

A11101 955046

A UNITED STATES
DEPARTMENT OF
COMMERCE
PUBLICATION



NBS
PUBLICATIONS

NSRDS—NBS 37



JANAF Thermochemical Tables

Second Edition

U.S.
DEPARTMENT
OF
COMMERCE
National
Bureau
of
Standards

OCT 6 1971

162031

BC 100
U573
No. 37
1971
Copy 2.

UNITED STATES DEPARTMENT OF COMMERCE • MAURICE H. STANS, *Secretary*

U.S. NATIONAL BUREAU OF STANDARDS • LEWIS M. BRANSCOMB, *Director*

JANAF Thermochemical Tables

SECOND EDITION

D. R. Stull and H. Prophet

Project Directors

Office of Standard Reference Data
National Bureau of Standards
Washington, D.C. 20234



NSRDS—NBS, 37.

t.ional and reference
Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 37, 1141 pages (June 1971)

CODEN: NSRDA

Issued June 1971

JANAF THERMOCHEMICAL TABLES

Second Edition

Superseding PB 168-370 and addenda 1, 2 and 3.

Prepared under
Air Force Contracts
F04611-67-C-0009
F04611-70-0028

by

The following personnel of the Dow Chemical Company:

D. R. Stull and H. Prophet, Project Directors

J. Chao,	1961-69	A. N. Syverud,	1963-70
A. T. Hu,	1965-70	T. E. Dergazarian,	1959-63
E. W. Phillips,	1963-66	A. C. Swanson,	1962-64
G. C. Karris,	1965-68	D. U. Webb,	1967-68
S. K. Wollert,	1963-65	L. A. DuPlessis,	1960-61
S. Levine,	1960-61	H. K. Unger,	1963-64
J. L. Curnutt,	1969-70	R. S. Orehotsky,	1963-64
J. A. Rizos,	1962-63	R. V. Petrella,	1961-62
B. H. Justice,	1964	S. T. Hadden,	1962
F. L. Oetting,	1961	G. C. Sinke,	1961, 65, 69, 70

at

The Thermal Research Laboratory
Dow Chemical Company
Midland, Michigan

Technically Assisted by
The Thermochemical Working Group
Interagency Chemical Rocket Propulsion Group

July 1970

Foreword

The National Standard Reference Data System provides effective access to the quantitative data of physical science, critically evaluated and compiled for convenience, and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, with responsibility to administer it assigned to the National Bureau of Standards.

The System now comprises a complex of data centers and other activities, carried on in academic institutions and other laboratories both in and out of government. The independent operational status of existing critical data projects is maintained and encouraged. Data centers that are components of the NSRDS produce compilations of critically evaluated data, critical reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. In addition, the centers and projects establish criteria for evaluation and compilation of data and make recommendations on needed improvements in experimental techniques. They are normally closely associated with active research in the relevant field.

The technical scope of the NSRDS is indicated by the principal categories of data compilation projects now active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

The NSDRS receives advice and planning assistance from the National Research Council of the National Academy of Sciences-National Academy of Engineering. An overall Review Committee considers the program as a whole and makes recommendations on policy, long-term planning, and international collaboration. Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The NSRDS-NBS series of publications is intended primarily to include evaluated reference data and critical reviews of long-term interest to the scientific and technical community.

The JANAF Thermochemical Tables Project, sponsored and monitored by agencies of the Defense Department, has been considered an important part of the National Standard Reference Data System. The tables have found wide utility in technical areas far removed from those for which the work was initiated. Consequently, when plans for a Second Edition of the JANAF Thermochemical Tables were under discussion, a suggestion was made that they be incorporated into the NSRDS-NBS publication series. This suggestion was accepted, and the present volume, NSRDS-NBS 37, is the outcome. It is hoped that this publication channel will lead to even wider distribution and greater use of these very valuable tables.

LEWIS M. BRANSCOMB, *Director*

PREFACE TO THE FIRST EDITION

Beginning in the mid-1950's, when elements other than the conventional carbon, hydrogen, oxygen, nitrogen, chlorine, and fluorine came into consideration as rocket propellant ingredients, formidable difficulties were encountered in conducting rigorous theoretical performance calculations for these new propellants. The first major problem was calculational techniques. The second was the lack of accurate thermodynamic data.

By the end of 1959, the calculational technique problem had been substantially resolved by applying the method of minimization of free energy to large, high-speed digital computers. At this point the calculations became as accurate as the thermodynamic data upon which they were based. However, serious gaps were present in the available data. For propellant ingredients, only the standard heat of formation is required to conduct a performance calculation. However, this must be known to a high degree of accuracy. For combustion products, the enthalpy and entropy must be known, as a function of temperature, in addition to the standard heat of formation.

In order to resolve the problem, a substantial experimental thermodynamic research program was initiated under the sponsorship and technical direction of Project PRINCIPIA of the Advanced Research Projects Agency. Simultaneously, a project was initiated to critically evaluate and compile consistent tables of thermodynamic properties of propellant combustion products for use by the aerospace industry. This project, known as the "JANAF Thermochemical Tables," was undertaken by the Dow Chemical Company. Since the objective of the project was to have one single source of "best available data" prepared for use by the entire industry, the JANAF Thermochemical Panel undertook the task of furnishing a critical review of the Tables prior to their publication and distribution. This approach was designed to insure that the Tables be of the highest possible quality.

Washington, D.C.
July 1964

G. V. Mock
Advanced Research Project Agency

PREFACE TO THE SECOND EDITION

It is appropriate to call attention to some of the reasons for the phenomenal success of the JANAF Thermochemical Tables in achieving, first, the initial limited objective of providing the standard data for the chemical rocket propulsion industry, and later, upon publication, world-wide recognition as thermodynamic reference data of the highest quality and timeliness.

First, and most obvious, there was the selection and continued support of a highly competent evaluation team, themselves engaged in a broad spectrum of thermodynamic research. The personnel of the Thermal Research Laboratory of the Dow Chemical Company, under the direction of Dr. D. R. Stull and Dr. H. Prophet, have filled this role to a degree of excellence not likely to be exceeded anywhere. Moreover, the group has heroically remained productive in spite of many battles to retain continuing support, and the actual sharp reduction of funding over the past two years to a less-than-viable level.

A second important factor is the unusual approach to format, evaluation, and distribution of the Tables, as it has been followed since their inception. The primary distribution is in frequently issued loose-leaf supplements. Each previously issued table may thus be revised as often as necessary to take account of improved data. Each loose-leaf table is accompanied on its reverse side by a complete explanation of the selection of the key data, together with all references.

The third vital distinction of these Tables has been the existence of a continuing cognizant working group composed of technological users of data, thermodynamicists, and government sponsors of both research and development. Independent prepublication review of the Tables has been an important contribution of some of the members of this group; but its annual technical meetings have resulted in even more far-reaching benefits. Together, the users and generators of data have been able to establish realistic priorities for the species to be included in the Tables; at the same time the course of experimental research has been guided by the demonstration of absence or inadequacy of needed data. Although the working group no longer enjoys official recognition, the members and participants have enthusiastically volunteered to continue meeting in this important work.

Special words of appreciation are due to Dr. Charles W. Beckett, who has lined up all the technical presentations at the last six annual meetings of the working group; and to Mr. Curtis C. Selph who has served with wisdom and insight as the Air Force project monitor for the JANAF Thermochemical Tables contracts.

JOSEPH F. MASI

Air Force Office of Scientific Research

Arlington, Virginia
October, 1970

Members of the JANAF Thermochemical Panel (1959-1961) and the JANAF Thermochemical Working Group (1961-1964) were:

T. O. Dobbins, Advanced Research Projects Agency (Past Chairman)
W. H. Jones, Institute for Defense Analysis; Aerospace Corporation (Past Chairman)
W. G. May, Institute for Defense Analyses; Esso Research and Engineering Company
(Past Chairman)
C. W. Beckett, National Bureau of Standards (Vice Chairman)
G. W. Avery, Chemical Propulsion Information Agency (Past Secretary)
B. K. Farris, Chemical Propulsion Information Agency (Past Secretary)
T. L. Reedy, Chemical Propulsion Information Agency (Secretary)
B. J. Alley, Army Materiel Command
P. W. Bender, University of Wisconsin
W. A. Burnett, Bureau of Naval Weapons
B. Brown, Hercules Powder Company
C. L. Funk, Jet Propulsion Laboratory
J. S. Gordon, Thiokol Chemical Corporation
L. J. Gordon, Aerojet-General Corporation
S. A. Greene, North American Aviation, Incorporated
C. B. Henderson, Atlantic Research Corporation
D. L. Hildenbrand, Philco Corporation
J. L. Margrave, University of Wisconsin
J. P. McCullough, U.S. Bureau of Mines
P. L. Nichols, Jr., Jet Propulsion Laboratory
C. C. Selph, Air Force Systems Command
D. R. Stull, Dow Chemical Company

The Thermochemical Working Group of the Interagency Chemical Rocket Propulsion Group (ICRPG) has consisted of the following at various times during its existence (1964-1969).

Members

J. F. Masi, Air Force Office of Scientific Research (Chairman)
C. W. Beckett, National Bureau of Standards (Vice Chairman)
T. O. Dobbins, Advanced Research Projects Agency
S. Gordon, National Aeronautics and Space Administration
R. Jackel, Office of Naval Research
J. Murrin, Naval Ordnance Systems Command
R. Odom, Army Materiel Command
C. E. Selph, Air Force Rocket Propulsion Laboratory
D. Squire, Army Research Office

Participants

G. S. Bahn, Marquardt Corporation
B. Brown, Hercules, Incorporated
H. F. Calcote, AeroChem Research Laboratories
J. P. Coughlin, Aerojet-General Corporation
J. S. Gordon, Atlantic Research Corporation
D. R. Douslin, U.S. Bureau of Mines
M. Farber, Space Sciences, Incorporated
R. M. Fristrom, Applied Physics Laboratory
C. B. Henderson, Atlantic Research Corporation
D. L. Hildenbrand, Douglas Aircraft Company
J. L. Margrave, Rice University

W. G. May, Esso Research and Engineering Company
W. Mitchell, Thiokol Chemical Corporation
C. F. Robillard, Jet Propulsion Laboratory
L. Schieler, Aerospace Corporation
C. H. Shomate, Naval Weapons Center
D. R. Stull, Dow Chemical Company
M. Zimmer, Naval Ordnance Station

Secretariat (Chemical Propulsion Information Agency)

T. Gilliland
M. McCormack
T. L. Reedy

Project Personnel

The Tables began under the direction of Daniel R. Stull in 1959. Major contributions in the first two years were made by Thomas E. Dergazarian, Samuel Levine and Louis A. DuPlessis. In the years from 1961 to 1969 the major contributors were Jing Chao, Harold Prophet, Alan N. Syverud and Andrew T. Hu. In 1969 Harold Prophet succeeded Daniel R. Stull as project director. At present Alan N. Syverud, Andrew T. Hu and Jerry L. Curnutt are the principal contributors.

Special mention must be made of Alan N. Syverud for his help in the technical editing of the Tables. Also G. C. Sinke has aided the project on numerous occasions with criticism, advice and tables.

We also wish to acknowledge the valuable assistance of Norma Dumont 1959-64, Viola E. Harrington 1964-66, Carol S. Scheffler 1966-67, Wildene B. Harris 1967-68 and Mary J. Walter since 1968 in the typing of these Tables. Isabel Carr has provided valuable services to the group in abstracting, searching and ordering documents, and proof reading the Tables.

We also wish to thank the staff of the Computation Research Laboratory for their assistance in the many facets of the production of these Tables.

DANIEL R. STULL
HAROLD PROPHET

Contents

	Page
Foreword	iii
Preface to the First Edition	iv
Preface to the Second Edition	v
Members of the JANAF Thermochemical Panel	vi
Project Personnel	vii
Constants Used	1
Symbols and Terminology	2
Evaluation of Thermodynamic Data	4
Calculation Methods	9
Notes	11
Index to Tables	13
Tables	Tables (Arranged by Chemical Symbols)

Library of Congress Catalog Card Number: 77-611423

C O N S T A N T S U S E D

The fundamental constants are those recommended by the International Union of Pure and Applied Chemistry as reported by F. D. Rossini, Pure and Applied Chemistry, 9, 453 (1964). The physical scale based on the atomic mass of $^{12}\text{C} = 12$ reported by A. E. Cameron and E. Wichers, J. Am. Chem. Soc. 84, 4175 (1962) is employed. The temperature scale is nominally the 1948 International Practical Temperature Scale for measured quantities and nominally the thermodynamic temperature scale for calculated gaseous quantities. The probable errors between these scales and the 1968 International Practical Temperature Scale are given by T. B. Douglas, J. Research Natl. Bur. Std. 73A, 451 (1969).

Fundamental Constants

<u>Name</u>	<u>Symbol</u>	<u>Value</u>	<u>Units</u>
Velocity of Light	c	2.997925×10^{10}	cm s ⁻¹
Planck Constant	h	6.6256×10^{-27}	erg s
Avogadro Constant	N	6.02252×10^{23}	mol ⁻¹
Faraday Constant	F	96,487.0	C mol ⁻¹
Absolute temperature of the "ice point", 0°C	T ₀ °C	273.1500	K
Molar volume of ideal gas (1 atm)	V ₀ °C	22,413.6	cm ³ mol ⁻¹
Pressure-Volume product for a mole of gas at 0°C and zero pressure	P=0 (PV) T ₀ °C	2271.06	J mol ⁻¹
Electronic Charge	e	1.60210×10^{-19}	C
Gas constant	R	8.3143	J deg ⁻¹ mol ⁻¹
		1.987165	cal deg ⁻¹ mol ⁻¹
Boltzmann Constant	k	1.38054×10^{-16}	erg deg ⁻¹ molecule ⁻¹
Second radiation constant	c ₂	1.43879	cm deg
Constant relating wave number and energy per mole E, in the relation $(\Delta E) = Nhc(\Delta \nu) = Z(\Delta \nu)$	Z	11.96255	J cm mol ⁻¹

Defined Constants

<u>Name</u>	<u>Symbol</u>	<u>Value</u>	<u>Units</u>
Standard gravity	g	980.665	cm s ⁻²
Standard atmosphere	atm	101 325	N m ⁻²
Standard millimeter of mercury pressure	mmHg	1/760	atm
Thermochemical calorie	cal	4.1840	J

SYMBOLS AND TERMINOLOGY

Throughout these tables, the symbols used are defined as follows:

amorph.	Amorphous state	S	Entropy
B	The rotational constant for diatomic or linear molecules	T	Temperature in degrees Kelvin ($T^\circ = t^\circ + 273.15^\circ$)
C_p	Molar heat capacity at constant pressure	t	Temperature in degrees Celsius
c	Crystalline state	V	Volume
D	Centrifugal distortion constant	V_0	Potential barrier
D_0	Dissociation energy required to break a bond at 0°K	x	First order vibrational anharmonicity constant
E	Internal or intrinsic energy	y	Second order vibrational anharmonicity constant
G or F	Gibbs energy = $E + PV - TS = H - TS$	α	Vibrational-rotational interaction constant
g_i	Quantum weight of electronic states	ϵ	Electronic energy level
()	Parentheses following a vibrational frequency are used to indicate the degeneracy	μ	Reduced mass of the molecule
g	Gaseous state, or statistical weight	ρ	Density
GFW	Gram Formula Mass	σ	Symmetry number
gls	Glassy state	ω	Vibrational frequency
H	Enthalpy (or heat content) = $E + PV$	[]	Square brackets enclose estimated quantities
I_A, I_B, I_C	Principal moments of inertia of a molecule	<u>Subscripts</u>	
$I_A I_B I_C$	Product of the principal moments of inertia of a molecule	a	Atomization
K	Equilibrium constant	b	Boiling point at one atmosphere pressure
k	Hooke's Law force constant	c	Combustion, or critical state
liq. or l	Liquid state	d	Dissociation
ln	Logarithm to the base e ($e = 2.7182818$)	e	Equilibrium position
log	Logarithm to the base 10	f	Formation from elements in their standard states
n	Number of potential maxima in an internal rotation	i	The i th quantity
P	Pressure in atmospheres	m	Melting
r	Internuclear distance	p	Constant pressure
		r	Reaction
		s	Sublimation
		t	Transition
		v	Vaporization

In addition to the above symbols, the spectroscopic symbols and terminology employed by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., and "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, are adopted.

Circular superscript, °, indicates the thermodynamic standard state.

Numerical subscript, as $_{298.15}$, denotes temperature in Kelvins.

Δ indicates the increment in a given property for a given process or reaction, taken as the value for the final state (or sum for the products) less that for the initial state (or sum for reactants).

ΔH , ΔG , ΔS , ΔC_p equal the increment in enthalpy, Gibbs energy, entropy and heat capacity, respectively, for a process or reaction.

ΔH_f° represents the standard enthalpy of formation, which is the increment in enthalpy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\Delta H_c^\circ_{298.15}$ symbolizes the enthalpy of combustion of a given substance, in gaseous oxygen to completely oxidized products at 25°C. and constant pressure, with all reactants and products in their appropriate standard states.

SYMBOLS AND TERMINOLOGY

$\Delta H_{r, 298.15}^{\circ}$ represents the enthalpy change in a given reaction at 25°C and constant pressure with all the reactants and products in their appropriate standard states.

When the reaction or process evolves heat, the sign of the change in enthalpy is negative. Conversely, when the reaction or process absorbs heat, the sign of the change in enthalpy is positive.

ΔG_f° or ΔF_f° denotes the standard Gibbs energy of formation, which is the increment in Gibbs energy associated with the reaction of forming the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

$\log_{10} K_p$ stands for the logarithm (to the base 10) of the thermodynamic equilibrium constant of formation for the reaction of forming the given compound from its elements at the indicated temperature.

$(H_T^{\circ} - H_{298.15}^{\circ})$ indicates the enthalpy (or heat content) in the standard state at the temperature T less the enthalpy in the standard state at 298.15 K.

$(G_T^{\circ} - H_{298.15}^{\circ})/T$ or $(F_T^{\circ} - H_{298.15}^{\circ})/T$ denotes the Gibbs energy function in the standard state at temperature T, and is defined as $-S_T^{\circ} + (H_T^{\circ} - H_{298.15}^{\circ})/T$.

S_T° represents the absolute entropy of the thermodynamic standard state at the absolute temperature T, omitting contributions from nuclear spins.

The Standard State is taken as the state at one atmosphere pressure and the temperature under consideration for the solid, liquid, and ideal gas. Only homogeneous substances are considered here.

The Reference State applies to elements in their stable standard state. Consequently the Reference State tables presented here are either single phase or polyphase tables.

CHANGES IN SYMBOLS ON TABLES DATED 6-30-66 OR LATER

The following symbols are used, without periods, to indicate units as follows:

<u>Symbol</u>	<u>Unit</u>	<u>Symbol</u>	<u>Unit</u>
Å	angstrom	eu	calories per degree-mole
atm	atmosphere	g	gram
cal	calorie	J	joule
deg	degree (temperature)	kcal	kilocalorie
°C	degree Celsius	mm	millimeter
°K	degree Kelvin	mol	mole
eV	electron volt	gibbs	calories per degree

Subscripts as defined earlier are used as symbol modifiers but are placed on the same line, thus, heat capacity is abbreviated as C_p° , enthalpy of formation as ΔH_f° , etc.

RELATIONSHIP TO SI UNITS

The symbols cal. mole⁻¹ deg⁻¹ and gibbs/mol are identical and refer to units of calories per degree-mole. These units can be converted to SI units of joules per degree-mole by multiplying the tabulated values by 4.184. Similarly values in kilocalories per mole can be converted to joules per mole by multiplying with the factor 4184. For further discussions of the SI system and for conversions from other units the reader should consult Pure and Applied Chemistry, 21, 1 (1970).

EVALUATION OF THERMODYNAMIC DATA

A. Interconsistency

The basic aim of these thermodynamic property tables is to provide a related and consistent set of enthalpies and Gibbs energies of formation. This allows the prediction of the enthalpy and Gibbs energy changes of any reaction among the constituents of the tables. Since the enthalpy and Gibbs energy of formation are related to each other by the entropy of formation we may choose to make consistent any two of these quantities. The entropy, which is an absolute quantity in thermochemical calculations, is ideal for this purpose. Since the enthalpy of reaction is the most common link between different materials, we adopt it as the other consistent quantity. Unfortunately enthalpies are not absolute quantities and in order to achieve consistency it is necessary to provide a consistent base. This is done by referring all enthalpies of formation to the elements in their reference states. By convention the enthalpy of formation of an element in its reference state is zero at all temperatures.

The reference state may be single phase or multiphase and examples of both kinds are found in this compilation. In these tables we have generally chosen the ideal diatomic gas for the reference state of permanent gases such as O_2 , N_2 , Cl_2 etc. For elements which are solid at room temperature we adopt the solid state up to the melting point, then the liquid up to the boiling point, and then the gas phase. These choices are arbitrary and vary in different compilations. Enthalpies or Gibbs energies of formation taken from different sources should be checked to ensure that the reference states are the same.

The choice of reference states is the first step in any scheme for interconsistency, and is the relation of all quantities to comparable bases. The next step in obtaining an interconsistent set of values, ideally, would be to take all the measured values of enthalpies, Gibbs energies and entropies of reaction and, after adjustment to the proper reference states, to solve the whole set simultaneously. This would provide values for enthalpies, Gibbs energies and entropies which when combined would yield the minimum overall deviations from the measured values. We have already taken this approach in a limited sense by treating groups of interrelated fluorides simultaneously. Hopefully with even larger memories in computers we shall be able to move towards the ultimate goal. As an interim solution it is necessary to fix, simultaneously when possible, certain key values for common reactants such as water, hydrochloric acid, etc., these can then be used to help fix smaller groups of interrelated compounds.

Because of the several revisions of these tables we do not claim to maintain perfect interconsistency. However, the consistency of the tables is a prime concern and a cause for revision if the effects are of the same order of magnitude as the stated uncertainties. As an example, over 100 fluoride tables have been revised since a new HF gas table was adopted in December 1968.

Another type of consistency is involved in systems where properties must be estimated. For example the estimation of certain properties of a series of halides must be done so that the proper graduation in properties occurs from fluoride to iodide and from polyhalide to monohalide. Similarly the evaluation of experimental data must be done in a consistent manner, and this is discussed in the next section.

B. General Evaluation Techniques

1. The Second-Law Method

Starting from the equation $\Delta G^\circ = -T\Delta nK$, by differentiation with respect to T and substitution of $d(\Delta G^\circ)/dT = -\Delta S^\circ$, we obtain $\Delta H^\circ = RT^2 d(\ln K)/dT$, the well known van't Hoff equation. By substituting $dT = -T^2 d(1/T)$ one obtains $\Delta H^\circ = -Rd(\ln K)/d(1/T)$, thus, the slope of a $\ln K$ versus $1/T$ plot is $-\Delta H^\circ/R$. If ΔH° is constant then the slope is constant and the plot is a straight line. Since the variation of ΔH° with temperature is often quite small it is customary to assume a straight line relationship. This method of obtaining heats of reaction from equilibrium measurements is known as a "second-law" calculation. However, it should be noted that for greatest accuracy the equilibrium measurements should extend over a wide range of temperature, and in this case ΔH° is probably not constant. Curvature corrections can be applied by assuming a specific form for the variation of ΔH° with temperature, however, the effects of such corrections are of significance only with very precise measurements. It should be noted that the second law cannot be applied to a single observation, but the third-law method, which is described below, can be used. The second-law method can be applied when only relative values of the equilibrium constant are available, for example, from mass-spectroscopic intensity measurements.

2. The Third-Law Method

The third-law method is based on a knowledge of the absolute entropy of the reactants and products. It allows the calculation of a reaction enthalpy from each data point when the change in the Gibbs-energy function for the reaction is known. The Gibbs-energy function is defined as $gef_T = (G_T^\circ - H_{ref}^\circ)/T$ and is easily calculated from the relation

$$S_T^\circ = -(G_T^\circ - H_{ref}^\circ)/T = (H_T^\circ - H_{ref}^\circ)/T - (G_T^\circ - H_{ref}^\circ)/T$$

thus,

$$gef_T = -S_T^\circ + (H_T^\circ - H_{ref}^\circ)/T.$$

From the definition we can write for the change in a reaction

$$\Delta G^\circ/T = \Delta gef_T + \Delta H_{ref}^\circ/T = -R\Delta nKp$$

thus,

$$\Delta H_{ref}^\circ/T = -R\Delta nKp - \Delta gef_T$$

where Δ signifies Σ products $-\Sigma$ reactants.

In the JANAF Thermochemical Tables, Gibbs-energy functions are based on 298 K and, thus, yield enthalpies at 298 K regardless of the temperature of the reaction. It should be noted that, since most of these tables are single phase tables, the Gibbs-energy functions of liquids are based on liquid at 298 K even though it may not exist at 298 K. This differs from the usual convention of combining all condensed phases into one table; in this case the enthalpy of reaction refers to the state stable at the base temperature. In these tables the functions always refer to the state of the table at 298 K regardless of its stability. For

example, if the vapor pressure over liquid copper is analysed using Cu(l) Gibbs-energy functions the enthalpy of vaporization at 298 K will result. To calculate the enthalpy of sublimation of Cu it is necessary to add the heat of melting at 298 K, which is the difference in the heat of formation of Cu(l) and Cu(c) at 298 K. It should also be noted that Gibbs-energy functions are always negative, thus the function $-(G_T^0 - H_T^0)/T$ is usually tabulated and the proper sign must be remembered when using these functions.

The analysis of data by the third law is generally considered superior to the second-law analysis. It is definitely superior if the Gibbs-energy functions are measured, because each data point is independent of the others. Thus, third-law analysis will often reveal trends in the equilibrium constants of a set of data that indicate nonequilibrium or erroneous values. We have found a combination of the two methods to be so valuable that a third-law calculation is always accompanied by a second-law treatment of the same data. The calculation is done in ascending temperature order to give ΔH_{298} and its deviation from the mean, δ , and the calculated $\log K_p$ and its deviation from the least-squares line. Third-law analyses enables bad points to be seen as deviations from the general trend of the differences; thus the method can be used even when the Gibbs-energy functions are estimated. If these bad points are located on the ends of the data set, the second-law line often fits quite well through them and by itself does not arouse suspicion. Moreover, the dropping of such points can bring widely discordant slopes into agreement with each other and often with the third-law values. The data sets given in Table 1 illustrate these comments. The first set of data contains all the reported points and is in disagreement with earlier values around 54 kcal/mole. The third-law analysis indicates the first two points are poor, and the effect of dropping these two is shown in the second set of data. This latter second-law slope has changed considerably; the heat is in good agreement with the earlier data and with the third law. The size of the third-law deviations in the second set indicates that the data are not very reproducible. A deviation of 0.5 kcal at 1000°K represents an uncertainty of 30% in the measured equilibrium constants.

If measured Gibbs-energy functions are available, third-law analysis is preferred; however, if the data are good, the second-law value should agree. When the Gibbs-energy functions are estimated, the third-law values derived from them must be handled carefully. Values that are constant and that agree with the second-law enthalpy indicate that the Gibbs-energy functions and equilibrium data are mutually consistent. A drift with temperature of the third-law values indicates errors in either the data or the functions. The magnitude of such drifts is often given in the table write-up and represents the entropy change required to bring the second- and third-law values into agreement. If the drift is within the experimental entropy uncertainty then the data are acceptable. Drifts which are much larger than reasonable entropy errors generally indicate failure to attain equilibrium.

Table 1. Analysis of Equilibrium Data
 $\text{PbF}_2(\text{c}) \rightarrow \text{PbF}_2(\text{g})$, data of Nesmeyanov and Iofa, Russ. J. Inorg. Chem. 4, 219 (1959)

Analysis I						Analysis II					
Third Law			Second Law			Third Law			Second Law		
T°K	ΔH_{298}	δ	Observed Log K_p	Calculated Log K_p	Difference	T°K	ΔH_{298}	δ	Observed Log K_p	Calculated Log K_p	Difference
792.0*	54.276	-1.105	-5.959	-6.016	0.057	852.0	54.980	-0.592	-5.222	-5.344	0.122
806.0*	54.004	-1.377	-5.653	-5.816	0.163	884.0	55.552	-0.020	-4.925	-4.900	-0.025
852.0	54.980	-0.401	-5.222	-5.207	-0.015	884.0	55.700	0.128	-4.962	-4.900	-0.061
884.0	55.552	0.171	-4.925	-4.820	-0.105	900.0	55.720	0.148	-4.754	-4.691	-0.063
884.0	55.700	0.319	-4.962	-4.820	-0.142	907.0	55.561	-0.011	-4.621	-4.601	-0.020
900.0	55.720	0.339	-4.754	-4.637	-0.117	911.0	55.824	0.253	-4.630	-4.551	-0.080
907.0	55.561	0.180	-4.621	-4.559	-0.062	921.0	54.998	-0.574	-4.301	-4.426	0.125
911.0	55.824	0.444	-4.630	-4.515	-0.115	936.0	55.988	0.416	-4.339	-4.245	-0.094
921.0	54.998	-0.383	-4.301	-4.407	0.106	941.0	55.757	0.185	-4.221	-4.186	-0.035
936.0	55.988	0.607	-4.339	-4.248	-0.091	950.0	54.957	-0.614	-3.923	-4.081	0.158
941.0	55.757	0.376	-4.221	-4.197	-0.024	958.0	56.122	0.550	-4.090	-3.989	-0.101
950.0	54.957	-0.423	-3.923	-4.105	0.182	984.0	55.661	0.089	-3.671	-3.701	0.030
958.0	56.122	0.741	-4.090	-4.025	-0.065	988.0	55.611	0.039	-3.614	-3.658	0.045
984.0	55.661	0.280	-3.671	-3.774	0.103	Average = 55.572			Standard deviation = 0.025		
988.0	55.611	0.230	-3.614	-3.737	0.123	$\Delta H_{298} = 55.57$			$\Delta H_{298} = 53.79$		
Average = 55.381			Standard deviation = 0.029								
$\Delta H_{298} = 55.38$			$\Delta H_{298} = 47.29$			* Deleted in Analysis II					

3. Heat Capacities

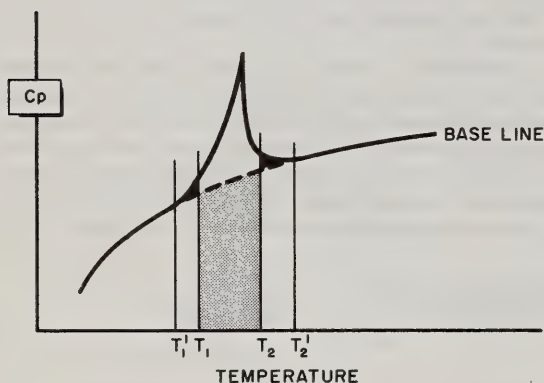
The evaluation of reported values is a relatively subjective procedure, but the analysis should be as objective as possible and therefore certain ground rules must be laid. The first step is the fitting by orthogonal polynomials and the computer-generated plotting of all information so that a general idea of the agreement can be visually obtained. If certain data sets differ from the majority, they are examined for possible causes of the difference. Calibration data, sample purity, and experimental scatter are checked. If the source of error can be located, the data are given appropriately less weight. Otherwise all data of equal reliability are considered equal, even if they disagree. Such data are then smoothed by a weighted orthogonal polynomial curvefit. Enthalpy data are smoothed similarly and heat capacities are derived directly from the differentiated polynomial. The smoothing of enthalpy data requires constraining the fit so that it passes through zero at the reference temperature. Additional constraints are often used to fix the heat capacity at 298 K, or to join enthalpy data smoothly with low-temperature heat capacities.

4. Transitions

The evaluation of solid state transitions involves first the recognition of the type of transition, which may not always be obvious. A first-order transition such as fusion involves a change of enthalpy and entropy at the transition point, whereas second-order transitions involve only discontinuities in heat capacity. Because of impurities and other factors, all first-order transitions do not occur at one temperature; rather, they spread a little on either side and are sometimes difficult to distinguish from λ -type second-order transitions. In order to evaluate the enthalpy of a first-order transition from heat-capacity data, an enthalpy change $(H_{T_2} - H_{T_1})$ from T_1 to T_2 °K must be reported on either side of the transition. The normal heat-capacity curve is extended forward and backward to the temperature of the transition-heat-capacity maximum to form a base line. If T_1' and T_2' are the temperatures at which the transitional heat capacity curve leaves and rejoins the base line, and ubl and obl designate under and over the base line, the heat of transition given by

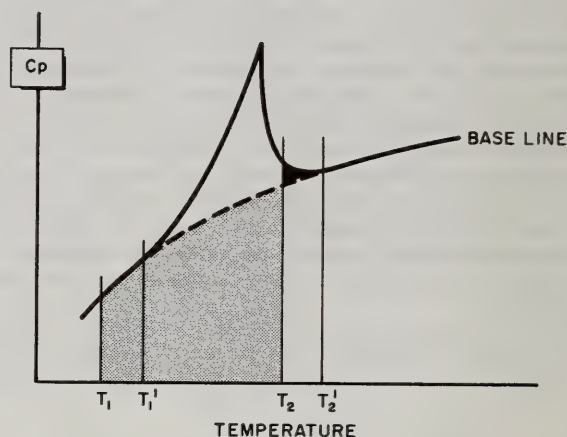
$$\Delta H_t = (H_{T_2} - H_{T_1}) - (H_{T_2} - H_{T_1})_{ubl} + (H_{T_1'} - H_{T_1})_{obl} + (H_{T_2'} - H_{T_2})_{obl}$$

Figures 1 and 2 show two possible cases. The shaded areas represent the enthalpy over the base line and cross-hatched areas the enthalpy under the base line.



EVALUATION OF TRANSITIONAL ENTHALPIES

FIGURE 1



EVALUATION OF TRANSITIONAL ENTHALPIES

FIGURE 2

Many enthalpies of fusion and enthalpies of solid-state transitions are obtained from enthalpy measurements and therefore require different treatment. Here the heats are given directly by the difference in enthalpy at the transition temperature. Normally, the enthalpy above and below can be smoothly extended to the temperature of transition, although the transition temperature may not be clearly obtainable from the enthalpy data.

The heats of the remaining transitions, vaporization and sublimation, are evaluated from equilibrium data by the second- and third-law methods just described except when calorimetric measurements are available.

5. Equilibrium

Perhaps the most significant factors to be established in evaluating equilibrium data are that equilibrium was attained and that the process was properly described. For example, in a sublimation process the most accurate measurements are valueless if the vapor phase is not uniquely defined. If polymerization or breakdown might have occurred, the first order of business is to establish the exact reaction. Because mass spectroscopy has shown that vapor phases are often extremely complex, it is almost a requirement that before equilibrium data can be accepted the vapor phases must be examined by a mass spectrometer to ensure their composition. Some methods of measurement are less accurate than others and should be given less weight. For example, equilibria determined in a mass spectrometer are usually quite rough because many approximations and uncertainties are involved in obtaining an absolute pressure measurement. On the other hand, measurements of the electromotive force of reversible cells can have great accuracy. Once the system is defined and equilibrium data are available, the data are analyzed by the second- and third-law methods.

CONSTRUCTION OF THE TABLES

1. Solid Phase

To produce a final table after all of the data have been evaluated or estimated, the enthalpy of formation, the entropy at 298 K, and the heat capacity at reasonable intervals through the temperature range of interest are needed. The enthalpy is obtained from the heat capacity by evaluating $\int_{298}^T C_p dT$. The entropy is similarly obtained from the heat capacity by evaluating $\int_{298}^T (C_p/T) dT$. The Gibbs energy function is then obtained from the relation $(G_T^\circ - H_{ref}^\circ)/T = -S_T^\circ + (H_T^\circ - H_{ref}^\circ)/T$. Enthalpies of

formation at temperatures other than 298 K require a knowledge of the enthalpies of the reference elements:

$$\Delta H_f^\circ = \Delta H_f^\circ_{298} + (H_T - H_{298})_{\text{compd}} - \sum (H_T - H_{298})_{\text{elements}}$$

The Gibbs energy of formation is readily calculated from the heat of formation when the entropies of the elements are known. Thus

$$\Delta G_f^\circ = \Delta H_f^\circ - T[S_T(\text{compd}) - \sum S_T(\text{elements})]$$

The logarithm of the equilibrium constant of formation is then found from the relation $\Delta G_f^\circ = -4.5756T \log K_p$.

Until now, we have only considered the calculation of values above 298 K; however, it is desirable to have data all the way to absolute zero. The temperature 0 K is a natural base for measurements involving gases in their lowest energy state, and values are needed in order to convert to the thermochemical reference temperature of 298 K. There is no basic difference in evaluating low-temperature data, but many more heat-capacity points are needed because of the large curvature. It is also necessary to evaluate the starting entropy at some temperature above 0 K because data rarely extend to below 5 K. In order to evaluate enthalpy it is necessary to start with a value above zero and integrate up to 298 K; then the value at 298 K is subtracted from the intermediate values, giving negative values below 298 K.

The tables extend to well above the normal melting point to facilitate the use of the tables by computers which can then interpolate values accurately right at the melting point. Dotted and solid lines indicate the end of the phase stability and solid-state transitions respectively.

2. Liquid Phase

The construction is identical with that used for the solid phase; however, the required data at 298 K are not usually readily available. The data are obtained by calculating a preliminary table using the chosen heat capacities with zero values for $\Delta H_f^\circ_{298}$ and S°_{298} . The correct starting values are then determined by comparing the values from the tables of crystal and liquid, using the following equations:

$$\Delta H_m^\circ = \Delta H_f^\circ(\ell) - \Delta H_f^\circ(c)$$

$$\Delta S_m^\circ = \frac{\Delta H_m^\circ}{T_m} = S^\circ_{T_m}(\ell) - S^\circ_{T_m}(c)$$

The correct values at 298 K may be obtained from the above relations. A typical liquid table is extrapolated both below the melting point and above the boiling point to facilitate interpolation near the phase boundaries.

3. Gas Phase

The data required for the various types of molecules are summarized below. The equations used are given in the section on Computational Methods. All molecules require the gram formula mass and enthalpy of formation at 298 K.

Additionally, monatomic species require: $\epsilon_0, \epsilon_1 \dots \epsilon_n$ and $g_0, g_1 \dots g_n$

Diatomic species require: $B_e, \sigma, x_e, \omega_e, \alpha_e, \epsilon_i, g_i$ ($i = 0, \dots, n$)

Linear polyatomic species require: B_e, σ, ω_i ($i = 1, \dots, 3N-5$), ϵ_i, g_i ($i = 0, \dots, n$)

Nonlinear polyatomic species require: $\sigma, \log I_A I_B I_C, \omega_i$ ($i = 1, \dots, 3N-6$), ϵ_i, g_i ($i = 0, \dots, n$)

ϵ_i is the energy of the i th electronic level

g_i is the statistical weight of the i th electronic level

B_e is the rotational constant

σ is the symmetry number

x_e is the anharmonicity correction = $\omega_e x_e / \omega_e$

ω_e is the fundamental frequency of a diatomic molecule

ω_i is a fundamental frequency of a polyatomic molecule

α_e is the rotational vibrational interaction constant

N is the number of atoms in the molecule

$I_A I_B I_C$ is the product of the moments of inertia

Monatomic species often have a large number of electronic levels; it is usual to average the higher levels taking account of the individual multiplicities. Diatomic and polyatomic species sometimes have several excited states which are low enough to make appreciable contributions. These states are treated by direct summation over the individual partition functions using anharmonic-oscillator approximations for each state. If vibrational and rotational constants for the higher states are not available the calculations are simplified by assuming the ground state values for each state.

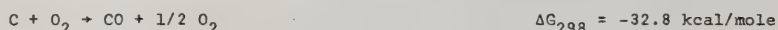
4. Multiphase Tables

Tables which show only values for the real phases at one atmosphere pressure are multiphase tables. In this compilation they are generally reference state tables, though some solid phase tables include more than one phase. Multiphase tables can always be recognized by the presence of solid lines, indicating phase transitions, on the table. They are prepared in a manner similar to tables for condensed phases. The functions are evaluated in the same manner as for a solid up to the first transition point; then the heat and entropy of transition are added and the integration is continued using the second-phase heat capacities. At each phase boundary the above process is repeated.

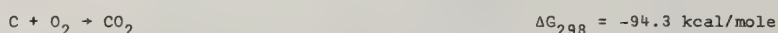
USE OF TABLES

The rapid proliferation of thermodynamic tabulations in recent years brings with it the possibility of serious abuse of the information in them. First, as we explained earlier, not all tabulations are based on the same reference states. To avoid this pitfall it is helpful to write down the reaction and check the value and state of each component. It is even better to utilize only a single compilation whenever possible, because values from different compilations may not be consistent or compatible. Second, the base temperatures of compilations differ between 0 and 298 K. Only enthalpies and Gibbs-energy functions are affected, but they can result in serious errors if used indiscriminately.

A different type of error is caused by misunderstanding the significance of negative Gibbs-energy changes. For example, many species in the JANAF Thermochemical Tables have large negative Gibbs energies of formation at 6000 K. This does not necessarily imply that the species are stable, but only that the Gibbs-energy change from the elemental reference state is negative. In fact, nearly all the elements are monatomic gases at 6000 K, and the reference states are generally unstable with respect to the atoms. Similarly, a negative Gibbs-energy change does not mean a reaction will occur, but means only that the reaction is favorable as written. For example, at 298 K



However, at normal pressures this reaction would generally be recognized as unlikely in view of



Similarly, in combining free energies of reaction, one should be careful not to combine impossible reactions with possible ones to obtain an over-all favorability:



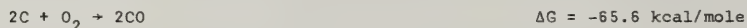
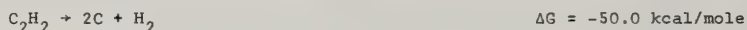
This equation is impossible because we cannot combine the reactions



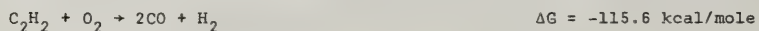
and



by simple addition. Both reactions must be written so that they are possible. They then become



Then by simple addition



Although these tables have been continuously revised it is not possible to keep all the tables fully revised with the latest data. Thus, each table indicates the dates of each revision at the foot of the tabular values. The latest date is most important since information generated after that date has not been incorporated. The frequency of revisions often indicates the level of research activity on the compound and may indicate further changes in the future.

CALCULATIONAL METHODS

The presentation of Mayer and Mayer "Statistical Mechanics", John Wiley & Sons, Inc., New York, (1940) forms the basis for the expressions given below for the ideal gas state. The calculations have been carried out by a Burroughs B5500 electronic computer.

I. Ideal Monatomic gas

(a) Translation

$$\begin{aligned} (H^\circ - H_0^\circ)/T &= C_p^\circ = 4.967913 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= 6.863426 \log M + 11.439043 \log T - 7.282868 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= 6.863426 \log M + 11.439043 \log T - 2.314954 \text{ cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

(b) Electronic

$$\begin{aligned} C_p^\circ &= \frac{4.113664}{T^2} \left[\frac{\sum \epsilon_i^2 g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} - \left(\frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} \right)^2 \right] \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ (H^\circ - H_0^\circ)/T &= \frac{2.859114}{T} \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= 4.575617 \log \sum g_i e^{-\frac{1.438790 \epsilon_i}{T}} \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= \frac{2.859114}{T} \frac{\sum \epsilon_i g_i e^{-\frac{1.438790 \epsilon_i}{T}}}{\sum g_i e^{-\frac{1.438790 \epsilon_i}{T}}} + 4.575617 \log \sum g_i e^{-\frac{1.438790 \epsilon_i}{T}} \text{ cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

II. Ideal Diatomic Gas

(a) Translation and Rotation

$$\begin{aligned} C_p^\circ &= 6.955079 + 0.0914148 (B/T)^2 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ (H^\circ - H_0^\circ)/T &= 6.955079 - 0.953038 (B/T) - 0.0914148 (B/T)^2 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) + 0.953038 (B/T) \\ &\quad + 0.0457074 (B/T)^2 - 8.005804 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= 6.863426 \log M + 11.439043 \log T - 4.575617 \log (B\sigma/T) - 0.0457074 (B/T)^2 - 1.050725 \\ &\quad \text{cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

where $B = (B_e - \alpha_e/2)$ when spectroscopic constants are available.

$$B = \frac{2.799076 \times 10^{-39}}{I} \text{ when calculated from a molecular model, (I in g cm}^2\text{)}$$

(b) Vibration

$$\begin{aligned} C_p^\circ &= 1.987165 u^2 e^{-u}/(1-e^{-u})^2 \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ (H^\circ - H_0^\circ)/T &= 1.987165 u e^{-u}/(1-e^{-u}) \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ -(G^\circ - H_0^\circ)/T &= -4.575617 \log (1-e^{-u}) \text{ cal deg}^{-1} \text{ mol}^{-1}. \\ S^\circ &= 1.987165 u e^{-u}/(1-e^{-u}) - 4.575617 \log (1-e^{-u}) \text{ cal deg}^{-1} \text{ mol}^{-1}. \end{aligned}$$

where $u = (1.438790/T) \cdot (\omega_e - 2\omega_e x_e)$ when spectroscopic constants are available.

$u = (1.438790/T)\omega$ where ω is the fundamental wave number of a harmonic oscillator.

(c) Electronic

Same as I(b) when the i th-state vibrational partition function, Q_v^i and the i th-state rotational partition function, Q_r^i , are equal to the respective ground state partition functions. In this case the partition function $Q = Q_t Q_v Q_r \sum_i Q_e^i$, otherwise all the thermodynamic functions are derived from $Q = Q_t \sum_i Q_e^i Q_v^i Q_r^i$, where Q_t is the translational partition function and $Q_e^i = g_i \exp(\epsilon_i/kT)$.

(d) Anharmonicity Corrections

$$C_p^\circ = 1.987615 \left[\frac{16\gamma}{u} - \frac{\delta u^2 e^u}{(e^u - 1)^2} + \frac{u^2 e^u (2\delta e^u - 4Xu - 8X)}{(e^u - 1)^3} + \frac{12Xu^3 e^{2u}}{(e^u - 1)^4} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{u(\delta e^u - 2X)}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$-(G^\circ - H_0^\circ)/T = 1.987165 \left[\frac{8\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{2Xu}{(e^u - 1)^2} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$S^\circ = 1.987165 \left[\frac{16\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{\delta u e^u}{(e^u - 1)^2} + \frac{4Xu^2 e^u}{(e^u - 1)^3} \right] \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

where u is $(\omega_e - 2\omega_e x_e) \cdot 1.438790/T$

$$X = (\omega_e x_e)/\omega_e; \quad \delta = \alpha_e/B_e; \quad \gamma = B_e/\omega_e.$$

III. Linear Polyatomic Molecule

- (a) Translation and rotation same as for II (a).
- (b) Vibration same as II (b) for 3N-5 vibrational degrees of freedom.
- (c) Electronic same as II (c) where levels and quantum weight are known.
- (d) Anharmonic corrections neglected.

IV. Nonlinear Polyatomic Molecule (Rigid Rotator, Harmonic Oscillator).

(a) Translation and Rotation

$$C_p^\circ = 7.948662 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$(H^\circ - H_0^\circ)/T = 7.948662 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$-(G^\circ - H_0^\circ)/T = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} - 10.297926 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

$$S^\circ = 6.863426 \log M + 18.302469 \log T - 4.575617 \log \sigma + 2.287809 \log I_A I_B I_C \times 10^{117} - 2.349265 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

- (b) Vibration same as II (b) for 3N-6 vibrational degrees of freedom.
- (c) Electronic same as II (c) where levels and quantum weight are known.
- (d) Anharmonic corrections neglected.

V. Condensed States

Evaluation of thermodynamic data for condensed states rests upon either measured or estimated information. Heat-capacity data are plotted, smoothed, and data for calculations read back at regular temperature intervals. Integration of this smoothed heat capacity data is carried out with the relations

$$H_T^\circ - H_{298.15}^\circ = \int_{298.15}^T C_p^\circ dT \quad S_T^\circ = \int_0^T \frac{C_p^\circ}{T} dT$$

by machine, three points at a time. The computer calculates the constants for a parabolic equation through the three points, and employs the constants to integrate the first temperature interval. The lowest point is discarded; the next higher point is combined with the two retained points; and a new set of parabolic constants calculated and used for integrating the next higher temperature interval. This recurrent procedure is well suited to this type of calculation. At the appropriate temperatures, transition enthalpies are added to the enthalpy total, while the quotient of the transition enthalpy divided by the absolute temperature is added to the entropy total.

NOTES

1. Indexing

The modified Hill indexing system, J. Am. Chem. Soc. 22, 478-94 (1900), for Chemical Compounds as used by Chemical Abstracts and the Classification Division of the U. S. Patent Office is used to index the chemical compounds in this data collection. The arrangement of atomic symbols in chemical formulas is alphabetical except for carbon compounds. Thus, the indexing of chemical compounds is as follows: Ac (actinium compounds), Ag (silver compounds), Al (aluminum compounds), Am (americium compounds), Ar (argon), As (arsenic compounds), Au (gold compounds), B (boron compounds), Ba (barium compounds), Be (beryllium compounds), and so on throughout the alphabet. Once the correct order of the elements in the formula is deduced, the location of a compound within the group is easily accomplished. This obviates the need for pagination, and the index page indicates the correct order.

Organic (carbon) compounds represent a gigantic group, so that for convenience this one class of compounds presents the exceptions to the alphabetical rule. In carbon compounds the C always comes first, followed immediately by H if hydrogen is present, and then followed by any other elements present in their normal alphabetical order. The number of atoms of the element indexed first also influences the order of indexing the compound; e.g., all formulas with C (one carbon atom only) come before those with C₂ (two carbon atoms), followed by C₃ compounds, and so on. Thus: CHBF₄O (formyl fluoride, compound with BF₃), CHCl₃ (chloroform), CH₂F₃P (trifluoromethylphosphine), CH₃NO₃ (methyl nitrate), CH₄Cl₂Si (dichloromethylsilane), CH₁₀N₄O₃ (hydrazine carbonate), CO (carbon monoxide), CO₂ (carbon dioxide), CO₃Zn (zinc carbonate), CZr (zirconium carbide), C₂Ba (barium acetylide), C₂BrClF₂ (bromochlorodifluoroethylene), C₂Ca (calcium carbide), and so on. See any formula index of Chemical Abstracts for further details and examples.

2. Selection of Enthalpy Reference Temperature

Since no enthalpy measurements can be made in the sense of an absolute quantity, and since all enthalpy measurements are made as a difference between an initial and a final state, it is necessary to select the thermodynamic state to which all other thermodynamic states will be referred. For these tables, the thermodynamic state selected is chosen as the state at one atmosphere total pressure tabulated at 298.15 K. Note that the temperature 298 K listed in the table actually refers to 298.15 K, but decimals have been omitted in the temperature column. Usage in theoretical work indicates the selection of the state existing at absolute zero, which is a hypothetical state that is even approached by relatively few measurements. Values of the difference in heat between 298.15 and 0 K will permit theoretical workers to use these tables, so it was decided to tabulate values at 0 K. Modern usage of thermodynamic data sometimes requires application to conditions below ambient, so the decision was made to tabulate values at 0, 100, and 200 K where the information is available.

3. Limitations of Calculated Quantities

Calculation of the contributions of rotation and translation involves the use of quantum statistics, but to obtain a numerical solution the quantum statistics are usually replaced by classical statistics at temperatures above about 100 K. Attempts to employ these methods below 100 K lead into a temperature range where the approximation afforded by classical statistics no longer holds. For this reason the equations presented under "Calculational Methods" fail in the vicinity of 0 K. In agreement with the third law concept, C_p^o and S^o are zero at 0 K. For a reference element, log K_p is zero at 0 K, while for compounds the absolute values of the free energy function and log K_p become infinite at 0 K.

4. Reference State of an Element

A related set of thermodynamic property tables requires that there be a reference table of the thermodynamic properties for each element to which all other forms of that element or any compound involving that element may be referred. If the temperature range of interest (6000 K here) can be represented by a single phase for that material (say hydrogen) the tabulated values in the reference table will be smooth and regular. If the temperature range of interest includes more than one phase (say magnesium) there will be a solid phase (from 0 to 922 K, the melting point), a liquid phase (922 to 1378 K, where the vapor pressure reaches one atmosphere), and a gas phase (1378 to 6000 K), the tabulated values in the reference table will be discontinuous at these phase boundaries. Practical usage dictates that in so far as possible the phase most stable at one atmosphere pressure (that is, the form most easily worked with) be selected. This practice is followed in these tables, and does lead to discontinuities in the thermodynamic functions. Attention is called to these discontinuities in the polyphase reference-state tables by insertion of a solid line at the temperature of a phase transition. The phase transitions considered are: first-order solid-state transformations from one crystal type to some other, solid to liquid, and solid or liquid to gas at one atmosphere.

5. Single-Phase Table

It is expected that these tables will be employed on various problems solved by automatic machine computation. Such calculations are carried out in numerous ways, and vary from one installation to another. Programs to perform these calculations are simplified if the thermodynamic functions are smooth and extend beyond the actual range of use permitting a wide latitude in iterative procedures. For this reason, most tables other than elemental reference states are tabulated as single-phase tables. Thus, tables for the solid state are extrapolated well past the melting point; those for the liquid state are extrapolated below the melting point (into the supercooled-liquid range to 298.15 K) and well above the atmospheric boiling point, while gas tables are tabulated from 0 K to 6000 K. Care has been taken to preserve the correct free energy relationships between the extrapolated-phase functions and the functions of the real phase. Attention is called to these extrapolations by insertion of a dotted line at the temperature where the indicated phase meets an adjacent more stable phase, but for reasons mentioned above the indicated phase is extrapolated into a temperature range where it is thermodynamically unstable.

NOTES

6. Mole

With each table and text there is listed either the atomic, molecular, or gram formula mass. It is generally understood that this mass in grams refers to Avogadro's number of atoms or molecules, and will be referred to simply as a "mole".

7. Point Groups and Ground-State Configurations

Throughout these tables the nomenclature and definition of the ground-state configurations and point groups are those in use by C. E. Moore, U. S. National Bureau of Standards Circular 467, (1949), and G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, (1950), and "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra", D. Van Nostrand Co., New York, (1945).

8. Decimal Places

Three decimal places have been arbitrarily carried in the tables even though in numerous cases the data do not warrant this accuracy. This has been done to preserve the proper relationship of the thermodynamic functions, and to facilitate machine interpolation of these values.

9. Higher Electronic Terms

A single electronic term of $30,000\text{ cm}^{-1}$ and above contributes a negligible amount to the thermodynamic functions at temperatures of 6000 K and below. On the other hand, a number of such terms cannot be neglected. In these cases, the number of terms and their values have been summed and their contribution included.

10. Estimated Vibrational Frequencies

Some vibrational frequencies have been estimated by analogy with related molecules. Occasionally, more than one frequency has been averaged at the same value. This is not to be confused with a true degeneracy which is indicated by placing the degeneracy value in parentheses following the frequency. However, when the information has been taken from another compilation, the degeneracies indicated by the compiler have been retained.

11. Quantum Weight

The term quantum weight is also referred to as statistical weight by many authors. The quantity is the product of the spin multiplicity and state degeneracy of the electronic level under consideration.

12. Isotope Effects

The functions calculated for gases from molecular constants are, in general, obtained from constants which have been corrected to the natural isotopic abundance.

INDEX TO TABLES

Filing Order	Table Title	Filing Order	Table Title
Al	Aluminum (ref. st.)	AlI ₃	Aluminum Triiodide (l)
Al	Aluminum (c)	AlI ₃	Aluminum Triiodide (g)
Al	Aluminum (l)	ALLiO ₂	Lithium Aluminate (c)
Al	Aluminum, Monatomic (g)	ALLiO ₂	Lithium Aluminate (l)
Al ⁺	Aluminum Unipositive Ion (g)	AlN	Aluminum Nitride (c)
AlBO ₂	Aluminum Boron Dioxide (g)	AlN	Aluminum Nitride (g)
AlBr	Aluminum Monobromide (g)	AlNaO ₂	Sodium Aluminate (c)
AlBr ₃	Aluminum Tribromide (c)	AlO	Aluminum Monoxide (g)
AlBr ₃	Aluminum Tribromide (l)	AlO ⁺	Aluminum Monoxide Unipositive Ion (g)
AlBr ₃	Aluminum Tribromide (g)	AlO ₂	Aluminum Dioxide (g)
AlCl	Aluminum Monochloride (g)	AlO ₂ ⁻	Aluminum Dioxide Uninegative Ion (g)
AlCl ⁺	Aluminum Monochloride Unipositive Ion (g)	AlS	Aluminum Sulfide (g)
AlClF	Aluminum Chlorofluoride (g)	Al ₂ BeO ₄	Beryllium Aluminate (c)
AlClF ₂	Aluminum Chlorodifluoride (g)	Al ₂ Br ₆	Aluminum Tribromide, Dimeric (g)
AlClO	Aluminum Oxychloride (c)	Al ₂ Cl ₆	Aluminum Trichloride, Dimer (g)
AlClO	Aluminum Oxychloride (g)	Al ₂ Cl ₉ K ₃	Potassium Nonachloroaluminate (c)
AlCl ₂	Aluminum Dichloride (g)	Al ₂ F ₆	Aluminum Trifluoride, Dimer (g)
AlCl ₂ ⁺	Aluminum Dichloride Unipositive Ion (g)	Al ₂ I ₆	Aluminum Triiodide, Dimeric (g)
AlCl ₂ ⁻	Aluminum Dichloride Uninegative Ion (g)	Al ₂ MgO ₄	Magnesium Aluminate (c)
AlCl ₂ F	Aluminum Dichlorofluoride (g)	Al ₂ O	Aluminum Suboxide (g)
AlCl ₃	Aluminum Trichloride (c)	Al ₂ O ⁺	Dialuminum Monoxide Unipositive Ion (g)
AlCl ₃	Aluminum Trichloride (l)	Al ₂ O ₂ ⁺	Aluminum Monoxide, Dimeric (g)
AlCl ₃	Aluminum Trichloride (g)	Al ₂ O ₂	Dialuminum Dioxide Unipositive Ion (g)
AlCl ₄ K	Potassium Tetrachloroaluminate (c)	Al ₂ O ₃	Aluminum Oxide (c, alpha)
AlCl ₄ Na	Sodium Tetrachloroaluminate (c)	Al ₂ O ₃	Aluminum Oxide (c, gamma)
AlCl ₆ K ₃	Tripotassium Hexachloroaluminate (c)	Al ₂ O ₃	Aluminum Oxide (l)
AlCl ₆ Na ₃	Trisodium Hexachloroaluminate (c)	Al ₂ O ₅ Si	Sillimanite (c)
AlF	Aluminum Monofluoride (g)	Al ₂ O ₅ Si	Andalusite (c)
AlF ⁺	Aluminum Monofluoride Unipositive Ion (g)	Al ₂ O ₅ Si	Kyanite (c)
AlFO	Aluminum Oxyfluoride (g)	Al ₆ O ₁₃ Si ₂	Mullite (c)
AlF ₂	Aluminum Difluoride (g)	B	Boron (ref. st.)
AlF ₂ ⁺	Aluminum Difluoride Unipositive Ion (g)	B	Boron, Beta-Rhombohedral (c)
AlF ₂ ⁻	Aluminum Difluoride Uninegative Ion (g)	B	Boron (l)
AlF ₃	Aluminum Trifluoride (c)	B	Boron, Monatomic (g)
AlF ₃	Aluminum Trifluoride (g)	B ⁺	Boron Unipositive Ion (g)
AlF ₄ Li	Lithium Tetrafluoroaluminate (g)	BBeO ₂	Beryllium Boron Dioxide (g)
AlF ₄ Na	Sodium Tetrafluoroaluminate (g)	BBr	Boron Monobromide (g)
AlF ₆ K ₃	Tripotassium Hexafluoroaluminate (c)	BBrCl	Boron Bromide Chloride (g)
AlF ₆ Li ₃	Trilithium Hexafluoroaluminate (c)	BBrCl ₂	Boron Bromide Dichloride (g)
AlF ₆ Li ₃	Trilithium Hexafluoroaluminate (l)	BBrF	Boron Bromide Fluoride (g)
AlF ₆ Na ₃	Cryolite (c)	BBrF ₂	Boron Bromide Difluoride (g)
AlF ₆ Na ₃	Cryolite (l)	BBrO	Boron Oxide Bromide (g)
AlH	Aluminum Monohydride (g)	BBr ₂	Boron Dibromide (g)
AlHO	Aluminum Monoxyhydride (g)	BBr ₂ Cl	Boron Dibromide Chloride (g)
AlHO	Aluminum Monohydroxide (g)	BBr ₂ F	Boron Dibromide Fluoride (g)
AlHO ⁺	Aluminum Monohydroxide Unipositive Ion (g)	BBr ₂ H	Boron Dibromide Hydride (g)
AlHO ⁻	Aluminum Monohydroxide Uninegative Ion (g)	BBr ₃	Boron Tribromide (l)
AlHO ₂	Aluminum Dioxyhydride (g)	BBr ₃	Boron Tribromide (g)
AlH ₄ Li	Lithium Aluminum Hydride (c)	BCl	Boron Monochloride (g)
AlI	Aluminum Monoiodide (g)	BCl ⁺	Boron Monochloride Unipositive Ion (g)
AlI ₃	Aluminum Triiodide (c)		

Filing Order	Table Title	Filing Order	Table Title
BClF	Boron Chloride Fluoride (g)	B ₂	Boron, Diatomic (g)
BClF ₂	Boron Chloride Difluoride (g)	B ₂ BeO ₄	Beryllium Diborate (g)
BClO	Boron Oxide Chloride (g)	B ₂ Be ₃ O ₆	Triberyllium Diborate (c)
BCl ₂	Boron Dichloride (g)	B ₂ Cl ₄	Boron Dichloride, Dimeric (g)
BCl ₂ ⁺	Boron Dichloride Unipositive Ion (g)	B ₂ F ₄	Boron Difluoride, Dimeric (g)
BCl ₂ ⁻	Boron Dichloride Uninegative Ion (g)	B ₂ H ₄ O ₄	Boron Dihydroxide, Dimeric (c)
BCl ₂ F	Boron Dichloride Fluoride (g)	B ₂ H ₄ O ₄	Boron Dihydroxide, Dimeric (g)
BCl ₂ H	Boron Dichloride Hydride (g)	B ₂ H ₆	Diborane (g)
BCl ₃	Boron Trichloride (g)	B ₂ Mg	Magnesium Diboride (c)
BF	Boron Monofluoride (g)	B ₂ O	Diboron Monoxide (g)
BFO	Boron Oxide Fluoride (g)	B ₂ O ₂	Boron Monoxide, Dimeric (g)
BF ₂	Boron Difluoride (g)	B ₂ O ₃	Boron Oxide (c)
BF ₂ ⁺	Boron Difluoride Unipositive Ion (g)	B ₂ O ₃	Boron Oxide (l)
BF ₂ ⁻	Boron Difluoride Uninegative Ion (g)	B ₂ O ₃	Boron Oxide (g)
BF ₂ H	Difluoroborane (g)	B ₂ O ₄ Pb	Lead Diborate (c)
BF ₂ HO	Boron Hydroxide Difluoride (g)	B ₂ Ti	Titanium Diboride (c)
BF ₂ O	Boron Oxide Difluoride (g)	B ₂ Ti	Titanium Diboride (l)
BF ₃	Boron Trifluoride (g)	B ₂ Zr	Zirconium Diboride (c)
BF ₄ K	Potassium Tetrafluoroborate (c)	B ₂ Zr	Zirconium Diboride (l)
BF ₄ K	Potassium Tetrafluoroborate (l)		
BF ₄ K	Potassium Tetrafluoroborate (g)	B ₃ Cl ₃ O ₃	Boron Oxide Chloride, Trimeric (g)
BH	Boron Monohydride (g)	B ₃ FH ₂ O ₃	Monofluoroboroxin (g)
BHO	Boron Oxide Hydride (g)	B ₃ F ₂ HO ₃	Difluoroboroxin (g)
BHO ⁺	Boron Oxide Hydride Unipositive Ion (g)	B ₃ F ₃ O ₃	Boron Oxide Fluoride, Trimeric (c)
BHO ₂	Metaboric Acid (c)	B ₃ F ₃ O ₃	Boron Oxide Fluoride, Trimeric (g)
BHO ₂	Metaboric Acid (g)	B ₃ H ₃ O ₃	Boroxin (c)
BH ₂	Boron Dihydride (g)	B ₃ H ₃ O ₃	Boroxin (g)
BH ₂ O ₂	Boron Dihydroxide (g)	B ₃ H ₃ O ₆	Metaboric Acid, Trimeric (g)
BH ₃	Boron Trihydride (g)	B ₃ H ₆ N ₃	Borazine (g)
BH ₃ O ₃	Boric Acid (c)		
BH ₃ O ₃	Boric Acid (g)	B ₄ K ₂ O ₇	Dipotassium Tetraboron Heptaoxide (c)
BH ₄ K	Potassium Tetrahydroborate (c)	B ₄ K ₂ O ₇	Dipotassium Tetraboron Heptaoxide (l)
BH ₄ Li	Lithium Tetrahydroborate (c)	B ₄ Li ₂ O ₇	Dilithium Tetraborate (c)
BH ₄ Na	Sodium Tetrahydroborate (c)	B ₄ Li ₂ O ₇	Dilithium Tetraborate (l)
BI	Boron Iodide (g)	B ₄ Mg	Magnesium Tetraboride (c)
BI ₂	Boron Diiodide (g)	B ₄ Na ₂ O ₇	Disodium Tetraborate (c)
BI ₃	Boron Triiodide (g)	B ₄ Na ₂ O ₇	Disodium Tetraborate (l)
BLiO ₂	Lithium Metaborate (c)	B ₄ O ₇ Pb	Lead Tetraborate (c)
BLiO ₂	Lithium Metaborate (l)	B ₅ H ₉	Pentaborane (l)
BLiO ₂	Lithium Metaborate (g)	B ₅ H ₉	Pentaborane (g)
BN	Boron Nitride (c)	B ₆ K ₂ O ₁₀	Dipotassium Hexaborate (c)
BN	Boron Nitride (g)	B ₆ Li ₂ O ₁₀	Dilithium Hexaborate (c)
BNaO ₂	Sodium Metaborate (c)	B ₆ Na ₂ O ₁₀	Disodium Hexaborate (c)
BNaO ₂	Sodium Metaborate (l)	B ₆ O ₁₀ Pb	Lead Hexaborate (c)
BNaO ₂	Sodium Metaborate (g)	B ₈ K ₂ O ₁₃	Dipotassium Octaborate (c)
BO	Boron Monoxide (g)	B ₈ K ₂ O ₁₃	Dipotassium Octaborate (l)
BO ₂	Boron Dioxide (g)	B ₈ Li ₂ O ₁₃	Dilithium Octaborate (c)
BO ₂ ⁻	Boron Dioxide Uninegative Ion (g)	B ₁₀ H ₁₄	Decaborane (c)
BS	Boron Monosulfide (g)	B ₁₀ H ₁₄	Decaborane (l)
BTi	Titanium Monoboride (c)	B ₁₀ H ₁₄	Decaborane (g)

Filing Order	Table Title
B ₁₀ O ₁₇ Pb ₂	Lead Decaborate (c)
Be	Beryllium (ref. st.)
Be	Beryllium (c)
Be	Beryllium (l)
Be	Beryllium (g)
Be ⁺	Beryllium Unipositive Ion (g)
BeBr	Beryllium Monobromide (g)
BeBr ₂	Beryllium Dibromide (c)
BeBr ₂	Beryllium Dibromide (l)
BeBr ₂	Beryllium Dibromide (g)
BeCl	Beryllium Monochloride (g)
BeCl ⁺	Beryllium Monochloride Unipositive Ion (g)
BeClF	Beryllium Chloride Fluoride (g)
BeCl ₂	Beryllium Dichloride (c,α)
BeCl ₂	Beryllium Dichloride (c,β)
BeCl ₂	Beryllium Dichloride (l)
BeCl ₂	Beryllium Dichloride (g)
BeF	Beryllium Monofluoride (g)
BeF ₂	Beryllium Difluoride (c)
BeF ₂	Beryllium Difluoride (l)
BeF ₂	Beryllium Difluoride (g)
BeF ₃ Li	Lithium Trifluoroberyllate (c)
BeF ₃ Li	Lithium Beryllium Fluoride (g)
BeF ₄ Li ₂	Dilithium Tetrafluoroberyllate (c)
BeF ₄ Li ₂	Dilithium Tetrafluoroberyllate (l)
BeH	Beryllium Monohydride (g)
BeH ⁺	Beryllium Monohydride Unipositive Ion (g)
BeHO	Beryllium Monohydroxide (g)
BeHO ⁺	Beryllium Monohydroxide Unipositive Ion (g)
BeH ₂	Beryllium Dihydride (g)
BeH ₂ O ₂	Beryllium Hydroxide (c,α)
BeH ₂ O ₂	Beryllium Hydroxide (c,β)
BeH ₂ O ₂	Beryllium Hydroxide (g)
BeI	Beryllium Monoiodide (g)
BeI ₂	Beryllium Diiodide (c)
BeI ₂	Beryllium Diiodide (l)
BeI ₂	Beryllium Diiodide (g)
BeN	Beryllium Nitride (g)
BeO	Beryllium Oxide (c)
BeO	Beryllium Oxide (l)
BeO	Beryllium Oxide (g)
BeO ₄ S	Beryllium Sulfate (c,α)
BeO ₄ S	Beryllium Sulfate (c,β)
BeO ₄ S	Beryllium Sulfate (c,γ)
BeO ₄ W	Beryllium Tungstate (c)
Be ₂ Cl ₄	Beryllium Dichloride, Dimeric (g)
Be ₂ F ₂ O	Dilithium Oxide Difluoride (g)
Be ₂ O	Diberyllium Oxide (g)
Be ₂ O ₂	Beryllium Oxide, Dimeric (g)
Be ₂ O ₄ Si	Beryllium Orthosilicate (c)

Filing Order	Table Title
Be ₃ N ₂	Beryllium Nitride (c,α)
Be ₃ N ₂	Beryllium Nitride (l)
Be ₃ O ₃	Beryllium Oxide, Trimeric (g)
Be ₄ O ₄	Beryllium Oxide, Tetrameric (g)
Be ₅ O ₅	Beryllium Oxide, Pentameric (g)
Be ₆ O ₆	Beryllium Oxide, Hexameric (g)
Br	Bromine, Monatomic (g)
BrCl	Bromine Monochloride (g)
BrF	Bromine Monofluoride (g)
BrF ₃	Bromine Trifluoride (g)
BrF ₅	Bromine Pentafluoride (g)
BrH	Hydrogen Bromide (g)
BrH ₄ N	Ammonium Bromide (c)
BrHg	Mercurous Bromide (g)
BrI	Iodine Monobromide (g)
BrK	Potassium Bromide (c)
BrK	Potassium Bromide (l)
BrK	Potassium Bromide (g)
BrLi	Lithium Bromide (c)
BrLi	Lithium Bromide (l)
BrLi	Lithium Bromide (g)
BrMg	Magnesium Monobromide (g)
BrN	Nitrogen Bromide (g)
BrNO	Nitrosyl Bromide (g)
BrNa	Sodium Bromide (c)
BrNa	Sodium Bromide (l)
BrNa	Sodium Bromide (g)
BrP	Phosphorus Monobromide (g)
BrPb	Lead Monobromide (g)
BrTi	Titanium Monobromide (g)
BrW	Tungsten Monobromide (g)
BrZr	Zirconium Monobromide (g)
Br ₂	Bromine (ref. st.)
Br ₂	Bromine (l)
Br ₂	Bromine, Diatomic (g)
Br ₂ Fe	Iron Dibromide (c)
Br ₂ Fe	Iron Dibromide (l)
Br ₂ Fe	Iron Dibromide (g)
Br ₂ Hg	Mercuric Bromide (c)
Br ₂ Hg	Mercuric Bromide (l)
Br ₂ Hg	Mercuric Bromide (g)
Br ₂ Hg ₂	Mercurous Bromide (c)
Br ₂ K ₂	Potassium Bromide, Dimeric (g)
Br ₂ Li ₂	Lithium Bromide, Dimeric (g)
Br ₂ Mg	Magnesium Dibromide (c)
Br ₂ Mg	Magnesium Dibromide (l)
Br ₂ Mg	Magnesium Dibromide (g)
Br ₂ Na ₂	Sodium Bromide, Dimeric (g)
Br ₂ Pb	Lead Dibromide (c)

Filing Order	Table Title
Br ₂ Pb	Lead Dibromide (l)
Br ₂ Pb	Lead Dibromide (g)
Br ₂ Ti	Titanium Dibromide (c)
Br ₂ Ti	Titanium Dibromide (g)
Br ₂ Zr	Zirconium Dibromide (c)
Br ₂ Zr	Zirconium Dibromide (l)
Br ₂ Zr	Zirconium Dibromide (g)
Br ₃ OP	Phosphoryl Bromide (g)
Br ₃ P	Phosphorus Tribromide (g)
Br ₃ PS	Thiophosphoryl Bromide (g)
Br ₃ Ti	Titanium Tribromide (c)
Br ₃ Ti	Titanium Tribromide (g)
Br ₃ Zr	Zirconium Tribromide (c)
Br ₃ Zr	Zirconium Tribromide (g)
Br ₄ Fe ₂	Iron Dibromide, Dimeric (g)
Br ₄ Pb	Lead Tetrabromide (g)
Br ₄ Ti	Titanium Tetrabromide (c)
Br ₄ Ti	Titanium Tetrabromide (l)
Br ₄ Ti	Titanium Tetrabromide (g)
Br ₄ Zr	Zirconium Tetrabromide (c)
Br ₄ Zr	Zirconium Tetrabromide (g)
Br ₅ W	Tungsten Pentabromide (c)
Br ₅ W	Tungsten Pentabromide (l)
Br ₅ W	Tungsten Pentabromide (g)
Br ₆ W	Tungsten Hexabromide (c)
Br ₆ W	Tungsten Hexabromide (g)
C	Carbon (ref. st., Graphite)
C	Carbon, Monatomic (g)
C ⁻	Carbon Uninegative Ion (g)
CaI	Aluminum Carbide (g)
CB	Boron Carbide (g)
CB ₄	Boron Carbide (c)
CB ₄	Boron Carbide (l)
CBe ₂	Beryllium Carbide (c)
CBe ₂	Beryllium Carbide (l)
CBr	Carbon Monobromide (g)
CBrF ₃	Bromotrifluoromethane (g)
CBrN	Cyanogen Bromide (g)
CBr ₄	Carbon Tetrabromide (g)
CCl	Carbon Monochloride (g)
CClFO	Carbonyl Chlorofluoride (g)
CClF ₃	Chlorotrifluoromethane (g)
CClN	Cyanogen Chloride (g)
CClO	Carbonyl Monochloride (g)
CCl ₂	Carbon Dichloride (g)
CCl ₂ F ₂	Dichlorodifluoromethane (g)
CCl ₂ O	Carbonyl Chloride (g)
CCl ₃	Trichloromethyl (g)
CCl ₃ F	Trichlorofluoromethane (g)
CCl ₄	Carbon Tetrachloride (g)

Filing Order	Table Title
CF	Carbon Monofluoride (g)
CFN	Cyanogen Fluoride (g)
CFO	Carbonyl Monofluoride (g)
CF ₂	Carbon Difluoride (g)
CF ₂ O	Carbonyl Fluoride (g)
CF ₃	Trifluoromethyl (g)
CF ₃ I	Trifluoroiodomethane (g)
CF ₄	Carbon Tetrafluoride (g)
CF ₄ O	Trifluoromethyl Hypofluorite (g)
CH	Methylidyne (g)
CHCl	Monochloromethylene (g)
CHClF ₂	Chlorodifluoromethane (g)
CHCl ₂ F	Dichlorofluoromethane (g)
CHCl ₃	Chloroform (g)
CHF	Monofluoromethylene (g)
CHFO	Formyl Fluoride (g)
CHF ₃	Trifluoromethane (g)
CHN	Hydrogen Cyanide (g)
CHNO	Hydrogen Isocyanate (g)
CHO	Formyl (g)
CHO ⁺	Formyl Unipositive Ion (g)
CHP	Methinophosphide (g)
CH ₂	Methylene (g)
CH ₂ ClF	Chlorofluoromethane (g)
CH ₂ Cl ₂	Dichloromethane (g)
CH ₂ F ₂	Difluoromethane (g)
CH ₂ O	Formaldehyde (g)
CH ₃	Methyl (g)
CH ₃ Cl	Methyl Chloride (g)
CH ₃ Cl ₃ Si	Trichloromethylsilane (g)
CH ₃ F	Fluoromethane (g)
CH ₃ F ₃ Si	Trifluoromethylsilane (g)
CH ₄	Methane (g)
CIN	Cyanogen Iodide (g)
CKN	Potassium Cyanide (c)
CKN	Potassium Cyanide (l)
CKN	Potassium Cyanide (g)
CK ₂ O ₃	Potassium Carbonate (c)
CK ₂ O ₃	Potassium Carbonate (l)
CLi ₂ O ₃	Lithium Carbonate (c)
CLi ₂ O ₃	Lithium Carbonate (l)
CMgO ₃	Magnesium Carbonate (c)
CN	Cyano (g)
CN ⁺	Cyano Unipositive Ion (g)
CN ⁻	Cyano Uninegative Ion (g)
CNNa	Sodium Cyanide (c)
CNNa	Sodium Cyanide (l)
CNNa	Sodium Cyanide (g)
CN ₂	CNN Radical (g)
CN ₂	NCN Radical (g)

Filing Order	Table Title
CNa ₂ O ₃	Sodium Carbonate (c)
CNa ₂ O ₃	Sodium Carbonate (l)
CO	Carbon Monoxide (g)
COS	Carbon Oxsulfide (g)
CO ₂	Carbon Dioxide (g)
CO ₂ ⁻	Carbon Dioxide Uninegative Ion (g)
CP	Carbon Phosphide (g)
CS	Carbon Monosulfide (g)
CS ₂	Carbon Disulfide (g)
CSi	Silicon Carbide (c,α)
CSi	Silicon Carbide (c,β)

CSi	Silicon Carbide (g)
CSi ₂	Disilicon Carbide (g)
CTi	Titanium Carbide (c)
CTi	Titanium Carbide (l)
CZr	Zirconium Carbide (c)
CZr	Zirconium Carbide (l)
C ₂	Carbon, Diatomic (g)
C ₂ ⁻	Dimeric Carbon Uninegative Ion (g)
C ₂ Be	Beryllium Carbide (g)
C ₂ Cl ₂	Dichloroacetylene (g)
C ₂ Cl ₄	Tetrachloroethylene (g)
C ₂ Cl ₆	Hexachloroethane (g)
C ₂ F ₂	Difluoroacetylene (g)
C ₂ F ₃ N	Trifluoroacetoneitrile (g)
C ₂ F ₄	Tetrafluoroethylene (g)
C ₂ F ₆	Hexafluoroethane (g)
C ₂ H	CCH Radical (g)
C ₂ HCl	Chloroacetylene (g)
C ₂ HF	Monofluorocetylene (g)
C ₂ H ₂	Acetylene (g)
C ₂ H ₄	Ethylene (g)
C ₂ H ₄ O	Ethylene Oxide (g)
C ₂ K ₂ N ₂	Potassium Cyanide, Dimeric (g)
C ₂ Li ₂	Lithium Carbide (c)
C ₂ Mg	Magnesium Carbide (c)
C ₂ N	CNC Radical (g)
C ₂ N ₂	Cyanogen (g)
C ₂ N ₂ Na ₂	Sodium Cyanide, Dimeric (g)
C ₂ O	CCO Radical (g)
C ₂ Si	Silicon Dicarbid (g)
C ₃	Carbon, Trimeric (g)
C ₃ Al ₄	Aluminum Carbide (c)
C ₃ Hg ₂	Magnesium Carbide (c)
C ₃ O ₂	Carbon Suboxide (g)
C ₄	Carbon, Tetratomic (g)
C ₄ H ₁₂ Si	Tetramethylsilane (g)
C ₄ N ₂	Carbon Subnitride (g)
C ₅	Carbon, Pentatomic (g)

Filing Order	Table Title
Ca	Calcium (ref. st.)
Ca	Calcium (α)
Ca	Calcium (β)
Ca	Calcium (l)
Ca	Calcium (g)
CaCl	Calcium Monochloride (g)
CaCl ₂	Calcium Chloride (c)
CaCl ₂	Calcium Chloride (l)
CaCl ₂	Calcium Chloride (g)
CaF	Calcium Monofluoride (g)
CaF ₂	Calcium Difluoride (c)
CaF ₂	Calcium Difluoride (l)
CaF ₂	Calcium Difluoride (g)
CaHO	Calcium Monohydroxide (g)
CaHO ⁺	Calcium Monohydroxide Unipositive Ion (g)
Cl	Chlorine, Monatomic (g)
Cl ⁺	Chlorine Unipositive Ion (g)
Cl ⁻	Chlorine Uninegative Ion (g)
ClCs	Cesium Monochloride (c)
ClCs	Cesium Monochloride (l)
ClCs	Cesium Monochloride (g)
ClCu	Copper Monochloride (c)
ClCu	Copper Monochloride (l)
ClCu	Copper Monochloride (g)
ClF	Chlorine Monofluoride (g)
ClFLi ₂	Lithium Chlorofluoride (g)
ClFMg	Magnesium Chloride Fluoride (g)
ClFO ₃	Perchloryl Fluoride (g)
ClF ₂ OP	Phosphoryl Difluorochloride (g)
ClF ₃	Chlorine Trifluoride (g)
ClF ₃ Si	Chlorotrifluorosilane (g)
ClF ₅	Chlorine Pentafluoride (g)
ClFe	Iron Monochloride (g)
ClH	Hydrogen Chloride (g)
ClHO	Hydrogen Oxychloride (g)
ClH ₃ Si	Chlorosilane (g)
ClH ₄ N	Ammonium Chloride (c)
ClH ₄ NO ₄	Ammonium Perchlorate (c)
ClHg	Mercurous Chloride (g)
ClI	Iodine Monochloride (c)
ClI	Iodine Monochloride (l)
ClI	Iodine Monochloride (g)
ClK	Potassium Chloride (c)
ClK	Potassium Chloride (l)
ClK	Potassium Chloride (g)
ClKO ₄	Potassium Perchlorate (c)
CLLi	Lithium Chloride (c)
CLLi	Lithium Chloride (l)
CLLi	Lithium Chloride (g)
CLLiO	Lithium Oxychloride (g)

Filing Order	Table Title
CLLiO ₄	Lithium Perchlorate (c)
CLLiO ₄	Lithium Perchlorate (l)
CLMg	Magnesium Monochloride (g)
CLMg ⁺	Magnesium Monochloride Unipositive Ion (g)
CLNO	Nitrosyl Chloride (g)
CLNO ₂	Nitryl Chloride (g)
CLNa	Sodium Chloride (c)
CLNa	Sodium Chloride (l)
CLNa	Sodium Chloride (g)
CLNaO ₄	Sodium Perchlorate (c)
ClO	Chlorine Monoxide (g)
ClOTi	Titanium Oxychloride (g)
ClO ₂	Chlorine Dioxide (g)
ClP	Phosphorus Monochloride (g)
ClPb	Lead Monochloride (g)
ClSi	Silicon Monochloride (g)
ClTi	Titanium Monochloride (g)
ClW	Tungsten Monochloride (g)
ClZr	Zirconium Monochloride (g)

Cl ₂	Chlorine, Diatomic (ref. st.,g)
Cl ₂ Cs ₂	Cesium Monochloride, Dimeric (g)
Cl ₂ Cu	Copper Dichloride (c)
Cl ₂ FOP	Phosphoryl Fluorodichloride (g)
Cl ₂ Fe	Iron Dichloride (c)
Cl ₂ Fe	Iron Dichloride (l)
Cl ₂ Fe	Iron Dichloride (g)
Cl ₂ H ₂ Si	Dichlorosilane (g)
Cl ₂ Hg	Mercuric Chloride (c)
Cl ₂ Hg	Mercuric Chloride (l)
Cl ₂ Hg	Mercuric Chloride (g)
Cl ₂ Hg ₂	Mercurous Chloride (c)
Cl ₂ K ₂	Potassium Chloride, Dimeric (g)
Cl ₂ Li ₂	Lithium Chloride, Dimeric (g)
Cl ₂ Mg	Magnesium Dichloride (c)
Cl ₂ Mg	Magnesium Dichloride (l)
Cl ₂ Mg	Magnesium Dichloride (g)
Cl ₂ MoO ₂	Molybdenum Dioxydichloride (g)
Cl ₂ Na ₂	Sodium Chloride, Dimeric (g)
Cl ₂ O	Chlorine Monoxide (g)
Cl ₂ OTi	Titanium Oxydichloride (g)
Cl ₂ O ₂ W	Tungsten Dioxydichloride (c)
Cl ₂ O ₂ W	Tungsten Dioxydichloride (g)
Cl ₂ Pb	Lead Dichloride (c)
Cl ₂ Pb	Lead Dichloride (l)
Cl ₂ Pb	Lead Dichloride (g)
Cl ₂ Si	Silicon Dichloride (g)
Cl ₂ Ti	Titanium Dichloride (c)
Cl ₂ Ti	Titanium Dichloride (g)
Cl ₂ W	Tungsten Dichloride (c)

Filing Order	Table Title
Cl ₂ W	Tungsten Dichloride (g)
Cl ₂ Zr	Zirconium Dichloride (c)
Cl ₂ Zr	Zirconium Dichloride (l)
Cl ₂ Zr	Zirconium Dichloride (g)
Cl ₃ Cu ₃	Copper Monochloride, Trimeric (g)
Cl ₃ FSi	Trichlorofluorosilane (g)
Cl ₃ Fe	Iron Trichloride (c)
Cl ₃ Fe	Iron Trichloride (l)
Cl ₃ Fe	Iron Trichloride (g)
Cl ₃ HSi	Trichlorosilane (g)
Cl ₃ Li ₃	Lithium Chloride, Trimeric (g)
Cl ₃ OP	Phosphoryl Chloride (g)
Cl ₃ P	Phosphorus Trichloride (g)
Cl ₃ PS	Thiophosphoryl Chloride (g)
Cl ₃ Si	Silicon Trichloride (g)
Cl ₃ Ti	Titanium Trichloride (c)
Cl ₃ Ti	Titanium Trichloride (g)
Cl ₃ Zr	Zirconium Trichloride (c)
Cl ₃ Zr	Zirconium Trichloride (g)

Cl ₄ Mg ₂	Magnesium Dichloride, Dimeric (g)
Cl ₄ Mo	Molybdenum Tetrachloride (c)
Cl ₄ Mo	Molybdenum Tetrachloride (l)
Cl ₄ Mo	Molybdenum Tetrachloride (g)
Cl ₄ OW	Tungsten Oxytetrachloride (c)
Cl ₄ OW	Tungsten Oxytetrachloride (l)
Cl ₄ OW	Tungsten Oxytetrachloride (g)
Cl ₄ Pb	Lead Tetrachloride (g)
Cl ₄ Si	Silicon Tetrachloride (g)
Cl ₄ Ti	Titanium Tetrachloride (c)
Cl ₄ Ti	Titanium Tetrachloride (l)
Cl ₄ Ti	Titanium Tetrachloride (g)
Cl ₄ W	Tungsten Tetrachloride (c)
Cl ₄ W	Tungsten Tetrachloride (g)
Cl ₄ Zr	Zirconium Tetrachloride (c)
Cl ₄ Zr	Zirconium Tetrachloride (g)
Cl ₅ Mo	Molybdenum Pentachloride (c)
Cl ₅ Mo	Molybdenum Pentachloride (l)
Cl ₅ Mo	Molybdenum Pentachloride (g)
Cl ₅ P	Phosphorus Pentachloride (g)
Cl ₅ W	Tungsten Pentachloride (c)
Cl ₅ W	Tungsten Pentachloride (l)
Cl ₅ W	Tungsten Pentachloride (g)
Cl ₆ Fe ₂	Iron Trichloride, Dimeric (g)
Cl ₆ Mo	Molybdenum Hexachloride (c)
Cl ₆ Mo	Molybdenum Hexachloride (g)
Cl ₆ W	Tungsten Hexachloride (c,α)
Cl ₆ W	Tungsten Hexachloride (c,β)
Cl ₆ W	Tungsten Hexachloride (l)
Cl ₆ W	Tungsten Hexachloride (g)

Filing Order	Table Title
Cl_{10}W_2	Tungsten Pentachloride, Dimeric (g)
Co	Cobalt (ref. st.)
Co	Cobalt (c)
Co	Cobalt (l)
Co	Cobalt (g)
Co^+	Cobalt Unipositive Ion (g)
CoF_2	Cobalt Difluoride (c)
CoF_2	Cobalt Difluoride (l)
CoF_2	Cobalt Difluoride (g)
Cs	Cesium (ref. st.)
Cs	Cesium (c)
Cs	Cesium (l)
Cs	Cesium (g)
Cs^+	Cesium Unipositive Ion (g)
CsF	Cesium Monofluoride (c)
CsF	Cesium Monofluoride (l)
CsF	Cesium Monofluoride (g)
CsO	Cesium Monoxide (g)
Cs_2	Cesium, Dimeric (g)
Cs_2F_2	Cesium Monofluoride, Dimeric (g)
Cs_2O	Dicesium Monoxide (g)
Cu	Copper (ref. st.)
Cu	Copper (c)
Cu	Copper (l)
Cu	Copper (g)
Cu^+	Copper Unipositive Ion (g)
CuF	Copper Monofluoride (c)
CuF	Copper Monofluoride (g)
CuF_2	Copper Difluoride (c)
CuF_2	Copper Difluoride (l)
CuF_2	Copper Difluoride (g)
CuH_2O_2	Copper Dihydroxide (c)
CuO	Copper Monoxide (c)
CuO	Copper Monoxide (g)
CuO_4S	Copper Sulfate (c)
Cu_2	Copper, Diatomic (g)
Cu_2O	Dicopper Monoxide (c)
Cu_2O	Dicopper Monoxide (l)
$\text{Cu}_2\text{O}_5\text{S}$	Copper Oxide Sulfate (c)
F	Fluorine, Monatomic (g)
F^-	Fluorine Uninegative Ion (g)
FFe	Iron Monofluoride (g)
FH	Hydrogen Fluoride (g)
FHO	Hydrogen Oxyfluoride (g)
FH_3Si	Fluorosilane (g)
FHg	Mercurous Fluoride (g)
FI	Iodine Monofluoride (g)

Filing Order	Table Title
FK	Potassium Fluoride (c)
FK	Potassium Fluoride (l)
FK	Potassium Fluoride (g)
FLi	Lithium Fluoride (c)
FLi	Lithium Fluoride (l)
FLi	Lithium Fluoride (g)
FLiO	Lithium Oxyfluoride (g)
FMg	Magnesium Monofluoride (g)
FN	Nitrogen Monofluoride (g)
FNO	Nitrosyl Fluoride (g)
FNO_2	Nitryl Fluoride (g)
FNO_3	Fluorine Nitrate (g)
FNa	Sodium Fluoride (c)
FNa	Sodium Fluoride (l)
FNa	Sodium Fluoride (g)
FO	Fluorine Monoxide (g)
FOti	Titanium Oxyfluoride (g)
FO_2	Monofluorine Dioxide (g)
FP	Phosphorus Monofluoride (g)
FPS	Phosphorus Thiofluoride (g)
FPb	Lead Monofluoride (g)
FSi	Silicon Monofluoride (g)
FTi	Titanium Monofluoride (g)
FW	Tungsten Monofluoride (g)
FZr	Zirconium Monofluoride (g)
F_2	Fluorine, Diatomic (ref.st.,g)
F_2Fe	Iron Difluoride (c)
F_2Fe	Iron Difluoride (l)
F_2Fe	Iron Difluoride (g)
F_2HK	Potassium Bifluoride (c)
F_2HK	Potassium Bifluoride (l)
$\text{F}_2\text{H}_2\text{Si}$	Difluorosilane (g)
F_2Hg	Mercuric Fluoride (c)
F_2Hg	Mercuric Fluoride (l)
F_2Hg	Mercuric Fluoride (g)
F_2Hg_2	Mercurous Fluoride (c)
F_2K^-	Potassium Difluoride Uninegative Ion (g)
F_2K_2	Potassium Fluoride, Dimeric (g)
F_2Li^-	Lithium Difluoride Uninegative Ion (g)
F_2Li_2	Lithium Fluoride, Dimeric (g)
F_2Mg	Magnesium Fluoride (c)
F_2Mg	Magnesium Fluoride (l)
F_2Mg	Magnesium Fluoride (g)
F_2N	Nitrogen Difluoride (g)
F_2N_2	Difluorodiazine, cis- (g)
F_2N_2	Difluorodiazine, trans- (g)
F_2Na^-	Sodium Difluoride Uninegative Ion (g)
F_2Na_2	Sodium Fluoride, Dimeric (g)
F_2O	Oxygen Difluoride (g)
F_2OS	Thionyl Fluoride (g)

Filing Order	Table Title	Filing Order	Table Title
F ₂ OSi	Silicon Oxydifluoride (g)	Fe	Iron (l)
F ₂ OTi	Titanium Oxydifluoride (g)	Fe	Iron (g)
F ₂ O ₂ S	Sulfuryl Fluoride (g)	FeH ₂ O ₂	Iron Dihydroxide (c)
F ₂ P	Phosphorus Difluoride (g)	FeH ₂ O ₂	Iron Dihydroxide (g)
F ₂ Pb	Lead Difluoride (c)	FeH ₃ O ₃	Iron Trihydroxide (c)
F ₂ Pb	Lead Difluoride (l)	FeI ₂	Iron Diiodide (c)
F ₂ Pb	Lead Difluoride (g)	FeI ₂	Iron Diiodide (l)
F ₂ Si	Silicon Difluoride (g)	FeI ₂	Iron Diiodide (g)
F ₂ Ti	Titanium Difluoride (g)	Fe _{0.947} O	Wüstite (c)
F ₂ Zr	Zirconium Difluoride (c)	FeO	Iron Oxide (c)
F ₂ Zr	Zirconium Difluoride (l)	FeO	Iron Oxide (l)
F ₂ Zr	Zirconium Difluoride (g)	FeO	Iron Oxide (g)
F ₃ Fe	Iron Trifluoride (c)	FeO ₄ S	Iron Sulfate (c)
F ₃ Fe	Iron Trifluoride (g)	Fe ₂ I ₄	Iron Diiodide, Dimeric (g)
F ₃ HSi	Trifluorosilane (g)	Fe ₂ O ₃	Hematite (c)
F ₃ Li ₃	Lithium Fluoride, Trimeric (g)	Fe ₂ O ₁₂ S ₃	Diiron Trisulfate (c)
F ₃ N	Nitrogen Trifluoride (g)	Fe ₃ O ₄	Magnetite (c)
F ₃ NO	Trifluoramine Oxide (g)	H	Hydrogen, Monatomic (g)
F ₃ OP	Phosphoryl Fluoride (g)	H ⁺	Proton (g)
F ₃ P	Phosphorus Trifluoride (g)	H ⁻	Hydrogen Uninegative Ion (g)
F ₃ PS	Thiophosphoryl Fluoride (g)	HHg	Mercury Monohydride (g)
F ₃ Si	Silicon Trifluoride (g)	HI	Hydrogen Iodide (g)
F ₃ Ti	Titanium Trifluoride (c)	HK	Potassium Hydride (c)
F ₃ Ti	Titanium Trifluoride (g)	HK	Potassium Hydride (g)
F ₃ Zr	Zirconium Trifluoride (c)	HKO	Potassium Hydroxide (c)
F ₃ Zr	Zirconium Trifluoride (g)	HKO	Potassium Hydroxide (l)
		HKO	Potassium Hydroxide (g)
F ₄ Mg ₂	Magnesium Difluoride, Dimeric (g)	HLi	Lithium Hydride (c)
F ₄ MoO	Molybdenum Oxytetrafluoride (g)	HLi	Lithium Hydride (l)
F ₄ N ₂	Tetrafluorohydrazine (g)	HLi	Lithium Hydride (g)
F ₄ OW	Tungsten Oxytetrafluoride (c)	HLiO	Lithium Hydroxide (c)
F ₄ OW	Tungsten Oxytetrafluoride (l)	HLiO	Lithium Hydroxide (l)
F ₄ OW	Tungsten Oxytetrafluoride (g)	HLiO	Lithium Hydroxide (g)
F ₄ Pb	Lead Tetrafluoride (g)	HMg	Magnesium Monohydride (g)
F ₄ S	Sulfur Tetrafluoride (g)	HMgO	Magnesium Monohydroxide (g)
F ₄ Si	Silicon Tetrafluoride (g)	HMgO ⁺	Magnesium Monohydroxide Unipositive Ion (g)
F ₄ Ti	Titanium Tetrafluoride (c)	HN	Imidogen (g)
F ₄ Ti	Titanium Tetrafluoride (g)	HNO	Nitroxyl (g)
F ₄ Zr	Zirconium Tetrafluoride (c)	HNO ₂	Nitrous Acid, cis- (g)
F ₄ Zr	Zirconium Tetrafluoride (g)	HNO ₂	Nitrous Acid, trans- (g)
F ₅ I	Iodine Pentafluoride (g)	HNO ₃	Nitric Acid (g)
F ₅ P	Phosphorus Pentafluoride (g)	HNa	Sodium Hydride (c)
F ₆ Mo	Molybdenum Hexafluoride (l)	HNa	Sodium Hydride (g)
F ₆ Mo	Molybdenum Hexafluoride (g)	HNaO	Sodium Hydroxide (c)
F ₆ S	Sulfur Hexafluoride (g)	HNaO	Sodium Hydroxide (l)
F ₆ W	Tungsten Hexafluoride (l)	HNaO	Sodium Hydroxide (g)
F ₆ W	Tungsten Hexafluoride (g)	HO	Hydroxyl (g)
F ₇ I	Iodine Heptafluoride (g)	HO ⁺	Hydroxyl Unipositive Ion (g)
		HO ⁻	Hydroxyl Uninegative Ion (g)
Fe	Iron (ref. st.)	HO ₂	Hydroperoxyl (g)
Fe	Iron (c)		

Filing Order	Table Title
HP	Phosphorus Monohydride (g)
HPb	Lead Monohydride (g)
HS	Sulfur Monohydride (g)
HSi	Silicon Monohydride (g)
HZr	Zirconium Hydride (g)
H ₂	Hydrogen, Diatomic (ref. st., g)
H ₂ K ₂ O ₂	Potassium Hydroxide, Dimeric (g)
H ₂ Li ₂ O ₂	Lithium Hydroxide, Dimeric (g)
H ₂ Mg	Magnesium Hydride (c)
H ₂ MgO ₂	Magnesium Dihydroxide (c)
H ₂ MgO ₂	Magnesium Dihydroxide (g)
H ₂ MoO ₄	Molybdic Acid (g)
H ₂ N	Amidogen (g)
H ₂ N ₂	Diimide (g)
H ₂ Na ₂ O ₂	Sodium Hydroxide, Dimeric (g)
H ₂ O	Water (g)
H ₂ O ₂	Hydrogen Peroxide (g)
H ₂ O ₄ S	Sulfuric Acid (l)
H ₂ O ₄ S	Sulfuric Acid (g)
H ₂ O ₄ W	Tungstic Acid (c)
H ₂ O ₄ W	Tungstic Acid (g)
H ₂ P	Phosphorus Hydride (g)
H ₂ S	Hydrogen Sulfide (g)
H ₂ Ti	Titanium Hydride (c)
H ₃ N	Ammonia (g)
H ₃ O ⁺	Hydronium Unipositive Ion (g)
H ₃ O ₄ P	Orthophosphoric Acid (c)
H ₃ O ₄ P	Orthophosphoric Acid (l)
H ₃ P	Phosphine (g)
H ₄ IN	Ammonium Iodide (c)
H ₄ N ₂	Hydrazine (l)
H ₄ N ₂	Hydrazine (g)
H ₄ Si	Silane (g)
Hg	Mercury (ref. st.)
Hg	Mercury (l)
Hg	Mercury, Monatomic (g)
HgI	Mercurous Iodide (g)
HgI ₂	Mercuric Iodide (c)
HgI ₂	Mercuric Iodide (l)
HgI ₂	Mercuric Iodide (g)
HgO	Mercuric Oxide (c)
HgO	Mercury Monoxide (g)
Hg ₂ I ₂	Mercurous Iodide (c)
Hg ₂ I ₂	Mercurous Iodide (l)
I	Iodine, Monatomic (g)
IK	Potassium Iodide (c)
IK	Potassium Iodide (l)
IK	Potassium Iodide (g)

Filing Order	Table Title
ILi	Lithium Iodide (c)
ILi	Lithium Iodide (l)
ILi	Lithium Iodide (g)
INO	Nitrosyl Iodide (g)
INa	Sodium Iodide (c)
INa	Sodium Iodide (l)
IPb	Lead Monoiodide (g)
ITi	Titanium Monoiodide (g)
IZr	Zirconium Monoiodide (g)
I ₂	Iodine (ref. st.)
I ₂	Iodine (l)
I ₂	Iodine, Diatomic (g)
I ₂ K ₂	Potassium Iodide, Dimeric (g)
I ₂ Li ₂	Lithium Iodide, Dimeric (g)
I ₂ Pb	Lead Diiodide (c)
I ₂ Pb	Lead Diiodide (l)
I ₂ Pb	Lead Diiodide (g)
I ₂ Ti	Titanium Diiodide (c)
I ₂ Ti	Titanium Diiodide (g)
I ₂ Zr	Zirconium Diiodide (c)
I ₂ Zr	Zirconium Diiodide (l)
I ₂ Zr	Zirconium Diiodide (g)
I ₃ Ti	Titanium Triiodide (c)
I ₃ Ti	Titanium Triiodide (g)
I ₃ Zr	Zirconium Triiodide (c)
I ₃ Zr	Zirconium Triiodide (g)
I ₄ Pb	Lead Tetraiodide (g)
I ₄ Ti	Titanium Tetraiodide (c)
I ₄ Ti	Titanium Tetraiodide (l)
I ₄ Ti	Titanium Tetraiodide (g)
I ₄ Zr	Zirconium Tetraiodide (c)
I ₄ Zr	Zirconium Tetraiodide (g)
K	Potassium (ref. st.)
K	Potassium (l)
K	Potassium, Monatomic (g)
K ⁺	Potassium Unipositive Ion (g)
KO	Potassium Monoxide (g)
KO ⁻	Potassium Monoxide Uninegative Ion (g)
K ₂	Potassium, Diatomic (g)
K ₂ O	Potassium Oxide (c)
K ₂ O ₂	Potassium Peroxide (c)
Li	Lithium (ref. st.)
Li	Lithium (c)
Li	Lithium (l)
Li	Lithium, Monatomic (g)
Li ⁺	Lithium Unipositive Ion (g)
LiN	Lithium Nitride (g)

Filing Order	Table Title	Filing Order	Table Title
LiNO	Lithium Nitroxide (g)	Mo	Molybdenum (c)
LiNaO	Lithium Sodium Oxide (g)	Mo	Molybdenum (l)
LiO	Lithium Monoxide (g)	Mo	Molybdenum, Monatomic (g)
LiO ⁻	Lithium Monoxide Uninegative Ion (g)	Mo ⁺	Molybdenum Unipositive Ion (g)
Li ₂	Lithium, Diatomic (g)	MoO	Molybdenum Monoxide (g)
Li ₂ O	Lithium Oxide (c)	MoO ₂	Molybdenum Dioxide (c)
Li ₂ O	Lithium Oxide (l)	MoO ₂	Molybdenum Dioxide (g)
Li ₂ O	Lithium Oxide (g)	MoO ₃	Molybdenum Trioxide (c)
Li ₂ O ₂	Lithium Peroxide (c)	MoO ₃	Molybdenum Trioxide (l)
Li ₂ O ₂	Lithium Monoxide, Dimeric (g)	MoO ₃	Molybdenum Trioxide (g)
Li ₂ O ₃ Si	Lithium Metasilicate (c)	N	Nitrogen, Monatomic (g)
Li ₂ O ₃ Si	Lithium Metasilicate (l)	NO	Nitric Oxide (g)
Li ₂ O ₃ Ti	Lithium Metatitanate (c)	NO ⁺	Nitric Oxide Unipositive Ion (g)
Li ₂ O ₃ Ti	Lithium Metatitanate (l)	NO ₂	Nitrogen Dioxide (g)
Li ₂ O ₅ Si ₂	Lithium Disilicate (c)	NO ₂ ⁻	Nitrogen Dioxide Negative Ion (g)
Li ₂ O ₅ Si ₂	Lithium Disilicate (l)	NO ₃	Nitrogen Trioxide (g)
Li ₃ N	Lithium Nitride (c)	NP	Phosphorus Nitride (g)
Mg	Magnesium (ref. st.)	NS	Sulfur Nitride (g)
Mg	Magnesium (c)	NSi	Silicon Nitride (g)
Mg	Magnesium (l)	NSi ₂	Disilicon Nitride (g)
Mg	Magnesium, Monatomic (g)	NTi	Titanium Nitride (c)
Mg ⁺	Magnesium Unipositive Ion (g)	NTi	Titanium Nitride (l)
MgN	Magnesium Nitride (g)	NZr	Zirconium Nitride (c)
MgO	Magnesium Oxide (c)	NZr	Zirconium Nitride (l)
MgO	Magnesium Oxide (l)	NZr	Zirconium Nitride (g)
MgO	Magnesium Oxide (g)	N ₂	Nitrogen (ref. st., g)
MgO ₃ Si	Magnesium Metasilicate (c)	N ₂ O	Dinitrogen Monoxide (g)
MgO ₃ Si	Magnesium Metasilicate (l)	N ₂ O ₃	Dinitrogen Trioxide (g)
MgO ₃ Ti	Magnesium Metatitanate (c)	N ₂ O ₄	Nitrogen Tetroxide (c)
MgO ₃ Ti	Magnesium Metatitanate (l)	N ₂ O ₄	Dinitrogen Tetroxide (l)
MgO ₄ S	Magnesium Sulfate (c)	N ₂ O ₄	Nitrogen Tetroxide (g)
MgO ₄ S	Magnesium Sulfate (l)	N ₂ O ₅	Dinitrogen Pentoxide (g)
MgO ₄ W	Magnesium Tungstate (c)	N ₄ Si ₃	Silicon Nitride (c,α)
MgO ₅ Ti ₂	Magnesium Dtitanate (c)	N ₅ P ₃	Triphosphorus Pentanitride (c)
MgO ₅ Ti ₂	Magnesium Dtitanate (l)	Na	Sodium (ref. st.)
MgS	Magnesium Sulfide (c)	Na	Sodium (c)
MgS	Magnesium Sulfide (g)	Na	Sodium (l)
Mg ₂ O ₄ Si	Magnesium Orthosilicate (c)	Na	Sodium Monatomic (g)
Mg ₂ O ₄ Si	Magnesium Orthosilicate (l)	Na ⁺	Sodium Unipositive Ion (g)
Mg ₂ O ₄ Ti	Magnesium Orthotitanate (c)	NaO	Sodium Monoxide (g)
Mg ₂ O ₄ Ti	Magnesium Orthotitanate (l)	NaO ⁻	Sodium Monoxide Uninegative Ion (g)
Mg ₂ Si	Magnesium Silicide (c)	NaO ₂	Sodium Superoxide (c)
Mg ₂ Si	Magnesium Silicide (l)	Na ₂	Sodium Diatomic (g)
Mg ₃ N ₂	Magnesium Nitride (c)	Na ₂ O	Disodium Monoxide (c)
Mg ₃ O ₈ P ₂	Magnesium Orthophosphate (c)	Na ₂ O	Disodium Monoxide (l)
Mg ₃ O ₈ P ₂	Magnesium Orthophosphate (l)	Na ₂ O ₂	Disodium Dioxide (c)
Mo	Molybdenum (ref. st.)	Na ₂ O ₃ Si	Sodium Metasilicate (c)
		Na ₂ O ₃ Si	Sodium Metasilicate (l)

Filing Order	Table Title
Na ₂ O ₄ S	Sodium Sulfate (c,V)
Na ₂ O ₄ S	Sodium Sulfate (c,III)
Na ₂ O ₄ S	Sodium Sulfate (c,I)
Na ₂ O ₄ S	Sodium Sulfate (c,δ)
Na ₂ O ₄ S	Sodium Sulfate (ℓ)
Na ₂ O ₄ W	Sodium Tungstate (c)
Na ₂ O ₅ Si ₂	Sodium Disilicate (c)
Na ₂ O ₅ Si ₂	Sodium Disilicate (ℓ)
Na ₂ S	Sodium Sulfide (c)
Na ₂ S	Sodium Sulfide (ℓ)
O	Oxygen, Monatomic (g)
O ⁻	Oxygen Uninegative Ion (g)
OP	Phosphorus Monoxide (g)
OPb	Lead Monoxide (c, Red)
OPb	Lead Monoxide (c, Yellow)
OPb	Lead Monoxide (ℓ)
OPb	Lead Monoxide (g)
OS	Sulfur Monoxide (g)
OS ₂	Disulfur Monoxide (g)
OSi	Silicon Monoxide (g)
OTi	Titanium Monoxide (c,α)
OTi	Titanium Monoxide (c,β)
OTi	Titanium Monoxide (ℓ)
OTi	Titanium Monoxide (g)
OW	Tungsten Monoxide (g)
OZr	Zirconium Monoxide (g)
O ₂	Oxygen, Diatomic (ref. st., g)
O ₂ ⁻	Diatomic Oxygen Uninegative Ion (g)
O ₂ P	Phosphorus Dioxide (g)
O ₂ Pb	Lead Dioxide (c)
O ₂ S	Sulfur Dioxide (g)
O ₂ Si	Quartz (c)
O ₂ Si	Cristobalite (c,low)
O ₂ Si	Cristobalite (c,high)
O ₂ Si	Silicon Dioxide (ℓ)
O ₂ Si	Silicon Dioxide (g)
O ₂ Ti	Anatase (c)
O ₂ Ti	Rutile (c)
O ₂ Ti	Titanium Dioxide (ℓ)
O ₂ Ti	Titanium Dioxide (g)
O ₂ W	Tungsten Dioxide (c)
O ₂ W	Tungsten Dioxide (g)
O _{2.72} W	Tungsten Oxide (c)
O _{2.90} W	Tungsten Oxide (c)
O _{2.96} W	Tungsten Oxide (c)
O ₂ Zr	Zirconium Dioxide (c)
O ₂ Zr	Zirconium Dioxide (ℓ)
O ₂ Zr	Zirconium Dioxide (g)

Filing Order	Table Title
O ₃	Ozone (g)
O ₃ PbSi	Lead Metasilicate (c)
O ₃ S	Sulfur Trioxide (g)
O ₃ Ti ₂	Dititanium Trioxide (c)
O ₃ Ti ₂	Dititanium Trioxide (ℓ)
O ₃ W	Tungsten Trioxide (c)
O ₃ W	Tungsten Trioxide (ℓ)
O ₃ W	Tungsten Trioxide (g)
O ₄ Pb ₂ Si	Lead Orthosilicate (c)
O ₄ Pb ₃	Lead Orthoplumbate (c)
O ₄ SiZr	Zirconium Orthosilicate (c)
O ₅ Ti ₃	Trititanium Pentoxide (c,α)
O ₅ Ti ₃	Trititanium Pentoxide (c,β)
O ₅ Ti ₃	Trititanium Pentoxide (ℓ)
O ₆ P ₄	Phosphorus Trioxide, Dimeric (g)
O ₆ W ₂	Tungsten Trioxide, Dimeric (g)
O ₈ W ₃	Tritungsten Octaoxide (g)
O ₉ W ₃	Tungsten Trioxide, Trimeric (g)
O ₁₀ P ₄	Phosphorus Pentoxide, Dimeric (c)
O ₁₀ P ₄	Phosphorus Pentoxide, Dimeric (g)
O ₁₂ W ₄	Tungsten Trioxide, Tetrameric (g)
P	Phosphorus (ref. st.)
P	Phosphorus (c, Red, V)
P	Phosphorus (c, White)
P	Phosphorus (ℓ)
P	Phosphorus (g)
PS	Phosphorus Sulfide (g)
P ₂	Phosphorus, Diatomic (g)
P ₄	Phosphorus, Tetratomic (g)
P ₄ S ₃	Phosphorus Sulfide (c)
P ₄ S ₃	Phosphorus Sulfide (ℓ)
P ₄ S ₃	Phosphorus Sulfide (g)
Pb	Lead (ref. st.)
Pb	Lead (c)
Pb	Lead (ℓ)
Pb	Lead (g)
Pb ₂	Lead, Diatomic (g)
S	Sulfur (ref. st.)
S	Sulfur (c)
S	Sulfur (ℓ)
S	Sulfur, Monatomic (g)
SSi	Silicon Monosulfide (g)
S ₂	Sulfur, Diatomic (g)
S ₂ Si	Silicon Disulfide (c)
S ₂ Si	Silicon Disulfide (ℓ)
S ₈	Sulfur Octatomic (g)

Filing Order	Table Title
Si	Silicon (ref. st.)
Si	Silicon (c)
Si	Silicon (l)
Si	Silicon, Monatomic (g)
Si ₂	Silicon, Diatomic (g)
Si ₃	Silicon, Triatomic (g)
Ti	Titanium (ref. st.)
Ti	Titanium (c,α)
Ti	Titanium (c,β)
Ti	Titanium (l)
Ti	Titanium, Monatomic (g)
Ti ⁺	Titanium Unipositive Ion (g)

Filing Order	Table Title
W	Tungsten (ref. st.)
W	Tungsten (c)
W	Tungsten (l)
W	Tungsten, Monatomic (g)
W ⁺	Tungsten Unipositive Ion
Zr	Zirconium (ref. st.)
Zr	Zirconium (c,α)
Zr	Zirconium (c,β)
Zr	Zirconium (l)
Zr	Zirconium (g)
Zr ⁺	Zirconium Unipositive Ion (g)
e ⁻	Electron Gas (ref. st.)

0 to 933°K. Crystal
933 to 2766.8°K. Liquid
2766.8 to 8000°K. Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	.000	INFINITE	- 1.084	.000	.000	.000
100	3.116	11.530	.988	.000	.000	.000
200	5.136	4.572	.7302	.000	.000	.000
298	5.866	6.769	.611	.000	.000	.000
300	5.814	6.805	.611	.000	.000	.000
400	6.163	6.528	.610	.000	.000	.000
500	6.450	6.334	.610	.000	.000	.000
600	6.717	6.134	.610	.000	.000	.000
700	6.994	5.934	.610	.000	.000	.000
800	7.270	5.734	.610	.000	.000	.000
900	7.546	5.534	.610	.000	.000	.000
1000	7.822	5.334	.610	.000	.000	.000
1100	8.098	5.134	.610	.000	.000	.000
1200	8.374	4.934	.610	.000	.000	.000
1300	8.650	4.734	.610	.000	.000	.000
1400	8.926	4.534	.610	.000	.000	.000
1500	9.202	4.334	.610	.000	.000	.000
1600	9.478	4.134	.610	.000	.000	.000
1700	9.754	3.934	.610	.000	.000	.000
1800	10.030	3.734	.610	.000	.000	.000
1900	10.306	3.534	.610	.000	.000	.000
2000	10.582	3.334	.610	.000	.000	.000
2100	10.858	3.134	.610	.000	.000	.000
2200	11.134	2.934	.610	.000	.000	.000
2300	11.410	2.734	.610	.000	.000	.000
2400	11.686	2.534	.610	.000	.000	.000
2500	11.962	2.334	.610	.000	.000	.000
2600	12.238	2.134	.610	.000	.000	.000
2700	12.514	1.934	.610	.000	.000	.000
2800	12.790	1.734	.610	.000	.000	.000
2900	13.066	1.534	.610	.000	.000	.000
3000	13.342	1.334	.610	.000	.000	.000
3100	13.618	1.134	.610	.000	.000	.000
3200	13.894	.934	.610	.000	.000	.000
3300	14.170	.734	.610	.000	.000	.000
3400	14.446	.534	.610	.000	.000	.000
3500	14.722	.334	.610	.000	.000	.000
3600	14.998	.134	.610	.000	.000	.000
3700	15.274	-.066	.610	.000	.000	.000
3800	15.550	-.266	.610	.000	.000	.000
3900	15.826	-.466	.610	.000	.000	.000
4000	16.102	-.666	.610	.000	.000	.000
4100	16.378	-.866	.610	.000	.000	.000
4200	16.654	-1.066	.610	.000	.000	.000
4300	16.930	-1.266	.610	.000	.000	.000
4400	17.206	-1.466	.610	.000	.000	.000
4500	17.482	-1.666	.610	.000	.000	.000
4600	17.758	-1.866	.610	.000	.000	.000
4700	18.034	-2.066	.610	.000	.000	.000
4800	18.310	-2.266	.610	.000	.000	.000
4900	18.586	-2.466	.610	.000	.000	.000
5000	18.862	-2.666	.610	.000	.000	.000
5100	19.138	-2.866	.610	.000	.000	.000
5200	19.414	-3.066	.610	.000	.000	.000
5300	19.690	-3.266	.610	.000	.000	.000
5400	19.966	-3.466	.610	.000	.000	.000
5500	20.242	-3.666	.610	.000	.000	.000
5600	20.518	-3.866	.610	.000	.000	.000
5700	20.794	-4.066	.610	.000	.000	.000
5800	21.070	-4.266	.610	.000	.000	.000
5900	21.346	-4.466	.610	.000	.000	.000
6000	21.622	-4.666	.610	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1955

Aluminum (Al)

(Crystal) At. Wt. = 26.9815

Al

ALUMINUM (Al)

(CRYSTAL)

AT. WT. = 26.9815

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	INFINITE	1.024	0.000	0.000	INFINITE
100	3.116	1.650	4.756	11.530	1.968	0.000	0.000	0.000
200	5.158	4.756	4.756	7.726	1.000	0.000	0.000	0.000
298	5.686	6.769	6.769	6.769	0.000	0.000	0.000	0.000
300	5.814	6.805	6.769	6.769	0.011	0.000	0.000	0.000
400	6.163	8.528	7.002	7.002	0.610	0.000	0.000	0.000
500	6.450	9.934	7.452	7.452	1.241	0.000	0.000	0.000
600	6.717	11.134	7.968	7.968	1.900	0.000	0.000	0.000
700	6.999	12.190	8.497	8.497	2.585	0.000	0.000	0.000
800	7.370	13.147	9.019	9.019	3.302	0.000	0.000	0.000
900	7.801	14.024	9.526	9.526	4.064	0.000	0.000	0.000
1000	8.430	14.907	10.023	10.023	4.883	0.000	0.000	0.000
1100	8.800	15.728	10.505	10.505	5.746	0.000	0.000	0.000
1200	9.080	16.506	10.973	10.973	6.640	0.000	0.000	0.000
1300	9.350	17.243	11.427	11.427	7.561	0.000	0.000	0.000
1400	9.600	17.945	11.868	11.868	8.509	0.000	0.000	0.000
1500	9.850	18.616	12.295	12.295	9.481	0.000	0.000	0.000

$$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 2.56 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = 78.0 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 6.769 \pm 0.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m^0 = 933^\circ \text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature heat capacity curve is based on the work of N. E. Phillips, *Phys. Rev.* **114**, 676 (1959) in the range 0.1 to 4°K; J. A. Kok and M. H. Keesom, *Physica* **4**, 835 (1937) from 1-20°K. and M. G. Glaue and P. F. Meads, *J. Am. Chem. Soc.* **65**, 1897 (1941). The high temperature enthalpy adopted here is that of R. A. McDonald, private communication, Dow Thermal Research Laboratory, Oct. 1965. This data is in general agreement with the measurements of J. H. Ambery and E. Griffiths, *Proc. Phys. Soc. (London)* **39**, 378 (1926); E. D. Eastman, A. M. Williams and T. F. Young, *J. Am. Chem. Soc.* **46**, 1178 (1924); M. B. Kendall and R. Hultgren, private communication to D. R. Stull from R. L. Orr, Mar. 28, 1960; S. Satoh, *Sci. Papers, Inst. Phys. Chem. Res. (Tokyo)* **29**, 19 (1936); P. Wust, A. Meuthen and R. Durrer, *Forsch. Arb. Ver. deut. Ing. No. 204 (1918). Other investigations have been discussed by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley "Selected Value of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, (1965). These other determinations generally lay below the adopted values.*

Melting Data.

The heat of melting was reported by McDonald, loc. cit., It is in good agreement with the selected value of Hultgren et al, loc. cit. The chosen value also has eliminated uncertainty due to reaction of the liquid aluminum and its vessel by use of BN and TiB₂ containers. The melting point of 933°K. was chosen at the limit of the "well established" 932 ± 1°K., as more likely representing pure aluminum. This choice was based mainly on the work of W. F. Roesser and H. T. Wensel, *J. Res. Natl. Bur. Std.* **14**, 247 (1935).

Sublimation Data.

See Al(g) for details.

At. Wt. = 26.9815

(Liquid)

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100						
200						
298	7.588	8.420	8.420	.000	2.072	1.589
300	7.588	8.467	8.420	-.014	2.075	1.576
400	7.588	10.650	8.718	-.773	2.235	1.386
500	7.588	12.343	9.290	-1.532	2.363	1.198
600	7.588	13.727	9.909	-2.280	2.462	.907
700	7.588	14.896	10.540	-3.049	2.536	.642
800	7.588	15.909	11.149	-3.808	2.578	.402
900	7.588	16.803	11.729	-4.567	2.575	.191
1000	7.588	17.603	12.277	-5.356	2.530	-.022
1100	7.588	18.326	12.795	-6.084	.000	.000
1200	7.588	18.986	13.283	-6.863	.000	.000
1300	7.588	19.594	13.746	-7.602	.000	.000
1400	7.588	20.156	14.184	-8.361	.000	.000
1500	7.588	20.679	14.600	-9.120	.000	.000
1600	7.588	21.169	14.995	-9.878	.000	.000
1700	7.588	21.629	15.372	-10.637	.000	.000
1800	7.588	22.063	15.732	-11.396	.000	.000
1900	7.588	22.473	16.076	-12.155	.000	.000
2000	7.588	22.862	16.405	-12.914	.000	.000
2100	7.588	23.233	16.722	-13.672	.000	.000
2200	7.588	23.585	17.026	-14.431	.000	.000
2300	7.588	23.923	17.318	-15.190	.000	.000
2400	7.588	24.246	17.600	-15.949	.000	.000
2500	7.588	24.555	17.872	-16.708	.000	.000
2600	7.588	24.853	18.135	-17.466	.000	.000
2700	7.588	25.139	18.389	-18.225	.000	.000
2800	7.588	25.415	18.635	-18.984	.000	.000
2900	7.588	25.682	18.874	-19.743	.000	.000
3000	7.588	25.939	19.105	-20.502	.000	.000
3100	7.588	26.188	19.330	-21.260	.000	.000
3200	7.588	26.429	19.548	-22.019	.000	.000
3300	7.588	26.662	19.760	-22.778	.000	.000
3400	7.588	26.889	19.966	-23.537	.000	.000
3500	7.588	27.109	20.167	-24.296	.000	.000
3600	7.588	27.322	20.363	-25.054	.000	.000
3700	7.588	27.530	20.554	-25.813	.000	.000
3800	7.588	27.733	20.740	-26.572	.000	.000
3900	7.588	27.930	20.922	-27.331	.000	.000
4000	7.588	28.122	21.099	-28.090	.000	.000

ALUMINUM (Al)

(LIQUID)

AT. WT. = 26.9815

$$S_{298.15}^{\circ} = 8.42 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = 2.072 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 2.56 \pm 0.05 \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = 69.497 \text{ kcal/mol}$$

$$T_m^{\circ} = 933^{\circ}\text{K}$$

$$T_b^{\circ} = 2766.8^{\circ}\text{K}$$

Heat of Formation

The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between $H_{298.15}^{\circ}$ for (c) and (l).

Heat Capacity and Entropy

The heat capacity is adopted from the enthalpy measurements of R. A. McDonald, private communication, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan, Oct. 1965. The liquid enthalpies were determined in crucibles of BN and TiB₂ sealed in a platinum-rhodium capsule. The liquid enthalpies are in agreement with the determination of J. W. Averbary and E. Griffiths, Proc. Phys. Soc. (London) 38, 378 (1976) and higher, by as much as 12 percent, than those of F. Wust, A. Meuthen and R. Dorrner, Forsch. Arb. Daut. Ing. No 204 (1918) and S. Umino, Sci. Repts. Tohoku. Imp. Univ. Ser. 1, 15, 597 (1926). The enthalpy data is adequately represented by a constant heat capacity. The entropy is calculated from that of the crystal in a manner analogous to the heat of formation.

Melting Data

See Al(c) for details.

Vaporization Data

The temperature of boiling and the heat of vaporization are derived from the adopted functions and the heat of sublimation in order to maintain thermodynamic consistency.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈)/T cal. mole ⁻¹	H° - H ₂₉₈ ΔH _f kcal. mole ⁻¹	Log K _p
0	0.000	INFINITE	77.440	INFINITE
100	6.020	33.385	77.923	163.365
200	5.290	37.231	78.1505	76.134
298	5.112	38.304	78.000	50.063
300	5.111	38.335	77.998	49.710
400	5.047	40.795	77.907	35.513
500	5.016	41.618	77.779	27.006
600	5.002	42.439	77.621	21.345
700	4.997	43.266	77.450	16.293
800	4.997	44.093	77.268	11.793
900	4.993	44.925	76.954	7.342
1000	4.986	45.760	76.516	3.126
1100	4.978	46.595	75.958	0.457
1200	4.976	47.426	75.297	-2.326
1300	4.975	48.256	74.533	-5.010
1400	4.974	49.085	73.675	-7.598
1500	4.973	49.914	72.613	-10.129
1600	4.973	50.743	71.452	-12.617
1700	4.972	51.572	70.193	-15.062
1800	4.972	52.401	68.836	-17.467
1900	4.971	53.230	67.383	-19.838
2000	4.971	54.059	65.836	-22.177
2100	4.971	54.888	64.193	-24.485
2200	4.971	55.717	62.454	-26.759
2300	4.970	56.546	60.620	-28.998
2400	4.970	57.375	58.693	-31.202
2500	4.970	58.204	56.673	-33.372
2600	4.970	59.033	54.560	-35.508
2700	4.970	59.862	52.354	-37.611
2800	4.970	60.691	50.059	-39.682
2900	4.970	61.520	47.678	-41.722
3000	4.971	62.349	45.211	-43.732
3100	4.971	63.178	42.658	-45.713
3200	4.971	64.007	40.019	-47.666
3300	4.971	64.836	37.294	-49.592
3400	4.971	65.665	34.483	-51.492
3500	4.971	66.494	31.586	-53.367
3600	4.971	67.323	28.603	-55.218
3700	4.971	68.152	25.534	-57.045
3800	4.971	68.981	22.380	-58.848
3900	4.971	69.810	19.141	-60.628
4000	4.971	70.639	15.817	-62.385
4100	4.971	71.468	12.408	-64.119
4200	4.971	72.297	8.914	-65.832
4300	4.971	73.126	5.335	-67.525
4400	4.971	73.955	1.670	-69.198
4500	4.971	74.784	-2.000	-70.852
4600	4.971	75.613	-5.535	-72.487
4700	4.971	76.442	-9.035	-74.103
4800	4.971	77.271	-12.500	-75.699
4900	4.971	78.100	-15.935	-77.276
5000	4.971	78.929	-19.340	-78.833
5100	4.971	79.758	-22.715	-80.371
5200	4.971	80.587	-26.060	-81.890
5300	4.971	81.416	-29.375	-83.390
5400	4.971	82.245	-32.660	-84.871
5500	4.971	83.074	-35.915	-86.333
5600	4.971	83.903	-39.140	-87.776
5700	4.971	84.732	-42.335	-89.200
5800	4.971	85.561	-45.500	-90.605
5900	4.971	86.390	-48.635	-92.000
6000	4.971	87.219	-51.740	-93.385

ALUMINUM (Al)

(IDEAL GAS)

AT. WT. = 26.9815

Ground State Configuration $2s^2 2p^6$
 $S_{298.15}^\circ = 39.304$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^\circ 0 = 77.44 \pm 0.9$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = 78.0 \pm 0.9$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ_1 , cm. ⁻¹	g_1	ϵ_1 , cm. ⁻¹	g_1	ϵ_1 , cm. ⁻¹	g_1
0	2	32700	18	42200	12
112	4	37689	2	43600	20
25548	2	38930	10	44430	18
29100	12	40275	6	46130	84
		41319	14		

Heat of Formation.

The heat of sublimation of aluminum has been derived from a second and third law analysis of the vapor pressure data of several investigators; the results are tabulated below.

Ref.	Range °K.	Method	Points	ΔH_{298}° subli. kcal. mole ⁻¹	Drift cal. deg. ⁻¹ mole ⁻¹
1	1273-1473	Knudsen	10*	76.5 ± 2.3	75.32 ± 0.7
2	1734-2237	Boiling	1	85.1 ± 0.3	74.58 ± 1.8
3	1383-1468	Knudsen	10	89.8 ± 32.9	77.29 ± 3.7
4	1410-1468	Knudsen	6	71.9 ± 19.2	78.4 ± 1.3
5	1511-1723	Mass Spec	11	77.2 ± 2	70.5
6	2473	Boiling	1	77.35	77.35
7	1476	Knudsen	1	80.3 ± 1.2	79.5 ± 0.3
8	1400-1611	Torsion	104		-0.3 ± 0.8

*1 point rejected due to failure of statistical test.

References:

1. Yu. A. Priselkov, Yu. A. Sepsnikov and A. V. Tselyuev, *Izv. Akad. Nauk. SSR, Otd. Tech. Nauk.* No. 1, 106 (1959).
2. E. Baur and R. Brunner, *Helv. Chim. Acta*, **17**, 556 (1934).
3. L. Brewer and A. W. Searcy, *J. Am. Chem. Soc.*, **73**, 5308 (1951).
4. Ref. 3 omitting data from TAC cells.
5. R. F. Porter, P. Schissel and M. O. Ingraham, *J. Chem. Phys.*, **23**, 339 (1955).
6. H. von Wartenberg, *Z. Elektrochem.*, **19**, 482 (1913).
7. L. Farkas, *Z. Physik*, **7**, 735 (1931).
8. N. D. Potter, Philco Corporation, Newport Beach, California. Private communication Jan. 11, 1966.

It is apparent that there is little real agreement in the data; in Ref. 3 some of this is due to diffusion of liquid Al through the TAC crucibles, while Ref. 8 reports surface oxidation of the sample. The data for Ref. 5 have been reworked since they corrected their data using ΔC_p between (1) and (g) of -2 cal. deg.⁻¹ mole⁻¹, where our tables give a value of -2.62 cal. deg.⁻¹ mole⁻¹. Ref. 8 has obtained by far the largest number of data points all of which are in good agreement, show no trend and little scatter. Ref. 1 has gone to a great deal of trouble to ensure uniform heating, total collection of effluents and good Knudsen conditions and also has no trend. It is difficult to imagine why these two series differ by a factor of 3 in the pressure. An intermediate value of the heat of sublimation has been adopted at 78 ± 2 kcal. mole⁻¹. This choice is also indicated by the decomposition of AlN(c) to Al(g) and 1/2 N₂(g), which has been well established as 153.7 ± 0.8 kcal. mole⁻¹, combined with the heat of formation of AlN(c) = -76 ± 0.3 kcal. mole⁻¹, to yield ΔH_{sub}° Al = 77.7 ± 0.9 kcal. mole⁻¹.

Heat Capacity and Entropy.

The electronic ground state configuration and the higher electronic levels are taken from C. E. Moore, *Natl. Bur. Stds. Circular* 467, "Atomic Energy Levels" Washington 1949.

Ground State Configuration $1s^2$
 $\Delta H_f^0 = 215.4 \pm .5$ kcal/mole
 $\Delta H_f^{298.15} = 217.3 \pm .5$ kcal/mole
 $S_{298.15}^0 = 35.813$ cal. deg.⁻¹ mole⁻¹

Electronic Levels and Quantum Weight

E_i , cm. ⁻¹	g_i	E_i , cm. ⁻¹	g_i
0.0	1	94084.5	1
37592.0	1	94146.8	3
37453.8	3	94267.7	5
37579.3	5	95348.2	1
5849.7	3	95546.8	7
85479.0	5	95547.9	5
91271.2	3	95548.8	3

Heat of Formation.

The heat of formation was calculated from the equation: $Al(g) - e^- \rightarrow Al^+(g)$ with the JANAP auxiliary value for $Al(g)$ using an I.P. = 4.827916 X 10⁴ cm.⁻¹ (138.047 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1×10^5 cm.⁻¹ were omitted because their contribution is negligible below 8000°K. The $H^\circ - H_{298}^\circ$ value at 0°K. is -1.481 kcal./mole.

T, °K.	C _v	S°	-(F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF°	Log K _p
0							
100	4.968	35.613	0.000	217.300	207.153	-151.840	
200	4.968	35.613	0.000	217.307	207.090	-150.858	
300	4.968	35.613	0.009	217.307	207.090	-150.858	
400	4.968	35.613	0.036	217.307	207.090	-150.858	
500	4.968	35.613	0.103	217.307	207.090	-150.858	
600	4.968	35.613	0.208	217.307	207.090	-150.858	
700	4.968	35.613	0.346	217.307	207.090	-150.858	
800	4.968	35.613	0.516	217.307	207.090	-150.858	
900	4.968	35.613	0.720	217.307	207.090	-150.858	
1000	4.968	35.613	0.960	217.307	207.090	-150.858	
1100	4.968	35.613	1.236	217.307	207.090	-150.858	
1200	4.968	35.613	1.550	217.307	207.090	-150.858	
1300	4.968	35.613	1.903	217.307	207.090	-150.858	
1400	4.968	35.613	2.296	217.307	207.090	-150.858	
1500	4.968	35.613	2.730	217.307	207.090	-150.858	
1600	4.968	35.613	3.206	217.307	207.090	-150.858	
1700	4.968	35.613	3.726	217.307	207.090	-150.858	
1800	4.968	35.613	4.282	217.307	207.090	-150.858	
1900	4.968	35.613	4.876	217.307	207.090	-150.858	
2000	4.968	35.613	5.510	217.307	207.090	-150.858	
2100	4.968	35.613	6.186	217.307	207.090	-150.858	
2200	4.968	35.613	6.906	217.307	207.090	-150.858	
2300	4.968	35.613	7.672	217.307	207.090	-150.858	
2400	4.968	35.613	8.486	217.307	207.090	-150.858	
2500	4.968	35.613	9.350	217.307	207.090	-150.858	
2600	4.968	35.613	10.266	217.307	207.090	-150.858	
2700	4.968	35.613	11.236	217.307	207.090	-150.858	
2800	4.968	35.613	12.262	217.307	207.090	-150.858	
2900	4.968	35.613	13.346	217.307	207.090	-150.858	
3000	4.968	35.613	14.490	217.307	207.090	-150.858	
3100	4.968	35.613	15.696	217.307	207.090	-150.858	
3200	4.968	35.613	16.966	217.307	207.090	-150.858	
3300	4.968	35.613	18.302	217.307	207.090	-150.858	
3400	4.968	35.613	19.706	217.307	207.090	-150.858	
3500	4.968	35.613	21.180	217.307	207.090	-150.858	
3600	4.968	35.613	22.726	217.307	207.090	-150.858	
3700	4.968	35.613	24.346	217.307	207.090	-150.858	
3800	4.968	35.613	26.042	217.307	207.090	-150.858	
3900	4.968	35.613	27.816	217.307	207.090	-150.858	
4000	4.968	35.613	29.670	217.307	207.090	-150.858	
4100	4.968	35.613	31.606	217.307	207.090	-150.858	
4200	4.968	35.613	33.626	217.307	207.090	-150.858	
4300	4.968	35.613	35.732	217.307	207.090	-150.858	
4400	4.968	35.613	37.926	217.307	207.090	-150.858	
4500	4.968	35.613	40.210	217.307	207.090	-150.858	
4600	4.968	35.613	42.586	217.307	207.090	-150.858	
4700	4.968	35.613	45.056	217.307	207.090	-150.858	
4800	4.968	35.613	47.622	217.307	207.090	-150.858	
4900	4.968	35.613	50.286	217.307	207.090	-150.858	
5000	4.968	35.613	53.050	217.307	207.090	-150.858	
5100	4.968	35.613	55.916	217.307	207.090	-150.858	
5200	4.968	35.613	58.886	217.307	207.090	-150.858	
5300	4.968	35.613	61.962	217.307	207.090	-150.858	
5400	4.968	35.613	65.146	217.307	207.090	-150.858	
5500	4.968	35.613	68.440	217.307	207.090	-150.858	
5600	4.968	35.613	71.846	217.307	207.090	-150.858	
5700	4.968	35.613	75.366	217.307	207.090	-150.858	
5800	4.968	35.613	78.994	217.307	207.090	-150.858	
5900	4.968	35.613	82.734	217.307	207.090	-150.858	
6000	4.968	35.613	86.588	217.307	207.090	-150.858	

Aluminum Boron Dioxide (AlBO₂)
(Ideal Gas) GFW = 69.7913

T, °K	Cp ^a	gibbs/mol S ^b - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈ kcal/mol	ΔHf°	Log Kp
0	∞	INFINITE	-2.670	-128.809	INFINITE
100	8.336	53.455	2.068	-128.832	263.792
200	10.455	59.955	1.577	-129.103	142.020
298	12.627	64.420	1.000	-129.400	95.436
300	12.663	64.498	0.923	-129.406	95.851
400	14.289	68.377	1.376	-129.685	72.260
500	15.445	71.697	2.866	-129.970	58.074
600	16.294	74.592	4.464	-130.271	48.596
700	16.936	77.154	6.117	-130.587	41.809
800	17.432	79.449	7.837	-130.927	36.707
900	17.821	81.526	9.600	-131.306	32.727
1000	18.129	83.420	11.398	-131.723	29.493
1100	18.377	85.160	13.224	-132.176	26.823
1200	18.578	86.768	15.072	-132.662	24.591
1300	18.743	88.261	16.938	-133.176	22.697
1400	18.879	89.655	18.820	-133.718	21.068
1500	18.993	90.962	20.713	-134.280	19.654
1600	19.089	92.191	22.618	-134.862	18.412
1700	19.171	93.351	24.531	-135.468	17.313
1800	19.240	94.448	26.451	-136.093	16.333
1900	19.300	95.490	28.379	-136.734	15.453
2000	19.353	96.482	30.311	-137.394	14.659
2100	19.398	97.427	32.249	-138.071	13.939
2200	19.438	98.330	34.191	-138.762	13.281
2300	19.473	99.195	36.136	-139.464	12.679
2400	19.504	100.025	38.085	-140.186	12.125
2500	19.531	100.821	40.037	-140.922	11.605
2600	19.556	101.588	41.991	-141.672	11.113
2700	19.578	102.326	43.948	-142.436	10.657
2800	19.598	103.039	45.907	-143.214	10.233
2900	19.616	103.727	47.868	-144.006	9.838
3000	19.632	104.392	49.830	-144.812	9.462
3100	19.647	105.036	51.794	-145.632	9.107
3200	19.660	105.660	53.759	-146.464	8.771
3300	19.673	106.265	55.726	-147.308	8.454
3400	19.684	106.853	57.694	-148.164	8.154
3500	19.694	107.423	59.663	-149.032	7.871
3600	19.704	107.978	61.633	-149.912	7.604
3700	19.713	108.518	63.603	-150.804	7.354
3800	19.721	109.044	65.575	-151.708	7.114
3900	19.728	109.557	67.548	-152.624	6.884
4000	19.735	110.056	69.521	-153.552	6.664
4100	19.742	110.544	71.495	-154.492	6.454
4200	19.748	111.019	73.469	-155.444	6.254
4300	19.753	111.484	75.444	-156.408	6.064
4400	19.759	111.938	77.420	-157.384	5.884
4500	19.763	112.382	79.396	-158.372	5.714
4600	19.768	112.817	81.372	-159.372	5.554
4700	19.772	113.242	83.349	-160.384	5.404
4800	19.776	113.658	85.327	-161.408	5.264
4900	19.780	114.066	87.305	-162.444	5.134
5000	19.784	114.468	89.283	-163.492	5.014
5100	19.787	114.858	91.261	-164.552	4.904
5200	19.790	115.242	93.240	-165.624	4.804
5300	19.793	115.619	95.220	-166.708	4.714
5400	19.796	115.989	97.199	-167.804	4.634
5500	19.799	116.352	99.179	-168.912	4.554
5600	19.801	116.709	101.159	-170.032	4.484
5700	19.804	117.059	103.139	-171.164	4.424
5800	19.806	117.404	105.120	-172.308	4.364
5900	19.808	117.742	107.100	-173.464	4.314
6000	19.810	118.075	109.081	-174.632	4.264

June 30, 1966

ALUMINUM BORON DIOXIDE (AlBO₂)
(IDEAL GAS) OFW = 69.7913

Point Group [C_{2v}]
S°_{298.15} = [64.4] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf° = -128.8 ± 4 kcal/mol
ΔHf°_{298.15} = -129.4 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Bond Distances: Al-O = [1.66] Å O-B = [1.36] Å B-O = [1.20] Å
Bond Angle: Al-O-B = [145]° O-B-O = [180]°

Product of the Moments of Inertia: I_AI_BI_C = [6.65357] X 10⁻¹¹⁵ g³ cm⁶ σ = 1

Heat of Formation.

The heat of formation, ΔHf°₂₉₈ (AlBO₂, g) = -129.4 ± 4 kcal/mol, was calculated from the heat of reaction, ΔH°₁₅₀₀ = -14.7 ± 3.2 kcal/mol for 1/2 Al₂O₃(g) + 1/2 B₂O₃(g) = AlBO₂(g), with all JANAF auxiliary data. The value of ΔH°₁₅₀₀ was obtained from the mass spectrometric determination of ion intensity ratios by A. Buchler, P. E. Blackburn and J. L. Stauffer, "Thermodynamics of Vaporization in the Aluminum Oxide-Boron Oxide System," ARPA Order No 315-62, Arthur D. Little, Inc., Cambridge, Mass.

Heat Capacity and Entropy.

The bent molecular structure, the bond distances O-B and B-O, and the bond angle O-B-O were assumed to be the same as those in LiBO₂(g). The bond distance Al-O and the bond angle Al-O-B were estimated to be the same as those in Al₂O(g). The three principal moments of inertia are I_A = 0.7255 X 10⁻³⁹, I_B = 29.9238 X 10⁻³⁹, and I_C = 30.6495 X 10⁻³⁹ g cm².

The vibrational frequencies were estimated by comparison with those in LiBO₂(g), Al₂O(g), B₂O₃(g), and AlCl(g).

AlBO₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	INFINITE	- 2.287	5.337	INFINITE
100	7.225	44.631	64.496	5.597	3.371
200	8.092	53.926	58.013	5.817	2.669
298	8.509	57.246	57.246	5.800	2.447
300	8.514	57.299	57.246	5.808	2.443
400	8.710	59.778	57.463	5.766	2.459
500	8.816	61.734	58.224	5.755	2.461
600	8.881	63.347	58.948	5.733	2.456
700	8.926	64.677	59.677	5.716	2.450
800	8.965	65.800	60.400	5.700	2.443
900	8.986	66.871	61.058	5.685	2.437
1000	9.009	67.919	61.667	5.672	2.431
1100	9.028	68.778	62.302	5.656	2.420
1200	9.042	69.520	62.871	5.641	2.411
1300	9.052	70.166	63.385	5.627	2.403
1400	9.078	70.962	63.933	5.613	2.396
1500	9.092	71.588	64.423	5.600	2.390
1600	9.106	72.176	64.869	5.587	2.384
1700	9.119	72.726	65.276	5.575	2.378
1800	9.130	73.244	65.651	5.563	2.372
1900	9.146	73.744	66.167	5.551	2.366
2000	9.158	74.213	66.558	5.540	2.360
2100	9.171	74.650	66.933	5.528	2.354
2200	9.183	75.056	67.288	5.516	2.348
2300	9.196	75.436	67.627	5.504	2.342
2400	9.208	75.887	67.947	5.492	2.336
2500	9.220	76.264	68.301	5.480	2.330
2600	9.232	76.625	68.615	5.468	2.324
2700	9.244	76.974	68.918	5.456	2.318
2800	9.256	77.312	69.206	5.444	2.312
2900	9.267	77.635	69.486	5.432	2.306
3000	9.279	77.950	69.773	5.420	2.300
3100	9.291	78.254	70.042	5.408	2.294
3200	9.303	78.549	70.303	5.396	2.288
3300	9.314	78.834	70.556	5.384	2.282
3400	9.326	79.114	70.805	5.372	2.276
3500	9.338	79.385	71.046	5.360	2.270
3600	9.349	79.648	71.281	5.348	2.264
3700	9.351	79.904	71.511	5.336	2.258
3800	9.362	80.154	71.734	5.324	2.252
3900	9.364	80.398	71.944	5.312	2.246
4000	9.366	80.635	72.156	5.300	2.240
4100	9.407	80.867	72.378	5.288	2.234
4200	9.410	81.094	72.592	5.276	2.228
4300	9.412	81.316	72.800	5.264	2.222
4400	9.442	81.533	72.979	5.252	2.216
4500	9.453	81.745	73.172	5.240	2.210
4600	9.465	81.953	73.360	5.228	2.204
4700	9.478	82.154	73.543	5.216	2.198
4800	9.488	82.354	73.727	5.204	2.192
4900	9.499	82.552	73.905	5.192	2.186
5000	9.511	82.744	74.080	5.180	2.180
5100	9.522	82.933	74.252	5.168	2.174
5200	9.534	83.118	74.420	5.156	2.168
5300	9.546	83.300	74.584	5.144	2.162
5400	9.557	83.478	74.749	5.132	2.156
5500	9.568	83.653	74.910	5.120	2.150
5600	9.579	83.826	75.067	5.108	2.144
5700	9.591	83.996	75.222	5.096	2.138
5800	9.602	84.164	75.375	5.084	2.132
5900	9.614	84.337	75.525	5.072	2.126
6000	9.625	84.488	75.673	5.060	2.120

Dec. 31, 1961, Sept. 30, 1964

Ground State Configuration $1\sum^+$
 $S_{298.15}^0 = 57.246$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 = 5.3 \pm 5.0$ kcal. mole⁻¹
 ΔH_f^0 298.15 = 3.6 ± 5.0 kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ_l , cm. ⁻¹	g_l
0	1

$\omega_e = 377.40$ cm.⁻¹
 $\omega_e x_e = 1.276$ cm.⁻¹
 $B_e = 0.1586$ cm.⁻¹
 $r_e = 2.295$ Å

Heat of Formation.

S. A. Semakovich, Zh. Fizik, Khim. 50, 933 (1957) measured the vapor pressure of the reaction $Al(l) + NaBr(l) \rightarrow Na(l) + AlBr(g)$ at 1175°K. By the third law method the heat of reaction (ΔH_f^0 298.15) was evaluated to be 108.31 kcal. mole⁻¹. The value of ΔH_f^0 298.15 for $AlBr(g)$ was calculated as 3.6 ± 5.0 kcal. mole⁻¹. Based on this value the dissociation energy (D_0) was derived to be 4.3 ± 0.2 e.v. which is in excellent agreement with the value, $D_0 = 4.3 \pm 0.2$ e.v., reported by A. G. Daydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The dissociation energy (D_0) of $AlBr(g)$ was reported to be 2.4 e.v. and 105 kcal. mole⁻¹ (4.55 e.v.) by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950 and R. P. Barrow, Trans. Faraday Soc. 56, 952 (1960), respectively. However, using these D_0 values, the corresponding values of ΔH_f^0 298.15 for $AlBr(g)$ were found to be 48.55 and -1.11 kcal. mole⁻¹. The adopted value was calculated from the vapor pressure data reported by S. A. Semakovich, loc. cit.

Heat Capacity and Entropy.

The spectroscopic constants were taken from G. Herzberg, loc. cit. and corrected to the average isotopic species.

Aluminum Boron Dioxide (AlBO₂)
(Ideal Gas) GFW = 69.7913

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o ₂₉₈)/T	H ^o - H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	-0.00	INFINITE	-2.870	-128.809	-128.809	INFINITE
100	8.336	53.455	2.068	-128.832	-128.832	283.792
200	10.453	59.825	1.137	-129.103	-130.789	142.920
298	12.627	64.420	0.000	-129.400	-131.560	96.436
300	12.663	64.498	0.023	-129.406	-131.574	95.851
400	14.226	68.457	1.816	-129.483	-132.400	58.074
500	15.495	71.657	2.866	-129.970	-132.862	58.074
600	16.294	74.592	4.454	-130.271	-133.413	48.596
700	16.936	77.154	6.117	-130.587	-133.912	41.809
800	17.432	79.459	8.053	-130.927	-134.365	36.707
900	17.819	81.486	10.262	-131.289	-134.783	32.285
1000	18.119	83.420	12.821	-131.666	-135.165	29.493
1100	18.377	85.160	15.738	-132.062	-135.504	26.823
1200	18.578	86.708	19.027	-132.476	-135.801	24.591
1300	18.740	88.083	22.697	-132.905	-136.056	22.656
1400	18.879	89.295	26.753	-133.357	-136.278	21.057
1500	18.993	90.362	31.213	-133.832	-136.469	19.654
1600	19.089	91.291	36.055	-134.329	-136.629	18.412
1700	19.171	92.091	41.281	-134.836	-136.762	17.313
1800	19.240	92.765	46.895	-135.353	-136.869	16.345
1900	19.299	93.321	52.800	-135.880	-136.942	15.493
2000	19.353	93.765	58.911	-136.416	-136.983	14.750
2100	19.398	94.107	65.234	-136.961	-137.000	14.113
2200	19.438	94.350	71.775	-137.516	-137.000	13.577
2300	19.473	94.500	78.531	-138.083	-137.000	13.125
2400	19.504	94.565	85.499	-138.661	-137.000	12.750
2500	19.531	94.551	92.672	-139.250	-137.000	12.445
2600	19.556	94.468	100.045	-139.850	-136.933	12.199
2700	19.578	94.318	107.612	-140.461	-136.772	12.005
2800	19.598	94.107	115.369	-141.083	-136.528	11.857
2900	19.616	93.832	123.317	-141.726	-136.200	11.743
3000	19.632	93.500	131.456	-142.390	-135.804	11.655
3100	19.647	93.118	139.785	-143.075	-135.336	11.587
3200	19.660	92.690	148.304	-143.781	-134.804	11.536
3300	19.671	92.225	156.911	-144.506	-134.216	11.493
3400	19.684	91.725	165.604	-145.250	-133.572	11.457
3500	19.694	91.195	174.381	-146.013	-132.875	11.427
3600	19.704	90.633	183.241	-146.794	-132.125	11.401
3700	19.713	90.045	192.183	-147.592	-131.325	11.378
3800	19.721	89.431	201.206	-148.406	-130.475	11.357
3900	19.728	88.792	210.310	-149.236	-129.578	11.337
4000	19.735	88.128	219.494	-150.081	-128.635	11.317
4100	19.742	87.440	228.757	-150.941	-127.648	11.297
4200	19.749	86.728	238.099	-151.816	-126.618	11.277
4300	19.755	86.000	247.519	-152.706	-125.548	11.257
4400	19.761	85.257	256.916	-153.611	-124.431	11.237
4500	19.767	84.500	266.390	-154.530	-123.268	11.217
4600	19.768	83.728	275.939	-155.463	-122.061	11.197
4700	19.776	82.937	285.562	-156.410	-120.811	11.177
4800	19.781	82.128	295.259	-157.371	-119.518	11.157
4900	19.784	81.300	305.030	-158.346	-118.183	11.137
5000	19.784	80.456	314.874	-159.334	-116.808	11.117
5100	19.787	79.598	324.791	-160.335	-115.393	11.097
5200	19.787	78.728	334.780	-161.348	-113.938	11.077
5300	19.789	77.847	344.840	-162.373	-112.443	11.057
5400	19.793	76.956	354.971	-163.410	-110.908	11.037
5500	19.799	76.056	365.174	-164.458	-109.333	11.017
5600	19.801	75.147	375.449	-165.517	-107.718	10.997
5700	19.806	74.229	385.794	-166.587	-106.063	10.977
5800	19.810	73.303	396.209	-167.667	-104.368	10.957
5900	19.814	72.370	406.694	-168.757	-102.633	10.937
6000	19.818	71.430	417.249	-169.856	-100.858	10.917

June 30, 1966

ALUMINUM BORON DIOXIDE (AlBO₂) (IDEAL GAS)

QPW = 69.7913

AlBO₂

Point Group [C₃]
S_{298.15} = [64.4] gibbs/mol
Ground State Quantum Weight = [1]
ΔH_f^o = -128.8 ± 4 kcal/mol
ΔH_f^o_{298.15} = -129.4 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω _h , cm ⁻¹	ω _h , cm ⁻¹
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Bond Distances: Al-O = [1.66] Å O-B = [1.36] Å B-O = [1.20] Å
Bond Angle: Al-O-B = [145]° O-B-O = [180]°
Product of the Moments of Inertia: I_AI_BI_C = [6.65357] X 10⁻¹¹⁵ g³ cm⁶
σ = 1

Heat of Formation.

The heat of formation, ΔH_f^o₂₉₈ (AlBO₂, g) = -129.4 ± 4 kcal/mol, was calculated from the heat of reaction, ΔH_f^o₁₅₀₀ = -14.7 ± 3.2 kcal/mol for 1/2 Al₂O₃(g) + 1/2 B₂O₃(g) = AlBO₂(g), with all JANAF auxiliary data. The value of ΔH_f^o₁₅₀₀ was obtained from the mass spectrometric determination of ion intensity ratios by A. Büchler, F. E. Blackburn and J. L. Stauffer, "Thermodynamics of Vaporization in the Aluminum Oxide-Boron Oxide System," ARPA Order No 315-62, Arthur D. Little, Inc., Cambridge, Mass.

Heat Capacity and Entropy.

The bent molecular structure, the bond distances O-B and B-O, and the bond angle O-B-O were assumed to be the same as those in LiBO₂(g). The bond distance Al-O and the bond angle Al-O-(B-O) were estimated to be the same as those in Al₂O(g). The three principal moments of inertia are I_A = 0.7255 X 10⁻³⁵, I_B = 29.9238 X 10⁻³⁵, and I_C = 30.6493 X 10⁻³⁵ g cm².

The vibrational frequencies were estimated by comparison with those in LiBO₂(g), Al₂O(g), B₂O₃(g), and AlCl(g).

AlBO₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	-0.000	INFINITE	-2.287	5.337	5.337	INFINITE
100	7.223	48.631	1.586	5.597	3.371	-
200	8.092	53.026	0.817	5.330	2.442	2.669
298	8.509	57.246	0.000	3.600	6.026	4.417
300	8.514	57.299	0.016	3.568	6.086	4.433
400	8.778	61.718	0.865	3.459	6.199	4.459
500	8.816	64.734	1.755	3.458	10.573	4.621
600	8.881	63.347	2.640	3.673	12.576	4.580
700	8.926	64.720	3.530	3.816	14.541	4.540
800	8.959	65.914	4.425	3.862	16.462	4.500
900	8.984	66.941	5.321	3.899	18.341	4.459
1000	9.009	67.919	6.222	4.307	20.035	4.378
1100	9.028	68.778	7.124	4.556	21.596	4.290
1200	9.046	69.565	8.027	4.804	23.134	4.213
1300	9.062	70.289	8.933	5.051	24.651	4.148
1400	9.077	70.952	9.842	5.298	26.148	4.092
1500	9.092	71.596	10.748	5.542	27.631	4.026
1600	9.106	72.176	11.648	5.787	29.096	3.974
1700	9.120	72.728	12.549	6.031	30.545	3.927
1800	9.133	73.250	13.452	6.274	31.981	3.882
1900	9.146	73.750	14.357	6.514	33.401	3.838
2000	9.158	74.213	15.211	6.757	34.809	3.804
2100	9.171	74.660	16.028	6.998	36.207	3.768
2200	9.183	75.087	16.845	7.238	37.592	3.734
2300	9.196	75.496	17.664	7.476	38.963	3.702
2400	9.208	75.887	18.485	7.711	40.320	3.672
2500	9.220	76.264	19.306	7.955	41.665	3.644
2600	9.232	76.625	20.028	8.192	43.028	3.617
2700	9.244	76.974	20.757	8.429	44.366	3.591
2800	9.256	77.310	21.522	8.671	45.687	3.567
2900	9.267	77.633	22.320	8.916	46.991	3.543
3000	9.279	77.950	23.111	9.163	48.278	3.520
3100	9.291	78.254	23.942	9.411	49.549	3.498
3200	9.303	78.549	24.769	9.659	50.804	3.476
3300	9.314	78.836	25.597	9.906	52.043	3.455
3400	9.325	79.116	26.420	10.153	53.267	3.434
3500	9.338	79.385	27.245	10.400	54.476	3.413
3600	9.349	79.648	28.066	10.646	55.671	3.393
3700	9.361	79.904	28.884	10.891	56.852	3.373
3800	9.372	80.154	29.698	11.135	58.019	3.353
3900	9.383	80.400	30.509	11.378	59.173	3.333
4000	9.396	80.635	31.316	11.620	60.314	3.313
4100	9.407	80.867	32.117	11.861	61.442	3.293
4200	9.419	81.094	32.915	12.101	62.557	3.273
4300	9.430	81.316	33.710	12.340	63.659	3.253
4400	9.441	81.535	34.502	12.578	64.749	3.233
4500	9.453	81.745	35.292	12.815	65.826	3.213
4600	9.465	81.953	36.076	13.051	66.891	3.193
4700	9.476	82.157	36.856	13.286	67.943	3.173
4800	9.488	82.356	37.632	13.519	68.983	3.153
4900	9.499	82.552	38.406	13.751	70.011	3.133
5000	9.511	82.744	39.176	13.981	71.027	3.113
5100	9.522	82.933	39.942	14.210	72.031	3.093
5200	9.534	83.118	40.706	14.438	73.023	3.073
5300	9.547	83.299	41.467	14.665	74.003	3.053
5400	9.558	83.476	42.232	14.891	74.971	3.033
5500	9.568	83.653	43.000	15.116	75.927	3.013
5600	9.579	83.826	43.764	15.340	76.871	3.000
5700	9.591	83.996	44.522	15.563	77.803	2.987
5800	9.602	84.162	45.275	15.785	78.723	2.973
5900	9.613	84.324	46.024	16.006	79.631	2.959
6000	9.625	84.488	46.767	16.226	80.527	2.945

Dec. 31, 1961; Sept. 30, 1964

ALUMINUM MONOBROMIDE (AlBr)

MOL. WT. = 106.896

Ground State Configuration $1\sum^+$
 $\Delta H_f^0 = 5.3 \pm 5.0$ kcal. mole⁻¹
 $\Delta H_f^0(298.15) = 57.246$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0(298.15) = 3.6 \pm 5.0$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

E_i , cm. ⁻¹	g_i
0	1

$\omega_e = 377.40$ cm.⁻¹
 $\sigma = 1$
 $\nu_e = 2.295 \text{ Å}$
 $\omega_e = 0.1586$ cm.⁻¹
 $\omega_e = 0.000849$ cm.⁻¹

Heat of Formation.

S. A. Semenovitch, Zh. Fizik, Khim. **50**, 933 (1957) measured the vapor pressure of the reaction $Al(1) + NaBr(1) \rightarrow Na(g) + AlBr(g)$ at 1175°K. By the third law method the heat of reaction ($\Delta H_f^0(298.15)$) was evaluated to be 108.31 kcal. mole⁻¹. The value of $\Delta H_f^0(298.15)$ for AlBr(g) was calculated as 3.6 ± 5.0 kcal. mole⁻¹. Based on this value the dissociation energy (D_0^0) was derived to be 4.3 ± 0.2 e.v. which is in excellent agreement with the value, $D_0 = 4.3 \pm 0.2$ e.v., reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The dissociation energy (D_0^0) of AlBr(g) was reported to be 2.4 e.v. and 105 kcal. mole⁻¹ (4.55 e.v.) by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950 and R. P. Barrow, Trans. Faraday Soc. **56**, 952 (1960), respectively. However, using these D_0^0 values, the corresponding values of $\Delta H_f^0(298.15)$ for AlBr(g) were found to be 48.55 and -1.11 kcal. mole⁻¹. The adopted value was calculated from the vapor pressure data reported by S. A. Semenovitch, loc. cit.

Heat Capacity and Entropy.

The spectroscopic constants were taken from G. Herzberg, loc. cit. and corrected to the average isotopic species.

AlBr

Aluminum Tribromide (AlBr₃)
(Crystal) $\text{GFW} = 266.7085$

AlBr₃

$\text{GFW} = 266.7085$

(CRYSTAL)

ALUMINUM TRIBROMIDE (AlBr₃)

$\Delta H_f^\circ = -121.4 \pm 3 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = -126.0 \pm 3 \text{ kcal/mol}$
 $\Delta H_m^\circ = 2.69 \text{ kcal/mol}$

$S_{298.15}^\circ = 43.08 \pm 0.25 \text{ gibbs/mol}$

$T_m = 370.6^\circ\text{K}$

Heat of Formation

The value of ΔH_{298}° for AlBr₃(c) is that selected by the National Bureau of Standards (1). The methods and auxiliary data used to obtain their value are not given. Their result is apparently based on the heats of reaction of aqueous solutions of AlBr₃ measured by Berthelot (2).

Heat Capacity and Entropy

The heat capacity of AlBr₃(c) has been measured from 11.6° to 308.1°K by Justice (3) and the enthalpy from 337° to 367°K by Fischer (4). The heat capacities used are derived from curve fits of these data. The Cp values above 370.6°K are obtained by graphical extrapolation. Justice (3) reported the value of $S_{298}^\circ = 0.951 \text{ eu}$.

Melting Data

Fischer (4) determined the melting temperature (T_m) of AlBr₃(c). The heat of melting (ΔH_m°) is calculated from the enthalpies of AlBr₃(c) and AlBr₃(l) at the melting temperature. The enthalpy of the crystal at the melting point was determined from the curve used for the heat capacity calculations. The enthalpy of the liquid at the melting point was determined from a linear least squares fit to the enthalpy data for AlBr₃(l) reported by Fischer (4).

References

1. U. S. Natl. Bur. Std. Tech. Note 270-2, 1966.
2. M. P. E. Berthelot, Ann. Chim. Phys. (5) 15, 185 (1878).
3. B. H. Justice, The Dow Chemical Co., Midland, Michigan, Quarterly Progress Report AFPRPL-TR-66, 175, October, 1966, Contract AFOW611-11201.
4. W. Fischer, Z. Anorg. Chem. 200, 332 (1931).

T, °K	Cp°	S°	$-(C_p^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	kcal/mol ΔH°	ΔG°	Log Kp
0	16.927	0.000	INFINITE	-5.239	-121.355	-121.355	INFINITE
100	16.927	20.655	62.555	-4.190	-121.416	-121.386	265.288
200	21.499	33.990	45.185	-2.239	-121.663	-121.277	132.526
298	24.040	43.075	43.075	-0.000	-126.000	-120.553	86.368
300	24.097	43.224	43.075	-0.045	-126.016	-120.514	87.798
370	28.150	50.702	46.067	2.684	-126.325	-116.513	61.660
500	29.400	57.190	46.061	5.565	-135.410	-111.659	48.806
600	29.700	62.597	48.380	8.530	-134.436	-107.002	38.875
700	29.720	67.167	50.677	14.591	-132.597	-94.352	22.913
800	29.760	70.524	52.963	17.449	-131.711	-83.889	22.799
900	29.780	73.651	55.263	20.426	-133.417	-89.546	16.570
1000	29.800	76.627	57.349	23.405	-132.550	-85.203	16.928
1100	29.820	83.220	61.232	29.386	-131.663	-80.727	14.411
1200	29.840	87.820	63.710	32.354	-129.948	-72.615	11.336
1300	29.860	89.831	66.320	35.341	-129.082	-68.552	9.988

AlBr₃

T, °K	C _p ^a	S ^b	-(G ^c -H ^{nas})/T	H ^c -H ^{nas}	ΔH ^c	ΔG ^c	Log K _p
0							
100	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
200	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
300	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
400	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
500	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
600	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
700	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
800	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
900	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
1000	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
1100	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
1200	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
1300	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
1400	29.869	58.130	49.352	.000	-123.633	-120.057	88.004
1500	29.869	58.130	49.352	.000	-123.633	-120.057	88.004

ALUMINUM TRIBROMIDE (AlBr₃)

(LIQUID)

GFW = 266.7085

S_{298.15}^a = 49.352 gibbs/molΔH_{f298.15}^a = -123.633 ± 3 kcal/molT_m = 370.6°KΔH_m^a = 2.68 kcal/molT_b = 529°K (to dimer gas)ΔH_v^a = 5.92 kcal/mol (to dimer gas)

Heat of Formation

The heat of formation (ΔH_{f298}^a) of AlBr₃(l) is calculated from ΔH_{f298}^a of AlBr₃(c) plus the heat of melting (ΔH_m^a) and the enthalpy differences (H₂₉₈^a - H₂₉₈^a) of the crystal and liquid.

Heat Capacity and Entropy

Fischer (1) has measured the enthalpy of AlBr₃(l) from 371° to 406°K. The heat capacity used is derived from a linear least squares fit to his data. The resulting constant value for the heat capacity is adopted for temperatures above 406°K. The entropy (S₂₉₈^a) of AlBr₃(2) was determined in a manner analogous to that for the heat of formation.

Melting Data

See AlBr₃(c) table for details.

Vaporization Data

The heat of vaporization (ΔH_v^a) of AlBr₃(l) is determined from the work of Fischer et al. (2). The boiling temperature (T_b) was calculated from their vapor pressure data. See Al₂Br₆(g) table for details.

References

1. W. Fischer, Z. Anorg. Chem., 200, 332 (1931).
2. W. Fischer, O. Rahlfs and R. B. Benze, Z. Anorg. Chem., 205, 1, (1932).

Aluminum Tribromide (AlBr₃)

(Ideal Gas) GFW = 266.7085

AlBr₃

ALUMINUM TRIBROMIDE (AlBr₃)

(IDEAL GAS)

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Log Kp

ΔG°

ΔH°

H°-H°₂₉₈

S°

ΔG°

ΔH°

ΔG°

ΔH°

Point Group [D_{3h}]

Ground State Configuration $1s^2 2s^2 2p^6 3s^2 3p^2$

GFW = 62.4345

$$\Delta H_f^\circ = -12.34 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -12.30 \pm 1.0 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 54.455 \pm 0.02 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weight

ϵ_1 , cm ⁻¹	0	24541	24615	24680
ϵ_2	1	2	2	2
ω_e	480.0 cm ⁻¹			
$\omega_e x_e$	1.94 cm ⁻¹			
B_e	0.24262 cm ⁻¹			
α_e	0.00159 cm ⁻¹			
r_e	2.1298 Å			

Heat of Formation

Equilibrium constants as a function of temperature for the reaction $2\text{Al}(t) + \text{AlCl}_3(g) + 3\text{AlCl}(g)$ have been reported by many investigators. The data were subjected to second and third law analyses with results as follows (Alr at 298.15°K refers to $2\text{Al}(c) + \text{AlCl}_3(g) \rightarrow 3\text{AlCl}(g)$):

Investigator(s)	Temp. Range °K	Number of Data Points	$\Delta H_{298.15}^\circ$, kcal/mol, AlCl_3	Drift eu
Rao and Dadage (1)	1125-1425	11	102.3±1.6	102.8±0.8
Frisch et al. (2)	931-1034	8	99.7±1.1	106.7±0.5
Gross et al. (3)	1225-1278	7	a	109.7±2.6
Ginsberg et al. (4)	1423-1500	8	91.4±1.8	104.7±0.8
Semenkovich (5)	1223-1473	6	89.2±0.4	98.5±1.3
Heingartner (6)	978-1383	13	58.8±2.5	100.0±9.5
Weiss (7)	1273-1473	3	93.1±3.4	86.3±1.2
Pinchuk et al. (8)	1173-1373	3	86.0±7.5	95.0±1.9
Mitani et al. (9)	1273-1473	b	88.9	99.1±2.1
Kikuchi et al. (10)	1273-1523	b	78.7	98.7±5.0
Tanabe et al. (11)	1173-1573	b	93.3	94.6±0.5
Russell et al. (12)	1388	1	103.8	

a. Temperature range too small for significant second law calculation.

b. These data available only as equations as given in Chemical Abstracts.

Unfortunately, most of the data are very discordant and of no help in defining $\Delta H_f^\circ(\text{AlCl}_3, g)$. The results of Rao and Dadage (1) cover a temperature range of 300°K, show good compatibility with the thermodynamic functions, are near an average of all the data, and are judged most acceptable. The third-law heat of reaction derived from their data is adopted and combined with the heat of formation of $\text{AlCl}_3(g)$ to give $\Delta H_f^\circ(298.15^\circ\text{K})$ for $\text{AlCl}(g)$.

Gross et al. (3) reported equilibrium constants for the reaction of aluminum with sodium chloride and potassium chloride and Pinchuk et al. (8) determined equilibrium constants for reaction of aluminum with sodium chloride and magnesium chloride. The results of Pinchuk et al. (8) are suspect in that the partial pressures of sodium and magnesium chlorides they calculate from their data exceed the saturation pressures calculated from JANAF data. The data of Gross et al. (3) were recalculated to allow for effects of dimer in sodium chloride and potassium chloride vapors (JANAF data):

Reaction	T , °K	$K_p(\text{atm})^2$	$\Delta H_{298.15}^\circ$, kcal/mol
$\text{NaCl}(s) + \text{Al}(t) + \text{AlCl}_3(g) \rightleftharpoons \text{Na}(g) + \text{AlCl}(g)$	1043	4.178×10^{-10}	-12.7 ± 1.0
$\text{KCl}(s) + \text{Al}(t) + \text{AlCl}_3(g) \rightleftharpoons \text{K}(g) + \text{AlCl}(g)$	1243	1.138×10^{-6}	-13.6 ± 1.5
$\text{KCl}(s) + \text{Al}(t) + \text{AlCl}_3(g) \rightleftharpoons \text{K}(g) + \text{AlCl}(g)$	1023	6.14×10^{-11}	-13.1 ± 1.5

The result for $\text{NaCl}(s)$ is the average of 12 experiments whereas the $\text{NaCl}(t)$ and $\text{KCl}(s)$ are based on 5 and 3 experiments, respectively, and the $\text{NaCl}(s)$ value is considered the most reliable. The derived heat of formation is in good agreement with the value selected on the basis of the Rao and Dadage data.

Barrow (13) has compared thermochemical and spectroscopic dissociation energies for monohalides of B, Al, Ga, In, and Tl. A short extrapolation of vibrational levels gives $D_0 = 124.1$ kcal/mol for AlCl while predissociation indicates $D_0 \leq 120.1$ kcal/mol. The maximum predissociation value gives $\Delta H_f^\circ(298.15^\circ\text{K})$ for $\text{AlCl}(g) = -14.1$ kcal/mol, in reasonable agreement with the selected value. Barrow (13) speculates that a potential maximum occurs in the A'' state of AlF and AlCl which causes extrapolation of vibrational levels to give erroneous heats of dissociation.

Heat Capacity and Entropy

The vibrational frequency and anharmonicity constants were taken from Herzberg (14) and the structural constants are based on microwave spectroscopy by Lide (15). The electronic levels were reported by Sharma (16).

References

1. D. A. Rao and V. V. Dadage, *J. Phys. Chem.*, **70**, 1349 (1966).
2. M. A. Frisch, M. A. Greenbaum, and M. J. P. Cantow, *J. Phys. Chem.*, **69**, 3001 (1965).
3. P. Gross, C. S. Campbell, P. J. C. Kent, and D. L. Levi, *Discuss. Faraday Soc.*, **4**, 206 (1948).
4. H. Ginsberg and V. Sparwald, *Aluminum*, **41**, 219 (1965).
5. S. A. Semakovich, *Zh. Prikl. Khim.*, **33**, 1781 (1960).
6. P. Heingartner, *Schweiz. Arch. Angew. Wiss. Tech.*, **18**, 241 (1952).
7. Y. M. Pinchuk and H. Nagai, *Nippon Kinzoku Gakkaishi*, **31**, 214 (1960).
8. Y. M. Pinchuk and H. Nagai, *Nippon Kinzoku Gakkaishi*, **31**, 214 (1960).
9. I. Tanabe, H. Kono, Y. Sawada, and T. Takahashi, *Trans. Japan Inst. Metals*, **12**, 71 (1964).
10. I. Tanabe, H. Kono, Y. Sawada, and T. Takahashi, *Denki Kagaku*, **32**, 285 (1964); *CA*, **62**, 4957f.
11. A. P. Russell, *Trans. Faraday Soc.*, **56**, 952 (1960).
12. G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed., Van Nostrand, New York, 1950.
13. D. R. Lide, Jr., *J. Chem. Phys.*, **42**, 1013 (1965).
14. D. Sharma, *Astrophys. J.*, **133**, 210 (1961).

T, °K	Cp°	S°	-G°-H° ₂₉₈ /T	H°-H° ₂₉₈	ΔH°	Log Kp
0	0.000	INFINITE	INFINITE	2.228	12.337	INFINITE
100	7.057	46.141	61.435	1.531	12.094	31.222
200	7.776	51.245	56.199	1.000	12.156	16.006
298	8.263	54.455	54.455	0.000	12.300	15.744
300	8.290	54.507	54.455	-0.015	12.303	13.959
400	8.559	56.932	54.764	1.659	12.473	20.690
500	8.773	58.860	55.413	1.723	12.667	11.932
600	8.902	60.416	56.124	2.599	12.884	9.002
700	8.965	61.619	56.483	3.463	13.125	6.326
800	8.910	63.005	54.371	4.371	13.356	28.584
900	8.945	64.057	56.207	5.264	13.710	7.397
1000	8.974	65.001	58.840	6.160	16.594	7.021
1100	8.998	65.857	59.460	7.059	16.903	6.688
1200	9.016	66.641	60.009	7.960	17.211	6.406
1300	9.037	67.363	60.546	8.862	17.518	6.162
1400	9.054	68.034	61.057	9.767	17.824	5.950
1500	9.070	68.659	61.543	10.673	18.130	5.763
1600	9.085	69.245	62.007	11.581	18.435	5.597
1700	9.099	69.796	62.449	12.490	18.739	5.447
1800	9.113	70.317	62.872	13.401	19.042	5.312
1900	9.126	70.810	63.277	14.313	19.345	5.190
2000	9.139	71.278	63.665	15.226	19.648	5.078
2100	9.152	71.724	64.038	16.161	19.950	4.975
2200	9.165	72.150	64.397	17.097	20.252	4.880
2300	9.177	72.558	64.743	17.974	20.553	4.791
2400	9.190	72.949	65.077	18.892	20.854	4.709
2500	9.202	73.324	65.400	19.812	21.155	4.633
2600	9.215	73.685	65.711	20.733	21.456	4.561
2700	9.228	74.033	66.013	21.737	21.757	4.494
2800	9.242	74.369	66.306	22.806	22.058	4.436
2900	9.256	74.694	66.589	23.950	22.359	4.380
3000	9.271	75.008	66.865	24.429	22.660	4.329
3100	9.287	75.312	67.132	25.387	22.961	4.283
3200	9.304	75.607	67.393	26.297	23.262	4.240
3300	9.323	75.894	67.646	27.216	23.563	4.198
3400	9.343	76.173	67.893	28.151	23.864	4.158
3500	9.364	76.444	68.133	29.107	24.165	4.120
3600	9.386	76.708	68.368	30.084	24.466	4.084
3700	9.409	76.965	68.597	31.092	24.767	4.049
3800	9.441	77.217	68.820	32.130	25.068	4.016
3900	9.472	77.462	69.039	32.653	25.369	3.984
4000	9.504	77.703	69.252	33.602	25.670	3.953
4100	9.539	77.938	69.461	34.584	25.971	3.923
4200	9.577	78.168	69.661	35.600	26.272	3.894
4300	9.618	78.394	69.866	36.649	26.573	3.866
4400	9.661	78.615	70.062	37.633	26.874	3.839
4500	9.707	78.833	70.255	38.602	27.175	3.813
4600	9.756	79.047	70.444	39.575	27.476	3.788
4700	9.807	79.257	70.629	40.552	27.777	3.764
4800	9.862	79.464	70.811	41.536	28.078	3.741
4900	9.919	79.668	70.990	42.525	28.379	3.718
5000	9.978	79.869	71.165	43.520	28.680	3.696
5100	10.040	80.067	71.336	44.521	28.981	3.675
5200	10.105	80.262	71.502	45.526	29.282	3.655
5300	10.171	80.456	71.675	46.542	29.583	3.636
5400	10.240	80.647	71.839	47.563	29.884	3.618
5500	10.311	80.835	72.001	48.590	30.185	3.601
5600	10.385	81.022	72.160	49.625	30.486	3.585
5700	10.462	81.208	72.316	50.666	30.787	3.570
5800	10.534	81.389	72.472	51.716	31.088	3.556
5900	10.611	81.570	72.625	52.774	31.389	3.543
6000	10.689	81.749	72.775	53.839	31.690	3.531

June 30, 1961; Sept. 30, 1964; June 30, 1970

Aluminum Monochloride Unipositive Ion (AlCl⁺)

(Ideal Gas) GFW = 62.4339

ALUMINUM MONOCHLORIDE UNIPOSITIVE ION (AlCl⁺) (IDEAL GAS) GFW = 62.4339

T, °K	Cp°	gibbs/mol S° - (C°-H° ₂₉₈)/T	kcal/mol H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0						
100						
200						
298	8.317	56.004	56.004	.000	196.777	- 144.242
300	8.324	56.056	56.004	.015	196.726	- 143.315
350	8.382	56.489	56.336	.862	193.917	- 105.951
400	8.426	56.921	56.965	1.728	191.026	- 83.497
500	8.615	62.021	57.678	2.405	205.922	- 68.076
600	8.674	63.384	58.398	3.490	206.179	- 66.507
700	8.918	64.572	59.097	4.380	206.405	- 65.080
800	8.952	65.625	59.765	5.273	206.589	- 63.734
900	8.979	66.589	60.399	6.170	206.720	- 62.466
1000	9.002	67.426	61.009	7.069	204.391	- 58.487
1100	9.023	68.210	61.568	7.970	204.580	- 54.429
1200	9.041	68.933	62.107	8.873	204.770	- 50.403
1300	9.058	69.604	62.619	9.778	204.961	- 46.415
1400	9.074	70.229	63.106	10.685	205.153	- 42.461
1500	9.088	70.815	63.570	11.593	205.345	- 38.541
1600	9.103	71.367	64.012	12.503	205.538	- 34.652
1700	9.116	71.887	64.438	13.414	205.732	- 30.793
1800	9.129	72.381	64.841	14.326	205.926	- 26.965
1900	9.142	72.849	65.230	15.239	206.120	- 23.167
2000	9.155	73.296	65.603	16.154	206.315	- 19.398
2100	9.167	73.722	65.963	17.070	206.510	- 15.650
2200	9.180	74.130	66.309	17.988	206.706	- 11.921
2300	9.192	74.521	66.642	18.906	206.902	- 8.212
2400	9.204	74.896	66.966	19.826	207.098	- 4.523
2500	9.216	75.257	67.278	20.747	207.295	- 0.834
2600	9.228	75.605	67.580	21.669	207.491	2.865
2700	9.240	75.941	67.872	22.593	207.687	5.616
2800	9.252	76.266	68.156	23.517	207.883	8.367
2900	9.264	76.579	68.432	24.443	208.079	11.118
3000	9.277	76.883	68.699	25.370	208.275	13.869
3100	9.289	77.178	68.960	26.298	208.471	16.620
3200	9.302	77.464	69.213	27.228	208.667	19.371
3300	9.315	77.742	69.460	28.159	208.863	22.122
3400	9.329	78.012	69.701	29.091	209.059	24.873
3500	9.343	78.275	69.935	30.025	209.255	27.624
3600	9.358	78.531	70.164	30.960	209.451	30.375
3700	9.373	78.781	70.387	31.896	209.647	33.126
3800	9.388	79.025	70.606	32.834	209.843	35.877
3900	9.402	79.263	70.819	33.774	210.039	38.628
4000	9.422	79.495	71.028	34.715	210.235	41.379
4100	9.440	79.722	71.234	35.658	210.431	44.130
4200	9.458	79.945	71.432	36.603	210.627	46.881
4300	9.477	80.162	71.628	37.550	210.823	49.632
4400	9.497	80.376	71.820	38.499	211.019	52.383
4500	9.518	80.585	72.009	39.449	211.215	55.134
4600	9.540	80.790	72.193	40.402	211.411	57.885
4700	9.563	81.001	72.374	41.357	211.607	60.636
4800	9.586	81.186	72.552	42.315	211.803	63.387
4900	9.611	81.362	72.727	43.275	212.000	66.138
5000	9.636	81.573	72.899	44.237	212.196	68.889
5100	9.662	81.760	73.067	45.202	212.392	71.640
5200	9.688	81.944	73.233	46.169	212.588	74.391
5300	9.716	82.116	73.396	47.140	212.784	77.142
5400	9.744	82.304	73.556	48.113	212.980	79.893
5500	9.773	82.480	73.714	49.088	213.176	82.644
5600	9.803	82.653	73.869	50.067	213.372	85.395
5700	9.833	82.824	74.022	51.049	213.568	88.146
5800	9.864	82.992	74.173	52.034	213.764	90.897
5900	9.896	83.156	74.321	53.022	213.960	93.648
6000						

June 30, 1968; June 30, 1970

Ground State Configuration [2]
S^{298.15} = [56.0 ± 0.5] gibbs/mol
ΔH_f^{298.15} = 205 ± 10 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[2]
[26000]	[4]
$\omega_e = [465]$ cm ⁻¹	$\omega_e x_e = [2]$ cm ⁻¹
$B_e = [0.2273]$ cm ⁻¹	$B_e = [0.0013]$ cm ⁻¹
$\sigma = 1$	$\tau_e = [2.2]$ Å

Heat of Formation

D. L. Hildenbrand, E. Murad, L. P. Theard and F. Ju, Aeronutronic Report No. U-3187, July 30, 1965, under contract AF 04(611)-10743, reported an appearance potential of 9.4 ± 0.4eV for AlCl⁺. They suggested that the magnitude of the value indicated formation by direct ionization of AlCl(g).

R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960), obtained an appearance potential of 19.7 ± 0.5eV for AlCl⁺ which they attributed to formation from AlCl₃(g). Assuming the process to be AlCl₃(g) + e⁻ → AlCl⁺(g) + 2Cl(g) + 2e⁻ ΔH = 454 kcal, one obtains ΔH_f²⁹⁸(AlCl⁺) = 257 kcal/mol, or an ionization potential of 11.6eV. This would almost certainly represent an upper limit, since the fragments could easily contain excess kinetic energy.

We adopt the ionization potential of 9.4 ± 0.4eV obtained by Hildenbrand et al., which yields ΔH_f²⁹⁸(AlCl⁺, g) = 205 ± 10 kcal/mol.

Heat Capacity and Entropy

AlCl⁺ is isoelectronic with MgCl, and the electronic configuration of the ground state and first excited state are estimated to be those for MgCl. The vibrational frequency, anharmonicity constant and bond length are estimated by comparison with those for MgCl and AlCl. The rotational constant is calculated from the bond length and atomic masses, and σ_e is calculated from the other constants assuming a Morse potential function. The enthalpy at 0°K is -2.236 kcal/mol.

AlCl⁺

Aluminum Chloride Difluoride (AlClF₂)

(Ideal Gas) Mol Wt. = 100.437

AlClF₂

MOL. WT. = 100.437

ALUMINUM CHLORIDE DIFLUORIDE (AlClF₂) (IDEAL GAS)

Point Group C_{2v}
 $\Delta H_f^\circ = [-235.8 \pm 20] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = [71.242] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = [-237.6 \pm 20] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 298.15$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[500] (1)	[250] (1)
[280] (1)	[800] (1)
[200] (1)	[900] (1)

Bond Distances: Al-F = [1.65] Å Al-Cl = [2.14] Å

Bond Angle: Cl-Al-F = [120]° F-Al-F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = 1.47245 \times 10^{-113} \text{ g. cm.}^2$

$\sigma^- = 2$

Heat of Formation.

The value of ΔH_f° 298.15 was calculated based on an assumption that $\Delta H_f^\circ = 0$ for the reaction $\text{AlCl}_3(\text{g}) + 2\text{AlF}_3(\text{g}) = 3\text{AlClF}_2(\text{g})$. The values of ΔH_f° 298.15 for $\text{AlF}_3(\text{g})$ and $\text{AlCl}_3(\text{g})$ used for calculation are -286.5 and -139.7 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for $\text{AlF}_2(\text{g})$ and $\text{AlCl}_3(\text{g})$. The bond distances of Al-F and Al-Cl atoms were assumed to be the same as those in $\text{AlF}_3(\text{g})$ and $\text{AlCl}_3(\text{g})$, respectively. The bond angles and ground state quantum weight were estimated by comparison with those for $\text{AlF}_3(\text{g})$. The three principal moments of inertia are 1.28827×10^{-38} , 2.79746×10^{-38} and $4.08573 \times 10^{-38} \text{ g. cm.}^2$.

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	-3.531	-236.830	-236.830	INFINITE
100	10.400	57.062	83.716	2.666	-236.329	-236.329	516.471
200	13.670	65.385	72.616	1.446	-237.399	-237.399	257.262
298	15.663	71.242	60.000	0.000	-237.600	-237.600	171.837
300	15.693	71.339	60.000	0.000	-237.603	-237.603	170.763
400	16.593	76.046	51.875	1.668	-237.766	-237.766	127.479
500	17.816	79.933	43.105	3.412	-237.883	-237.883	101.494
600	18.349	83.232	34.529	5.222	-237.976	-237.976	84.163
700	18.757	86.032	26.076	7.096	-238.069	-238.069	71.777
800	19.086	88.446	18.846	8.986	-238.162	-238.162	62.483
900	19.334	90.847	12.776	10.865	-238.255	-238.255	55.248
1000	19.566	92.871	8.046	12.785	-238.348	-238.348	49.418
1100	19.766	94.712	5.133	14.717	-238.441	-238.441	44.628
1200	19.944	96.400	3.000	16.657	-238.534	-238.534	40.633
1300	20.100	97.954	1.666	18.600	-238.627	-238.627	37.248
1400	20.234	99.408	1.000	20.548	-238.720	-238.720	34.353
1500	20.354	100.757	0.577	22.515	-238.813	-238.813	31.839
1600	20.462	102.023	0.313	24.476	-238.906	-238.906	29.638
1700	20.560	103.213	0.166	26.441	-239.000	-239.000	27.695
1800	20.648	104.334	0.086	28.406	-239.093	-239.093	25.983
1900	20.727	105.402	0.046	30.376	-239.186	-239.186	24.422
2000	20.798	106.413	0.023	32.346	-239.279	-239.279	23.029
2100	20.861	107.375	0.013	34.319	-239.372	-239.372	21.769
2200	20.916	108.293	0.006	36.292	-239.465	-239.465	20.623
2300	20.963	109.166	0.003	38.265	-239.558	-239.558	19.581
2400	21.002	110.011	0.001	40.242	-239.651	-239.651	18.615
2500	21.034	110.818	0.000	42.219	-239.744	-239.744	17.731
2600	21.078	111.594	0.000	44.197	-239.837	-239.837	16.915
2700	21.114	112.341	0.000	46.175	-239.930	-239.930	16.156
2800	21.151	113.060	0.000	48.152	-240.023	-240.023	15.446
2900	21.188	113.755	0.000	50.133	-240.116	-240.116	14.781
3000	21.226	114.426	0.000	52.113	-240.209	-240.209	14.164
3100	21.266	115.075	0.000	54.093	-240.302	-240.302	13.594
3200	21.306	115.705	0.000	56.074	-240.395	-240.395	13.067
3300	21.346	116.314	0.000	58.055	-240.488	-240.488	12.581
3400	21.386	116.903	0.000	60.037	-240.581	-240.581	12.134
3500	21.426	117.480	0.000	62.019	-240.674	-240.674	11.726
3600	21.466	118.038	0.000	64.001	-240.767	-240.767	11.356
3700	21.506	118.576	0.000	66.000	-240.860	-240.860	11.021
3800	21.546	119.111	0.000	68.000	-240.953	-240.953	10.719
3900	21.586	119.629	0.000	70.000	-241.046	-241.046	10.446
4000	21.626	120.127	0.000	72.000	-241.139	-241.139	10.201
4100	21.666	120.617	0.000	74.000	-241.232	-241.232	9.981
4200	21.706	121.094	0.000	76.000	-241.325	-241.325	9.781
4300	21.746	121.562	0.000	78.000	-241.418	-241.418	9.601
4400	21.786	122.016	0.000	80.000	-241.511	-241.511	9.440
4500	21.826	122.464	0.000	82.000	-241.604	-241.604	9.296
4600	21.866	122.900	0.000	84.000	-241.697	-241.697	9.167
4700	21.906	123.327	0.000	86.000	-241.790	-241.790	9.051
4800	21.946	123.744	0.000	88.000	-241.883	-241.883	8.946
4900	21.986	124.154	0.000	90.000	-241.976	-241.976	8.851
5000	22.026	124.554	0.000	92.000	-242.069	-242.069	8.766
5100	22.066	124.948	0.000	94.000	-242.162	-242.162	8.691
5200	22.106	125.334	0.000	96.000	-242.255	-242.255	8.626
5300	22.146	125.711	0.000	98.000	-242.348	-242.348	8.571
5400	22.186	126.082	0.000	100.000	-242.441	-242.441	8.526
5500	22.226	126.446	0.000	102.000	-242.534	-242.534	8.491
5600	22.266	126.804	0.000	104.000	-242.627	-242.627	8.466
5700	22.306	127.157	0.000	106.000	-242.720	-242.720	8.441
5800	22.346	127.503	0.000	108.000	-242.813	-242.813	8.426
5900	22.386	127.840	0.000	110.000	-242.906	-242.906	8.411
6000	22.426	128.174	0.000	112.000	-243.000	-243.000	8.401

AlClF₂

Aluminum Oxide Chloride (AlOCl)
(Crystal) Mol. Wt. = 78.437

ALUMINUM OXIDE CHLORIDE (AlOCl) (CRYSTAL) MOL. WT. = 78.437

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ Kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
100						
200						
298	13.600	13.000	+0.00	-189.600	-176.208	129.158
300	13.650	13.084	+0.025	-189.600	-176.126	128.301
400	15.370	14.298	+1.025	-189.600	-175.850	125.300
500	16.540	20.858	14.674	-189.519	-187.201	73.080
600	17.360	23.952	15.968	-189.089	-162.799	59.297
700	17.970	26.676	17.307	-188.836	-158.437	49.464
800	18.710	29.684	18.653	-188.575	-154.113	42.100
900	19.480	32.384	19.977	-188.312	-149.830	36.716
1000	19.940	34.273	21.157	-188.058	-145.571	31.769
1100	19.143	35.088	22.342	-190.232	-140.868	27.886
1200	19.290	36.760	23.475	-189.484	-136.395	24.840
1300	19.400	38.100	24.557	-189.527	-131.953	22.182
1400	19.450	39.250	25.595	-189.527	-127.642	19.840
1500	19.598	41.102	26.581	-188.797	-123.148	17.942
1600	19.650	42.369	27.529	-188.427	-118.783	16.224
1700	19.703	43.862	28.437	-188.054	-114.441	14.712
1800	19.783	44.758	29.307	-187.682	-110.123	13.370
1900	19.810	46.773	30.161	-187.312	-105.832	12.106
2000	19.829	47.740	31.730	-186.937	-101.544	11.006
2100	19.829	47.740	31.730	-186.565	-97.285	10.124
2200	19.840	48.663	32.479	-186.196	-93.042	9.242
2300	19.850	49.595	33.202	-185.829	-88.816	8.439
2400	19.850	50.539	33.909	-185.466	-84.616	7.709
2500	19.852	51.200	34.576	-185.107	-80.410	7.029
2600	19.852	51.979	35.231	-184.750	-76.230	6.407
2700	19.850	52.728	35.865	-184.398	-72.063	5.833
2800	19.850	53.440	36.480	-184.050	-67.916	5.311
2900	19.850	54.120	37.080	-183.706	-63.786	4.840
3000	19.850	54.820	37.658	-183.366	-59.670	4.419

Mar. 31, 1964

ΔH_f^o 0 = Unknown

S_{298.15} = [13 ± 1] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = -189.6 ± 0.3 kcal. mole⁻¹

ΔH_m^o = Unknown

T_m = Unknown

T_d = [500]°K.

Heat of Formation.

The heat of formation (ΔH_f^o 298.15) for AlOCl(c) was calculated from ΔH_f^o 298 = 21.05 kcal. mole⁻¹ for the reaction AlOCl(c) + Cl₂(g) = AlCl₃(c) + 1/2 O₂(g) reported by H. Schafer, F. E. Wittig, and W. Wilborn, Z. anorg. allgem. Chem. 297, 48 (1958). This reaction is the overall reaction of the following four separate reactions.

Chemical Reaction	ΔH _f ^o 298, kcal. mole ⁻¹
AlOCl(c) + 2(HCl·299.5 H ₂ O) = AlCl ₃ ·600 H ₂ O(l)	-46.9
AlCl ₃ ·600 H ₂ O(l) = AlCl ₃ (c) + 600 H ₂ O(l)	+79.3
H ₂ (g) + Cl ₂ (g) = 2(HCl·299.5 H ₂ O)	-79.67
H ₂ O(l) = H ₂ (g) + 1/2 O ₂ (g)	+68.32
AlOCl(c) + Cl ₂ (g) = AlCl ₃ (c) + 1/2 O ₂ (g)	+21.05

Heat Capacity and Entropy.

The heat capacities for AlOCl(c) were estimated based on the assumption that ΔC_p = 0 for the reaction AlCl₃(c) + Al₂O₃(c) = 3AlOCl(c). S_{298.15} was estimated by H. Schafer, F. E. Wittig, and W. Wilborn, loc. cit.

Temperature of Decomposition.

T_d is estimated as the temperature at which the free energy change of the reaction 6AlOCl(c) → 3Al₂O₃(c) + Al₂Cl₆(g) approaches zero.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.749	48.785	68.944	- 82.698	- 82.698	INFINITE
200	10.774	55.633	80.520	- 82.800	- 83.178	181.778
298	11.907	59.471	83.430	- 83.030	- 83.478	91.216
300	11.989	59.545	83.471	- 83.203	- 83.667	90.948
400	12.935	63.135	90.054	- 83.320	- 83.802	45.785
500	13.511	66.089	96.095	- 83.415	- 83.912	36.676
600	13.877	68.587	101.976	- 83.512	- 84.003	30.596
700	14.120	70.745	106.768	- 83.626	- 84.076	26.248
800	14.288	72.642	110.516	- 83.763	- 84.131	22.083
900	14.409	74.333	113.194	- 83.927	- 84.167	20.438
1000	14.498	75.855	114.866	- 84.114	- 84.189	18.357
1100	14.565	77.241	116.429	- 84.320	- 84.193	16.635
1200	14.617	78.510	117.892	- 84.545	- 84.185	15.198
1300	14.658	79.682	119.264	- 84.788	- 84.169	13.931
1400	14.691	80.769	120.558	- 85.048	- 84.137	12.816
1500	14.718	81.784	121.784	- 85.322	- 84.091	11.830
1600	14.740	82.736	122.951	- 85.609	- 84.033	11.235
1700	14.758	83.629	124.064	- 85.908	- 83.965	10.533
1800	14.774	84.473	125.129	- 86.218	- 83.888	9.908
1900	14.787	85.272	126.154	- 86.538	- 83.803	9.348
2000	14.798	86.031	127.138	- 86.866	- 83.711	8.844
2100	14.808	86.753	128.079	- 87.202	- 83.613	8.386
2200	14.816	87.442	128.984	- 87.545	- 83.510	7.970
2300	14.824	88.101	129.851	- 87.892	- 83.404	7.599
2400	14.830	88.732	130.684	- 88.242	- 83.295	7.240
2500	14.836	89.339	131.489	- 88.596	- 83.183	6.918
2600	14.841	89.917	132.269	- 88.955	- 83.068	6.620
2700	14.846	90.479	133.024	- 89.318	- 82.951	6.344
2800	14.850	91.019	133.754	- 89.685	- 82.833	6.088
2900	14.854	91.541	134.464	- 90.056	- 82.715	5.850
3000	14.857	92.044	135.154	- 90.431	- 82.598	5.628
3100	14.860	92.531	135.824	- 90.809	- 82.482	5.420
3200	14.863	93.004	136.474	- 91.190	- 82.367	5.224
3300	14.865	93.461	137.104	- 91.574	- 82.253	5.040
3400	14.867	93.904	137.714	- 91.961	- 82.140	4.866
3500	14.869	94.335	138.304	- 92.350	- 82.028	4.702
3600	14.871	94.756	138.874	- 92.741	- 81.917	4.548
3700	14.873	95.162	139.424	- 93.133	- 81.807	4.404
3800	14.875	95.558	139.954	- 93.526	- 81.698	4.269
3900	14.878	95.945	140.464	- 93.921	- 81.590	4.143
4000	14.879	96.321	140.954	- 94.317	- 81.483	4.026
4100	14.880	96.689	141.424	- 94.714	- 81.377	3.916
4200	14.882	97.047	141.874	- 95.112	- 81.272	3.811
4300	14.881	97.398	142.304	- 95.511	- 81.168	3.710
4400	14.882	97.740	142.714	- 95.911	- 81.065	3.613
4500	14.883	98.074	143.104	- 96.312	- 80.963	3.520
4600	14.884	98.401	143.474	- 96.714	- 80.862	3.431
4700	14.885	98.721	143.824	- 97.117	- 80.762	3.346
4800	14.886	99.035	144.154	- 97.521	- 80.663	3.265
4900	14.887	99.342	144.464	- 97.926	- 80.565	3.188
5000	14.887	99.642	144.754	- 98.331	- 80.468	3.114
5100	14.888	99.937	145.024	- 98.736	- 80.372	3.043
5200	14.889	100.226	145.274	- 99.141	- 80.277	2.975
5300	14.889	100.510	145.504	- 99.546	- 80.183	2.910
5400	14.890	100.788	145.714	- 99.951	- 80.090	2.847
5500	14.890	101.062	145.904	- 100.356	- 80.000	2.787
5600	14.891	101.330	146.074	- 100.761	- 79.911	2.729
5700	14.891	101.593	146.224	- 101.166	- 79.823	2.674
5800	14.892	101.852	146.364	- 101.571	- 79.736	2.621
5900	14.892	102.107	146.494	- 101.976	- 79.650	2.570
6000	14.892	102.357	146.614	- 102.381	- 79.565	2.520

ALUMINUM OXIDE CHLORIDE (AlOCl)

(IDEAL GAS)

MOL. WT. = 78.437

Point Group C_{2v}
 $\Delta H_f^0 = [-82.7 \pm 5.0] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [59.471] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{298.15} = [-83.2 \pm 5.0] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	
(450) (1)	
(350) (2)	
(900) (1)	

Bond Distance: O-Al = [1.62] Å Al-Cl = [2.14] Å
 Bond Angle: O-Al-Cl = 180°
 Rotational Constant: B₀ = [0.097703] cm.⁻¹
 $\sigma^- = 1$

Heat of Formation.

The free energy change of the reaction $1/3 \text{ Al}_2\text{O}_3(\text{s}) + 1/3 \text{ AlCl}_3(\text{g}) = \text{AlOCl}(\text{g})$, $\Delta G_f^0 = 28 \pm 3 \text{ kcal. mole}^{-1}$, has been determined by M. A. Greenbaum, et al., Marent Corporation, California, private communication, August 26, 1964. Incorporating appropriate auxiliary data the heat of reaction was derived to be 82.9 kcal. mole⁻¹, yielding $\Delta H_f^0 = -83.2 \pm 5 \text{ kcal. mole}^{-1}$ for AlOCl(g).

Heat Capacity and Entropy.

Point group, ground state quantum weight and vibrational frequencies were obtained from J. Hilaenrath, W. H. Evans and H. W. Woolley, National Bureau of Standards Report 6484, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine", July 1, 1959. The bond distances of ⁷⁰Al and ⁷¹Al-Cl were assumed to be the same as those in AlO(g) and AlCl(g) molecules, respectively. The three principal moments of inertia are I_A = 0 and I_B = I_C = 2.86467 X 10⁻³⁸ g. cm.²

Aluminum Dichloride (AlCl₃)

(Ideal Gas) Mol. Wt. = 97.894

ALUMINUM DICHLORIDE (AlCl₃) (IDEAL GAS)

MOL. WT. = 97.894

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(H° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	-	3.012	-	74.724	INFINITE
100	9.134	57.108	76.936	-	2.483	-	75.720	105.497
200	11.166	64.107	76.943	-	1.861	-	77.011	63.850
298	12.571	68.615	76.945	-	0.000	-	77.011	56.866
300	12.356	68.892	68.615	0.023	-	75.003	-	56.549
400	12.943	72.536	69.308	1.291	-	75.162	-	42.876
500	13.260	75.461	70.256	2.603	-	75.330	-	34.055
600	13.466	77.807	71.332	3.290	-	75.510	-	29.161
700	13.554	79.079	72.422	3.290	-	75.735	-	25.227
800	13.642	81.796	73.483	6.550	-	75.975	-	22.267
900	13.697	83.406	74.468	8.017	-	76.245	-	19.957
1000	13.737	84.851	75.462	9.369	-	76.539	-	18.062
1100	13.766	86.162	76.376	10.764	-	76.861	-	16.489
1200	13.789	87.351	77.242	12.142	-	77.217	-	15.175
1300	13.807	88.465	78.064	13.522	-	77.605	-	14.000
1400	13.821	89.489	78.844	14.903	-	78.028	-	13.102
1500	13.832	90.443	79.585	16.286	-	80.151	-	12.269
1600	13.842	91.336	80.292	17.670	-	80.375	-	11.528
1700	13.850	92.175	80.967	19.054	-	80.600	-	10.891
1800	13.856	92.967	81.612	20.440	-	80.825	-	10.315
1900	13.862	93.716	82.229	21.826	-	81.051	-	9.797
2000	13.866	94.428	82.822	23.212	-	81.280	-	9.331
2100	13.871	95.104	83.390	24.599	-	81.508	-	8.908
2200	13.874	95.750	83.938	25.986	-	81.739	-	8.522
2300	13.877	96.366	84.465	27.374	-	81.970	-	8.168
2400	13.880	96.957	84.973	28.761	-	82.204	-	7.843
2500	13.882	97.524	85.464	30.150	-	82.439	-	7.543
2600	13.885	98.068	85.938	31.538	-	82.676	-	7.265
2700	13.886	98.592	86.397	32.926	-	82.916	-	7.008
2800	13.888	99.097	86.842	34.315	-	83.151	-	6.759
2900	13.890	99.585	87.273	35.704	-	83.383	-	6.525
3000	13.891	100.056	87.691	37.093	-	83.615	-	6.303
3100	13.892	100.511	88.097	38.482	-	83.844	-	6.095
3200	13.893	100.952	88.492	39.872	-	84.068	-	5.900
3300	13.894	101.380	88.876	41.261	-	84.287	-	5.717
3400	13.895	101.794	89.250	42.650	-	84.502	-	5.549
3500	13.896	102.197	89.614	44.040	-	84.714	-	5.395
3600	13.897	102.589	89.969	45.430	-	84.922	-	5.250
3700	13.898	102.970	90.316	46.819	-	85.127	-	5.113
3800	13.898	103.340	90.653	48.209	-	85.329	-	5.000
3900	13.899	103.701	90.983	49.596	-	85.528	-	4.899
4000	13.900	104.053	91.306	50.989	-	85.725	-	4.809
4100	13.900	104.396	91.621	52.379	-	85.919	-	4.728
4200	13.901	104.731	91.929	53.769	-	86.110	-	4.652
4300	13.901	105.058	92.231	55.159	-	86.298	-	4.582
4400	13.902	105.378	92.526	56.549	-	86.483	-	4.517
4500	13.902	105.690	92.815	57.940	-	86.665	-	4.456
4600	13.902	105.994	93.098	59.330	-	86.844	-	4.399
4700	13.903	106.295	93.376	60.720	-	87.020	-	4.345
4800	13.903	106.588	93.648	62.110	-	87.193	-	4.294
4900	13.903	106.874	93.915	63.501	-	87.363	-	4.246
5000	13.904	107.155	94.177	64.891	-	87.530	-	4.201
5100	13.904	107.431	94.434	66.281	-	87.693	-	4.158
5200	13.904	107.701	94.687	67.672	-	87.853	-	4.117
5300	13.904	107.965	94.935	69.062	-	88.010	-	4.077
5400	13.905	108.225	95.178	70.453	-	88.163	-	4.038
5500	13.905	108.480	95.418	71.843	-	88.313	-	4.000
5600	13.905	108.731	95.654	73.234	-	88.460	-	3.963
5700	13.905	108.977	95.885	74.624	-	88.604	-	3.927
5800	13.906	109.219	96.113	76.015	-	88.745	-	3.892
5900	13.906	109.457	96.337	77.405	-	88.883	-	3.857
6000	13.906	109.690	96.558	78.796	-	89.018	-	3.823

June 30, 1981/ Sept. 30, 1984

Point Group C_{2v}

S°_{298.15} = [68.815] cal. deg⁻¹ mole⁻¹

ΔH_f⁰ = [-75 ± 20] kcal. mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm⁻¹

[430] (1)

[210] (1)

[540] (1)

Bond Distances: Al-Cl = [2.14] Å

Bond Angle: Cl-Al-Cl = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [6.62845 X 10⁻¹¹⁴] g.³ cm.⁶σ⁻ = 2

Heat of Formation.

The value of ΔH_f⁰ 298.15 for AlCl₃(g) was calculated based on an assumption that ΔH_f⁰ = 0 for the reaction AlCl(g) + AlCl₃(g) = 2AlCl₂(g). The values of ΔH_f⁰ 298.15 for AlCl(g) and AlCl₃(g) used for calculation are -11.2 and -139.7 Kcal. mole⁻¹, respectively.

Heat Capacity and Entropies.

The vibrational frequencies were calculated by valence force field method described by O. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950, using force constants, k₁ = 2.05 X 10⁵ and k_f/12 = 0.25 X 10⁵ dynes/cm., estimated from those for AlCl(g) and other similar compounds. The bond distance was assumed to be the same as that for AlCl(g). The bond angle and ground state quantum weight were estimated to be consistent with those for AlF₃(g). The three principal moments of inertia are I_A = 4.04243 X 10⁻³⁸, I_B = 3.7149 X 10⁻³⁹ and I_C = 4.41392 X 10⁻³⁸ g. cm.²

AlCl₃

Aluminum Dichloride Unipositive Ion (AlCl₂⁺)

(Ideal Gas) GFW = 97.887

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
100							
200							
298	13.255	62.959	62.959	0.000	110.000	107.648	- 78.908
300	13.270	63.041	62.959	0.025	110.008	107.633	- 78.410
400	13.862	66.951	63.488	1.385	110.436	106.777	- 58.340
500	14.214	70.088	64.505	2.792	110.856	105.814	- 46.251
600	14.410	72.468	65.458	4.224	111.267	104.767	- 38.162
700	14.534	74.530	66.428	5.671	111.637	103.655	- 32.362
800	14.617	76.376	67.465	7.159	111.969	102.450	- 27.959
900	14.675	78.001	68.553	8.594	112.299	101.284	- 24.595
1000	14.718	80.150	70.064	10.064	112.639	100.228	- 21.905
1100	14.745	81.554	71.044	11.537	112.983	99.232	- 19.716
1200	14.773	82.839	71.994	13.013	113.333	98.207	- 17.686
1300	14.792	84.022	72.874	14.492	113.687	97.155	- 16.333
1400	14.808	85.119	73.710	15.972	114.046	96.081	- 14.999
1500	14.820	86.141	74.505	17.453	114.410	94.982	- 13.639
1600	14.830	87.098	75.263	18.936	114.779	93.863	- 12.421
1700	14.838	87.997	75.986	20.419	115.152	92.727	- 11.521
1800	14.845	88.845	76.677	21.903	115.524	91.569	- 11.118
1900	14.851	89.648	77.339	23.388	115.896	90.398	- 10.398
2000	14.856	90.410	77.973	24.873	116.264	89.207	- 9.748
2100	14.861	91.135	78.583	26.359	116.630	87.998	- 9.158
2200	14.864	91.826	79.169	27.846	116.994	86.778	- 8.621
2300	14.868	92.487	79.734	29.332	117.356	85.546	- 8.129
2400	14.871	93.120	80.279	30.819	117.714	84.300	- 7.677
2500	14.873	93.727	80.805	32.306	118.069	83.038	- 7.259
2600	14.876	94.310	81.313	33.794	118.421	81.767	- 6.873
2700	14.878	94.872	81.805	35.281	118.770	80.483	- 6.515
2800	14.879	95.413	82.281	36.769	119.116	79.187	- 6.246
2900	14.881	95.935	82.743	38.257	119.459	77.881	- 6.003
3000	14.883	96.440	83.191	39.745	119.800	76.566	- 5.785
3100	14.884	96.928	83.626	41.234	120.138	75.242	- 5.584
3200	14.885	97.400	84.050	42.722	120.473	73.909	- 5.397
3300	14.886	97.858	84.461	44.211	120.805	72.567	- 5.247
3400	14.887	98.303	84.862	45.699	121.134	71.216	- 5.119
3500	14.888	98.734	85.252	47.188	121.459	69.856	- 5.007
3600	14.889	99.154	85.632	48.677	121.780	68.487	- 4.910
3700	14.890	99.562	86.003	50.166	122.097	67.110	- 4.826
3800	14.891	99.959	86.365	51.655	122.411	65.725	- 4.759
3900	14.891	100.346	86.719	53.144	122.721	64.336	- 4.693
4000	14.892	100.723	87.064	54.633	123.028	62.941	- 4.631
4100	14.892	101.090	87.402	56.123	123.332	61.540	- 4.571
4200	14.893	101.449	87.732	57.612	123.633	60.134	- 4.516
4300	14.893	101.800	88.055	59.101	123.931	58.723	- 4.465
4400	14.894	102.142	88.357	60.590	124.226	57.307	- 4.417
4500	14.894	102.477	88.661	62.080	124.519	55.886	- 4.371
4600	14.895	102.804	88.965	63.569	124.809	54.461	- 4.327
4700	14.895	103.124	89.262	65.058	125.096	53.032	- 4.284
4800	14.895	103.438	89.554	66.548	125.380	51.599	- 4.242
4900	14.896	103.745	89.840	68.038	125.661	50.162	- 4.201
5000	14.896	104.046	90.114	69.528	125.939	48.721	- 4.160
5100	14.896	104.341	90.416	71.017	126.214	47.276	- 4.119
5200	14.897	104.630	90.707	72.507	126.486	45.827	- 4.077
5300	14.897	104.914	90.993	73.996	126.755	44.374	- 4.035
5400	14.897	105.193	91.274	75.486	127.021	42.917	- 3.993
5500	14.897	105.466	91.547	76.976	127.284	41.456	- 3.951
5600	14.898	105.734	91.823	78.466	127.544	40.000	- 3.909
5700	14.898	106.000	92.100	79.955	127.801	38.539	- 3.867
5800	14.898	106.257	92.375	81.445	128.055	37.074	- 3.825
5900	14.898	106.512	92.645	82.935	128.306	35.605	- 3.783
6000	14.898	106.762	92.912	84.425	128.554	34.131	- 3.741

June 30, 1968



ALUMINUM DICHLORIDE UNIPosITIVE ION (AlCl₂⁺)

Point Group [D_{2h}]

S_{298.15} = [63 ± 2] Gibbs/mol

Ground State Quantum Weight = [1]

GFW = 97.887

ΔHf°₀ = [110 ± 40] kcal/mol

ΔHf°_{298.15} = [110 ± 40] kcal/mol

Vibrational Frequencies and Degeneracies
ω, cm⁻¹
[590] (1)
[180] (2)
[380] (1)

σ = 2

Bond Distance: Al-Cl = [2.17] Å

Bond Angle: Cl-Al-Cl = [180°]

Rotational Constant: B₀ = [0.0505] cm⁻¹

Heat of Formation

R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960), reported an appearance potential of 13.4 ± 0.5eV (309 ± 12 kcal) for AlCl₂⁺; they indicated that AlCl₂(g) was the probable parent molecule. Assuming the formation reaction to be AlCl₃ + e⁻ → AlCl₂⁺ + Cl + 2 e⁻, we obtain ΔHf°(AlCl₂⁺, g) = 140 kcal/mol or an ionization potential of 215 kcal or 9.3eV.

Since there is a possibility of the fragments containing excess kinetic energy, the ionization potential represents an upper limit to the true value. A comparison of the ionization potentials of BF₃ and BCl₃ indicates that the chloride is lower by 1eV per atom; on this basis we would obtain an ionization potential of 7eV using the value for AlF₂ of 8eV.

The National Bureau of Standards Report No. 8628, Jan. 1, 1965, gives an estimate of 8 ± 1eV (185 ± 25 kcal); we adopt this value as being representative of the probable range of values. The adopted ionization potential yields ΔHf°_{298.15}(AlCl₂⁺, g) = 110 ± 40 kcal/mol in conjunction with ΔHf°₂₉₈(AlCl₃, g) = -75 ± 20 kcal/mol.

Heat Capacity and Entropy

AlCl₂⁺ is isoelectronic with MgCl₂ and on this basis we assume the ground state to be singlet and linear in accordance with the predictions of A. D. Walsh, J. Chem. Soc. 2766 (1953). The vibrational frequencies are estimated to lie between those for AlCl₂ and MgCl₂. The bond length is estimated as the sum of the covalent radii of the atoms.

The enthalpy at 0°K is -3.128 kcal/mol.



Aluminum Dichloride Uninegative Ion (AlCl₂⁻)

(Ideal Gas) GFW = 97.888

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	12.269	67.441	67.441	.000	- 80.714	59.165
300	12.304	67.517	67.442	.023	- 80.719	58.403
400	12.906	71.149	67.933	1.266	- 80.675	44.177
500	13.233	74.067	68.677	2.595	- 81.347	35.327
600	13.426	76.498	69.950	3.929	- 82.038	29.377
700	13.548	78.578	71.038	5.278	- 82.748	25.091
800	13.629	80.392	72.096	6.637	- 83.489	21.848
900	13.687	82.001	73.109	8.003	- 84.272	19.302
1000	13.728	83.445	74.072	9.374	- 85.095	17.200
1100	13.759	84.755	74.984	10.748	- 85.940	15.458
1200	13.783	85.954	75.849	12.125	- 86.807	13.968
1300	13.801	87.058	76.670	13.504	- 87.696	12.732
1400	13.816	88.081	77.449	14.885	- 88.619	11.749
1500	13.828	89.035	78.190	16.268	- 89.573	10.900
1600	13.838	89.927	78.896	17.651	- 90.559	9.463
1700	13.846	90.767	79.569	19.035	- 91.580	8.119
1800	13.853	91.558	80.214	20.420	- 92.643	6.951
1900	13.859	92.307	80.831	21.806	- 93.748	5.949
2000	13.864	93.018	81.422	23.192	- 94.895	5.102
2100	13.868	93.695	81.991	24.578	- 96.081	4.404
2200	13.872	94.340	82.538	25.965	- 97.309	3.847
2300	13.875	94.957	83.064	27.353	- 98.578	3.426
2400	13.878	95.547	83.572	28.740	- 99.888	3.117
2500	13.880	96.114	84.063	30.128	- 101.239	2.872
2600	13.883	96.658	84.537	31.516	- 102.633	2.672
2700	13.885	97.182	84.995	32.905	- 104.074	2.511
2800	13.887	97.687	85.440	34.293	- 105.563	2.381
2900	13.888	98.175	85.870	35.682	- 107.102	2.281
3000	13.889	98.645	86.288	37.071	- 108.691	2.201
3100	13.891	99.101	86.694	38.460	- 110.330	2.141
3200	13.892	99.542	87.089	39.849	- 112.020	2.091
3300	13.893	99.969	87.473	41.238	- 113.761	2.051
3400	13.894	100.384	87.847	42.628	- 115.553	2.021
3500	13.895	100.787	88.211	44.017	- 117.406	1.991
3600	13.896	101.178	88.565	45.407	- 119.320	1.961
3700	13.897	101.559	88.911	46.796	- 121.295	1.931
3800	13.897	101.930	89.249	48.186	- 123.330	1.901
3900	13.898	102.291	89.579	49.576	- 125.425	1.871
4000	13.898	102.643	89.901	50.966	- 127.580	1.841
4100	13.899	102.986	90.216	52.355	- 129.795	1.811
4200	13.900	103.321	90.524	53.745	- 132.070	1.781
4300	13.900	103.648	90.826	55.135	- 134.405	1.751
4400	13.901	103.967	91.121	56.525	- 136.799	1.721
4500	13.901	104.280	91.410	57.915	- 139.253	1.691
4600	13.901	104.585	91.693	59.306	- 141.767	1.661
4700	13.902	104.884	91.970	60.696	- 144.340	1.631
4800	13.902	105.177	92.242	62.086	- 146.973	1.601
4900	13.902	105.464	92.509	63.476	- 149.666	1.571
5000	13.903	105.745	92.771	64.866	- 152.419	1.541
5100	13.903	106.020	93.028	66.257	- 155.232	1.511
5200	13.903	106.290	93.281	67.647	- 158.105	1.481
5300	13.904	106.555	93.529	69.037	- 161.038	1.451
5400	13.904	106.815	93.772	70.428	- 164.031	1.421
5500	13.904	107.070	94.012	71.818	- 167.084	1.391
5600	13.904	107.320	94.247	73.208	- 170.197	1.361
5700	13.904	107.566	94.479	74.599	- 173.370	1.331
5800	13.905	107.808	94.706	75.989	- 176.603	1.301
5900	13.905	108.046	94.931	77.380	- 179.896	1.271
6000	13.905	108.279	95.151	78.770	- 183.249	1.241

June 30, 1968

ALUMINUM DICHLORIDE UNINEGATIVE ION (AlCl₂⁻)

(IDEAL GAS)

GFW = 97.888

Point Group [C_{2v}']

ΔH_f^o = [-80 ± 40] kcal/mol

S_{298.15} = [67.4 ± 0.5] gibbs/mol

ΔH_f^o_{298.15} = [-80 ± 40] kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\frac{\omega}{\text{cm}^{-1}}$	
[550] (1)	
[200] (1)	
[450] (1)	

Bond Distance: Al-Cl = [2.14] Å

Bond Angle: Cl-Al-Cl = [120°]

σ = 2

Product of the Moments of Inertia: I_AI_BI_C = [6.634 × 10⁻³³] g³ cm⁶

Heat of Formation

AlCl₂⁻ is isoelectronic with SiCl₂ and an estimate of its heat of formation may be obtained by assuming the binding energy to be the same in the two molecules. This leads to ΔH_f^o₂₉₈(AlCl₂⁻, g) = -80 kcal/mol or an electron affinity of 5 kcal. An alternative route assumes that the heat of reaction is identical for the processes AlCl₃(g) + AlCl₂⁻(g) + Cl⁺(g) and AlCl₃(g) + Al⁺(g) + Cl⁺(g). Using the electron affinity of Al(g) given in National Bureau of Standards Report No. 8628, Jan. 1, 1965, we obtain ΔH_f^o₂₉₈(AlCl₂⁻, g) = -63 kcal/mol or an electron affinity of -12 kcal. In addition, using the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953), the electron must go into a non-bonding orbital; thus the binding energy should be close to that of AlCl₂. The dissociation energy of AlCl₂ is 211 kcal which leads to ΔH_f^o₂₉₈(AlCl₂⁻, g) = -87 kcal/mol or an electron affinity of 12 kcal. We adopt an intermediate value for the electron affinity of 5 ± 20 kcal/mol, or ΔH_f^o₂₉₈(AlCl₂⁻, g) = -80 ± 40 kcal/mol using ΔH_f^o₂₉₈(AlCl₂⁻, g) = -75 ± 20 kcal/mol.

Heat Capacity and Entropy

As noted earlier, AlCl₂⁻ is isoelectronic with SiCl₂ and with 18 valence electrons, should be definitely bent according to the correlation scheme of A. D. Walsh, loc. cit. The vibrational frequencies are estimated to lie between those of SiCl₂ and AlCl₂. The bond length and angle are estimated as equal to those for AlCl₂(g). By analogy with SiF₂ (see G. Herzberg "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Company Inc., New York, 1966) we do not expect any low lying electronic levels. The enthalpy at 0°K is -3.006 kcal/mol. The three principal moments of inertia are: I_A = 3.7155 × 10⁻³⁹, I_B = 4.0438 × 10⁻³⁹, and I_C = 4.4154 × 10⁻³⁸ g cm².

AlCl₂⁻

Aluminum Dichloride Fluoride (AlCl₂F)

(Ideal Gas) Mol. Wt. = 116.894

T, K.	C _p ^o	S ^o - (F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	11.238	59.274	3.734	-187.991	-187.991	INFINITE
200	15.238	87.557	2.828	-187.449	-187.449	409.849
300	17.410	104.410	2.428	-186.600	-186.600	106.072
400	18.429	116.438	2.136	-185.623	-185.623	136.219
500	18.859	124.557	1.936	-184.612	-184.612	160.862
600	18.700	129.763	1.786	-183.577	-183.577	180.236
700	18.582	133.936	1.673	-182.525	-182.525	196.481
800	18.498	137.256	1.586	-181.457	-181.457	209.651
900	18.434	140.013	1.517	-180.373	-180.373	220.273
1000	18.385	142.419	1.460	-179.270	-179.270	229.430
1100	18.347	144.527	1.413	-178.152	-178.152	237.197
1200	18.316	146.387	1.374	-177.023	-177.023	243.682
1300	18.290	148.046	1.342	-175.883	-175.883	248.918
1400	18.268	149.557	1.316	-174.733	-174.733	252.936
1500	18.249	150.963	1.294	-173.573	-173.573	255.885
1600	18.232	152.297	1.275	-172.406	-172.406	257.807
1700	18.217	153.581	1.258	-171.233	-171.233	258.732
1800	18.203	154.823	1.243	-170.057	-170.057	258.787
1900	18.190	156.033	1.229	-168.878	-168.878	257.987
2000	18.178	157.213	1.216	-167.696	-167.696	256.357
2100	18.167	158.367	1.203	-166.512	-166.512	253.844
2200	18.157	159.500	1.191	-165.327	-165.327	251.491
2300	18.147	160.613	1.179	-164.142	-164.142	249.266
2400	18.138	161.706	1.167	-162.957	-162.957	247.142
2500	18.129	162.780	1.156	-161.772	-161.772	245.107
2600	18.120	163.835	1.145	-160.587	-160.587	243.152
2700	18.111	164.871	1.134	-159.402	-159.402	241.277
2800	18.102	165.888	1.123	-158.217	-158.217	239.482
2900	18.093	166.886	1.112	-157.032	-157.032	237.757
3000	18.084	167.864	1.101	-155.847	-155.847	236.092
3100	18.075	168.822	1.090	-154.662	-154.662	234.487
3200	18.066	169.760	1.079	-153.477	-153.477	232.942
3300	18.057	170.678	1.068	-152.292	-152.292	231.457
3400	18.048	171.576	1.057	-151.107	-151.107	230.032
3500	18.039	172.454	1.046	-149.922	-149.922	228.667
3600	18.030	173.312	1.035	-148.737	-148.737	227.362
3700	18.021	174.150	1.024	-147.552	-147.552	226.117
3800	18.012	174.968	1.013	-146.367	-146.367	224.932
3900	18.003	175.766	1.002	-145.182	-145.182	223.807
4000	17.994	176.544	0.991	-144.000	-144.000	222.742
4100	17.985	177.302	0.980	-142.815	-142.815	221.737
4200	17.976	178.040	0.969	-141.630	-141.630	220.792
4300	17.967	178.758	0.958	-140.445	-140.445	219.907
4400	17.958	179.456	0.947	-139.260	-139.260	219.082
4500	17.949	180.134	0.936	-138.075	-138.075	218.317
4600	17.940	180.792	0.925	-136.890	-136.890	217.612
4700	17.931	181.430	0.914	-135.705	-135.705	216.967
4800	17.922	182.048	0.903	-134.520	-134.520	216.382
4900	17.913	182.646	0.892	-133.335	-133.335	215.857
5000	17.904	183.224	0.881	-132.150	-132.150	215.392
5100	17.895	183.782	0.870	-130.965	-130.965	214.987
5200	17.886	184.320	0.859	-129.780	-129.780	214.642
5300	17.877	184.838	0.848	-128.595	-128.595	214.357
5400	17.868	185.336	0.837	-127.410	-127.410	214.132
5500	17.859	185.814	0.826	-126.225	-126.225	213.967
5600	17.850	186.272	0.815	-125.040	-125.040	213.862
5700	17.841	186.710	0.804	-123.855	-123.855	213.817
5800	17.832	187.128	0.793	-122.670	-122.670	213.832
5900	17.823	187.526	0.782	-121.485	-121.485	213.907
6000	17.814	187.904	0.771	-120.300	-120.300	214.042

Dec. 31, 1960; Sept. 30, 1961

ALUMINUM DICHLORIDE FLUORIDE (AlCl₂F)

(IDEAL GAS)

Point Group C_{2v}

ΔH_f^o 0 = [-188.0 ± 20] kcal. mole⁻¹

S_{298.15}^o = [74.356] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = [-188.6 ± 20] kcal. mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[420] (1)	[200] (1)
[260] (1)	[650] (1)
[150] (1)	[820] (1)

Bond Distances: Al-F = [1.65] Å Al-Cl = [2.14] Å

Bond Angle: F-Al-Cl = [120]° Cl-Al-Cl = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [4.64645 X 10⁻¹¹³] g.³ cm.⁶

σ⁻ = 2

Heat of Formation.

The value of ΔH_f^o 298.15 was calculated based on an assumption the ΔH_f^o = 0 for the reaction AlF₃(g) + 2AlCl₃(g) = 3AlCl₂F(g). The values of ΔH_f^o 298.15 for AlF₃(g) and AlCl₃(g) used for calculation are -286.5 and -139.7 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for AlF₃(g) and AlCl₃(g). The bond distances of Al-F and Al-Cl atoms were assumed to be the same as those in AlF₃(g) and AlCl₃(g), respectively. The bond angles and ground state quantum weight were estimated by comparison with those for AlF₃(g). The three principal moments of inertia are 4.04374 X 10⁻³⁶, 1.92508 X 10⁻³⁶, and 5.96882 X 10⁻³⁶ g.³ cm.⁶

AlCl₂F

Aluminum Trichloride (AlCl₃)

(Crystal)

GFW = 133.341

T, °K	Cp*	S*	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	INFINITE	4.058	-168.323	-168.323	INFINITE
100	11.260	7.361	43.251	3.589	-169.004	-169.004	-169.004	355.605
200	16.930	17.950	86.035	2.015	-168.981	-168.981	-168.982	171.115
298	21.760	26.120	110.393	.000	-168.959	-168.959	-168.959	110.393
300	21.820	26.255	110.420	.040	-168.643	-150.474	-109.621	109.621
400	23.920	32.620	127.001	2.322	-168.200	-145.482	-78.922	78.922
500	26.020	38.383	137.734	4.824	-167.614	-136.517	-60.549	60.549
600	28.120	43.313	142.760	7.531	-166.449	-122.485	-46.403	46.403
700	30.220	47.805	147.479	10.448	-164.954	-107.291	-31.792	31.792
800	32.320	51.977	151.977	13.579	-163.073	-92.641	-16.641	16.641
900	34.420	55.905	156.211	16.912	-160.833	-77.534	-1.534	1.534
1000	36.520	59.641	160.159	20.459	-158.260	-61.960	13.960	13.960
1100	38.620	63.220	163.820	24.216	-155.388	-45.988	28.988	28.988
1200	40.720	66.670	167.183	28.183	-152.125	-29.512	43.487	43.487
1300	42.820	70.012	170.280	32.360	-148.468	-12.540	56.912	56.912
1400	44.920	73.263	173.147	36.747	-144.412	4.512	69.400	69.400
1500	47.020	76.433	175.810	41.344	-140.000	19.968	81.968	81.968

Dec. 31, 1960; June 30, 1961; June 30, 1963; Mar. 31, 1964; June 30, 1970

Heat of Formation

Gross and Hayman (1) measured the enthalpy of direct combination of "spectrographically pure" aluminum and carefully purified chlorine and derived ΔH_f° 298.15 = -168.80 \pm 0.16 kcal/mol. Siemsen (2) also reported the enthalpy of direct combination and is in agreement at -167.5 kcal/mol within his relatively large uncertainty interval of ± 1.1 kcal/mol.

Coughlin (3) determined the enthalpy of solution of 99.99+ pure Al in 4.360 M HCl and also (4) the enthalpy of solution of anhydrous AlCl₃ in the same solvent. Enthalpies of mixing were measured to close a thermochemical cycle at 303.15°K (adjusted to 1961 at. wts.):

Reaction	ΔH_f° 303.15 cal.
(1) Al(c) + 3H ⁺ (sol) = Al ³⁺ (sol) + 3/2 H ₂ (g)	-127.047 \pm 120
(2) 3(HCl-12.731 H ₂ O)(l) = 3H ⁺ (sol) + 3Cl ⁻ (sol) + 36.193 H ₂ O(sol)	0 \pm 10
(3) AlCl ₃ (c) = Al ³⁺ (sol) + 3Cl ⁻ (sol)	-72.504 \pm 50
(4) 38.193 H ₂ O(l) = 38.193 H ₂ O(sol)	-3.050 \pm 20
(5) Al(c) + 3(HCl-12.731 H ₂ O)(l) = AlCl ₃ (c) + 36.193 H ₂ O(l) + 3/2 H ₂ (g)	-51.503 \pm 140

With heat capacity data for Al, AlCl₃, and H₂ from the JANAF tables and for HCl(12.731 H₂O) from Parker (5), the enthalpy of reaction 5 at 298.15°K is -51.910 \pm 140 cal/mol AlCl₃. Interpolation of data for ΔH_f° 298.15(HCl, aq) selected by Wagman et al. (6) yields ΔH_f° 298.15(AlCl₃, c) = -168.37 kcal/mol. The overall uncertainty is estimated as 300 cal/mol.

Earlier investigations on the enthalpies of solution of Al were adjusted to the conditions of Coughlin's experiments by means of the data of Smith and Bess (7) for the effects of HCl concentration and H₂O dilution on ΔH_f° (AlCl₃, aq) and estimates of ΔC_p of solution of Al of +20 gibbs/mol.

Investigator(s)	ΔH (soln) as reported kcal/mol Al	ΔH (soln) adjusted kcal/mol Al
Young (8)	-126.83	-126.79
Roth and Wolf (9)	-124.01	-127.29
Cannari and Rossi (10)	-125.40	-126.80
Somermeier (11)	-128.36	-126.42
Richards and Burgess (12)	-126.00	-124.06

Only Richards and Burgess deviate more than expected; they report a value for Mg in good agreement with modern values and it seems likely their sample of Al was impure.

Several values for the enthalpy of solution of AlCl₃(c) in water have also been published and are listed here along with Coughlin's value recalculated to solution in pure water at 20°K.

Investigator(s)	ΔH (soln) in H ₂ O at 20°K (kcal/mol AlCl ₃)
Coughlin (3)	-78.22 (adjusted)
Thomsen (13)	-76.85
Berthelot (13)	-76.3
Said (13)	-77.6
Stoll (13)	-77.6
Roth and Böhner (14)	-77.9
Roth and Börgen (15)	-79.3
Klemm and Tanke (16)	-77.7 (adjusted)

Klemm and Tanke (16) measured the enthalpy of solution of AlCl₃ in HCl-20 H₂O at 0°K. A weighted average of the values of Gross and Hayman (1) and of Coughlin (4) is adopted for ΔH_f° 298.15(AlCl₃, c) = -168.65 \pm 0.20 kcal/mol.

Heat Capacity and Entropy

Justice (17) reported low temperature heat capacity data (13° to 310°K) and presented smoothed thermodynamic functions, including $S_{298.15}^\circ$ = 26.12 gibbs/mol, of which 0.086 gibbs/mol is extrapolation below 13°K. Heat content relative to 273.15°K was measured by Fischer (18) from 298°K to 504°K and heat content relative to 298.15°K was measured by McDonald (19) from 310° to 493°K. The heat content data for the crystal can be fit within about 2% by integration of C_p (c) (gibbs/mol) = 15.52 + 0.021T, which is an extrapolation of C_p data reported by Justice (17).

Melting Data

See table for AlCl₃(t).

Sublimation Data

See table for Al₂Cl₆(g).

References

1. F. Gross and C. Hayman, *Trans. Faraday Soc.*, **55**, 30 (1970).
2. H. Siemsen, *Z. Elektrochem.*, **55**, 327 (1951).
3. J. P. Coughlin, *J. Amer. Chem. Soc.*, **79**, 5749 (1957).
4. J. P. Coughlin, *J. Amer. Chem. Soc.*, **79**, 5750 (1957).
5. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-1965.
6. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
7. M. B. Smith and G. E. Bess, *J. Chem. Eng. Data*, **9**, 342 (1963).
8. F. E. Young, *J. Amer. Chem. Soc.*, **58**, 777 (1944).
9. R. A. Roth and U. Wolf, *Z. Elektrochem.*, **46**, 732 (1940).
10. E. Somermeier, *Phys. Rev.*, **1**, 141 (1913).
11. E. Somermeier, *Phys. Rev.*, **1**, 141 (1913).
12. T. W. Richards and L. L. Burgess, *J. Amer. Chem. Soc.*, **32**, 431 (1910).
13. F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances", Reinhold, New York, 1936, p. 331.
14. W. A. Roth and A. Böhner, *Z. Elektrochem.*, **40**, 87 (1934).
15. W. A. Roth and E. Börgen, *Z. Elektrochem.*, **41**, 540 (1935).
16. K. Klemm and E. Tanke, *Z. Elektrochem.*, **41**, 540 (1935).
17. B. H. Justice, *J. Chem. Eng. Data*, **9**, 342 (1963).
18. W. Fischer, *Z. Anorg. Chem.*, **200**, 327 (1931).
19. R. A. McDonald, *The Dow Chemical Co.*, Midland, Mich., unpublished data.

Aluminum Trichloride (AlCl₃)

(Liquid) GFW = 133.341

AlCl₃

ALUMINUM TRICHLORIDE (AlCl₃) (LIQUID) GFW = 133.341

S^o_{298.15} = 41.326 ± 0.5 gibbs/mol

ΔHf^o_{298.15} = -161.28 ± 0.40 kcal/mol

T_m = 465.7 ± 0.2°K

ΔH_m = 8.45 ± 0.20 kcal/mol

Heat of Formation

ΔHf^o_{298.15}(l) was obtained from ΔHf^o_{298.15}(c) by adding ΔH_m and the difference between (H_{465.7-H_{298.15}}) for crystal and liquid.

Melting Point

Kendall et al. (1) observed AlCl₃ to melt "sharply" at 463.4°K, Foster (2) noted that AlCl₃ began melting and melted completely in the range 465.7 ± 0.2°K, Nisels' son et al. (3) reported T_m = 467.2°K, and Ostrikova et al. (4) reported T_m = 466°K. Smits and Meijering (5) and Treadwell and Terebesi (6) derived triple point temperatures of 465.8°K and 466.5°K, respectively, from intersection of vapor pressure curves for crystal and liquid. The value of Foster is adopted as most accurate. The vapor pressure at the triple point is 2.3 atm.

Heat of Fusion and Heat Capacity

Fischer (7) and McDonald (8) measured heat content data for the liquid over a short range (473°-504°K) of temperature. Their data can be represented within 2% by the heat capacity equation derived for the crystal (see AlCl₃(c) table), a heat of fusion of 8.45 kcal/mol, and a liquid heat capacity of 30.0 gibbs/mol. Fischer's data are high, while McDonald's points lie below the selected values.

References

1. J. Kendall, E. D. Crittenden, and H. K. Miller, J. Amer. Chem. Soc. **55**, 863 (1933).
2. L. M. Foster, J. Amer. Chem. Soc. **72**, 1902 (1950).
3. L. A. Nisels' son, A. I. Pustil'nik, O. R. Gavrilov, and V. A. Rodin, Zh. Neorg. Khim. **10**, 2339 (1965).
4. N. V. Ostrikova, Z. A. Miroschnik, V. D. Kuleshova, N. P. Dudkina, and A. I. Ilyushchenko, Zh. Neorg. Khim. **14**, 2229 (1969).
5. A. Smits and J. L. Meijering, Z. Physik. Chem. **B11**, 98 (1938).
6. W. D. Treadwell and L. Terebesi, Helv. Chim. Acta **15**, 1053 (1932).
7. W. Fischer, Z. Anorg. Chem. **200**, 332 (1931).
8. R. A. McDonald, The Dow Chemical Co., Midland, Mich., Unpublished measurements.

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	30,000	41.326	41.326	-	161.280	-147.751	108.304
300	30,000	41.512	41.327	0.055	-161.258	-147.667	107.576
400	30,000	50.182	42.503	3.056	-160.102	-143.313	78.303
500	30,000	56.836	44.725	6.056	-159.013	-139.243	60.863
600	30,000	62.306	47.213	9.056	-157.975	-135.387	49.315
700	30,000	66.931	49.708	12.056	-156.977	-131.702	41.119
800	30,000	70.937	52.117	15.055	-156.023	-128.156	35.011
900	30,000	74.470	54.408	18.055	-155.120	-124.799	30.288
1000	30,000	77.631	56.475	21.055	-154.264	-121.616	26.492
1100	30,000	80.490	58.421	24.056	-153.499	-117.702	23.385
1200	30,000	83.100	60.354	27.056	-152.808	-114.270	20.811
1300	30,000	85.502	62.382	30.056	-152.119	-110.911	18.646
1400	30,000	87.725	64.114	33.056	-151.434	-107.619	16.400
1500	30,000	89.195	65.758	36.056	-150.752	-104.393	15.210

AlCl₃

Vibrational Frequencies and Depressions

$\frac{\omega_e}{\text{cm}^{-1}}$	$\frac{\omega_e}{\text{cm}^{-1}}$
371 (1)	146 (2)
[185] (1)	810 (2)

Bond Distance: Al-Cl = 2.08 Å

Bond Angle: Cl-Al-Cl = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 1.0618 \times 10^{-112.3} \text{ g cm}^8$ $\sigma = 8$

Heat of Formation

The heat of formation is calculated from the value adopted for Al₂Cl₆(g) and the heat of dissociation of Al₂Cl₆, derived from equilibrium P-V-T data on aluminum chloride vapor as listed below.

Investigator(s)	Temp. Range °K	Number of Data Points	$\Delta H_{288.15}^\circ$ (kcal/mol Al ₂ Cl ₆)	2nd Law	3rd Law
Smits and Meijering (1)	869-926	6		29.28	30.12
Fischer et al. (2)	647-869	16 ^a		30.82	30.35
Vrieland and Stull (3)	669-825	19 ^b		30.22	30.40

Twenty three points reported, points at 838, 881, 944, 734, 808, 605, and 688°K rejected by statistical test.

Twenty six points reported, points at 627.9, 643.1, 671.3, 638.4, 671.6, 722.5, and 686.9°K rejected by statistical test.

The three investigations are in reasonable agreement. Giving consideration also to equilibrium data on the reaction of AlCl₃(g) and Al(l) to form AlCl₃(g) (see AlCl₃(g) table), there is selected as a best value $\Delta H_{288.15}^\circ = 30.24$ kcal/mol Al₂Cl₆, which yields $\Delta H_{288.15}^\circ(\text{AlCl}_3, \text{g}) = -139.70$ kcal/mol.

Heat Capacity and Entropy

Zasorin and Rambidi (4) carried out electron diffraction experiments on aluminum chloride vapor at 800°K where the monomer should predominate. They found a planar symmetrical structure with Al-Cl = 2.06 ± 0.01 Å and Cl-Al-Cl angles of 120°. The individual moments of inertia are $I_A = I_B = 3.7466 \times 10^{-38} \text{ g cm}^2$ and $I_C = 7.4932 \times 10^{-38} \text{ g cm}^2$. For aluminum chloride vapor at high temperatures (monomer predominant), Klemperer (5) observed a band at 610 cm⁻¹ in the infrared spectrum and Beattie and Horder (6) reported Raman bands at 371 cm⁻¹ and 146 cm⁻¹. The remaining frequency should be infrared active but presumably was beyond the range of Klemperer's measurements. Zasorin and Rambidi (7) give 95 ± 15 cm⁻¹ based on amplitudes of vibration observed in electron diffraction measurements. However, this frequency gives thermodynamic functions clearly not compatible with the equilibrium P-V-T data. Force constant ratios in the boron halides also suggest a higher wavenumber. An estimate of 185 cm⁻¹ was therefore adopted as an optimum value for fitting both the Al₂Cl₆ dissociation data and the equilibrium data for AlCl₃(g) + 2Al(l) + 3AlCl(g) (see AlCl₃(g) table).

References

1. A. Smits and J. L. Meijering, Z. Phys. Chem. B41, 98 (1938).
2. W. Fischer, O. Rehfs, and B. Benze, Z. Anorg. Chem. 205, 1 (1932).
3. E. Vrieland and D. R. Stull, J. Chem. Eng. Data 12, 532 (1967).
4. E. Z. Zasorin and N. G. Rambidi, Zh. Strukt. Khim. 8, 391 (1967).
5. W. Klemperer, J. Chem. Phys. 24, 353 (1956).
6. I. R. Beattie and J. R. Horder, J. Chem. Soc. 1959, 2655.
7. E. Z. Zasorin and N. G. Rambidi, Zh. Strukt. Khim. 8, 531 (1967).

Potassium Tetrachloroaluminate (KAlCl_4)

(Crystal) Mol. Wt. = 207.908

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	37.400	47.000	47.000	0.000	-286.000	-261.610	191.756
300	37.440	47.231	47.001	0.059	-285.985	-261.459	190.464
400	39.250	56.294	48.495	3.920	-285.705	-253.302	187.521
500	41.060	64.271	51.300	11.260	-285.210	-243.200	184.200
600	43.780	75.128	54.708	12.252	-283.569	-237.534	86.518
700	45.600	82.019	58.127	16.724	-282.256	-229.964	71.705
800	47.000	88.204	61.507	21.358	-280.822	-222.593	60.807
900	47.800	93.789	64.789	26.100	-279.319	-215.402	52.804
1000	48.300	98.654	67.946	30.908	-260.292	-208.199	45.500
1100	48.407	103.462	70.969	35.743	-297.588	-200.043	38.743
1200	48.500	107.678	73.854	40.589	-295.739	-191.257	34.831
1300	48.580	111.564	76.608	45.443	-293.886	-182.627	30.701
1400	48.647	115.166	79.235	50.304	-292.030	-174.186	27.183
1500	48.700	118.225	81.743	55.172	-290.171	-165.789	24.133
1600	48.763	121.670	84.142	60.045	-288.311	-157.547	21.519
1700	48.825	124.628	86.437	64.924	-286.448	-149.431	19.210
1800	48.885	127.420	88.637	69.810	-284.582	-141.427	17.171
1900	48.943	130.065	90.746	74.701	-282.715	-133.521	15.359
2000	49.000	132.577	92.777	79.599	-280.847	-125.717	13.737

AlCl_4K

MOL. WT. = 207.908

(CRYSTAL)

POTASSIUM TETRACHLOROALUMINATE (KAlCl_4)

$\Delta H_f^\circ \text{O} = \text{Unknown}$

$\Delta H_f^\circ 298.15 = -286.0 \pm 2.5 \text{ kcal. mole}^{-1}$

$\Delta H_m^\circ = \text{Unknown}$

$S_{298.15}^\circ = [47 \pm 2] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 529^\circ\text{K.}$

Heat of Formation.

The heat of reaction of aluminum chloride and potassium chloride was measured by E. Baud, Ann. Chim. Phys. 1, 8 (1904). From $\Delta H_f^\circ = -26.38 \text{ kcal. mole}^{-1}$ for the reaction: $\text{Al}_2\text{Cl}_6(\text{c}) + 2\text{KCl}(\text{c}) = 2\text{KAlCl}_4(\text{c})$, the value of $\Delta H_f^\circ 298.15$ for $\text{KAlCl}_4(\text{c})$ was calculated to be $-286 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those for $\text{KAlCl}_3(\text{c})$, reported by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). $S_{298.15}^\circ$ was estimated according to the methods suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, 1958 and K. K. Kelley, private communication, June, 1960.

Temperature of Melting.

T_m was reported by W. Fischer and A.-L. Simon, Z. anorg. allgem. Chem. 305, 1 (1960).

AlCl_4K

Sodium Tetrachloroaluminate (NaAlCl₄)
(Crystal) Mol. Wt. = 191.799

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0							
100	37.040	45.000	45.000	.0000	- 273.000	- 248.956	182.481
200							
298	37.080	45.229	45.001	.069	- 272.984	- 248.806	181.247
300	37.080	45.229	45.001	.069	- 272.984	- 248.806	181.247
400	39.900	50.296	50.582	3.900	- 272.784	- 240.824	133.874
500	41.800	55.237	56.355	7.941	- 271.787	- 232.948	101.816
600	43.600	59.001	52.564	12.203	- 270.640	- 225.285	82.056
700	45.200	70.850	56.068	16.647	- 269.345	- 217.828	68.006
800	46.250	85.960	59.430	21.224	- 267.951	- 210.563	57.820
900	47.150	91.464	62.688	25.868	- 266.494	- 203.475	49.408
1000	47.800	96.459	65.819	30.639	- 265.503	- 196.369	42.914
1100	47.869	101.008	68.815	35.413	- 265.019	- 189.334	37.815
1200	48.100	105.184	71.674	40.212	- 264.560	- 181.965	33.142
1300	48.294	109.042	74.402	45.032	- 264.126	- 173.261	28.126
1400	48.450	112.627	77.006	49.869	- 263.699	- 164.677	23.706
1500	48.594	115.974	79.493	54.722	- 263.225	- 156.225	22.761
1600	48.700	119.114	81.872	59.587	- 262.213	- 147.895	20.201
1700	48.769	122.069	84.151	64.461	- 261.353	- 139.679	17.656
1800	48.800	124.857	86.335	69.339	- 260.494	- 131.578	15.975
1900	48.850	127.497	88.433	74.222	- 259.632	- 123.573	14.213
2000	48.900	130.004	90.449	79.109	- 258.775	- 115.673	14.640

SODIUM TETRACHLOROALUMINATE (NaAlCl₄) (CRYSTAL)

MOL. WT. = 191.799

ΔH_f° O = Unknown

S_{298.15}° = {45 ± 2} cal. deg.⁻¹ mole⁻¹

ΔH_f° 298.15 = -273 ± 1 kcal. mole⁻¹

ΔH_m° = Unknown

T_m = 424°K.

Heat of Formation.

The heat of formation at 298.15°K. was calculated from ΔH_f° = -11.9 kcal. mole⁻¹ for the reaction Al₂Cl₃(c) + 2NaCl(c) = 2NaAlCl₄(c) measured by E. Baud, Ann. chim. phys. 1, 6 (1904).

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those of KAlCl₄(c). S_{298.15} was estimated according to the methods suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, 1958 and K. K. Kelley, private communication, June, 1960.

Temperature of Melting.

T_m was reported by H. Fischer and A.-L. Simon, Z. anorg. allgem. Chem. 302, 1 (1960).

AlCl₄Na

Tripotassium Hexachloroaluminate (K_3AlCl_6)
(Crystal) Mol. Wt. = 357.022

T, °K.	C_p°	$\int_0^T C_p^\circ dT - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _f
0					
100					
200					
298	59.490	90.000	0.000	-463.325	339.610
300	59.580	90.368	11.0	-463.098	337.350
400	61.940	107.069	6.227	-458.001	297.350
500	64.450	122.043	12.548	-438.126	191.496
600	66.800	134.004	18.112	-425.854	155.110
600	66.800	134.004	18.112	-425.854	155.110
700	68.900	147.537	24.592	-413.767	109.784
800	70.900	159.895	30.626	-401.887	82.732
900	72.390	172.193	36.227	-390.242	72.290
1000	73.800	184.458	41.426	-378.569	63.212
1100	75.175	196.695	46.226	-366.813	54.231
1200	76.400	208.900	50.657	-355.067	45.253
1300	77.480	221.076	54.787	-343.332	36.231
1400	78.400	233.226	58.592	-331.607	27.239
1500	79.188	245.352	62.062	-320.000	18.239
1600	79.900	257.458	65.194	-308.500	9.239
1700	80.536	269.546	67.987	-297.115	0.239
1800	81.088	281.618	70.432	-285.846	-9.239
1900	81.558	293.676	72.532	-274.684	-18.239
2000	82.000	305.724	74.287	-263.632	-27.239

MOL. WT. = 357.022

(CRYSTAL)

TRIPOTASSIUM HEXACHLOROALUMINATE (K_3AlCl_6)

$AlCl_6K_3$

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_f^\circ 298.15 = -500 \pm 1 \text{ kcal. mole}^{-1}$

$\Delta H_m^\circ = \text{Unknown}$

$S_{298.15}^\circ = [30 \pm 2] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = [800]^\circ K.$

Heat of Formation.

The heat of formation at $298.15^\circ K.$ was recalculated from the same quantity given in National Bureau of Standards (U. S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952. The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(c) + 6KCl(c) = 2K_3AlCl_6(c)$ measured by E. Baud, Ann. chim. phys. 2, 8 (1904).

Heat Capacity and Entropy.

Both C_p and $S_{298.15}^\circ$ were estimated by comparison with the corresponding values of the sum of the constituent halides for $Na_3AlF_6(c)$.

Temperature of Melting.

T_m was estimated by comparison with that for $K_2AlF_6(c)$.

$AlCl_6K_3$

Trisodium Hexachloroaluminate (Na_3AlCl_6)

(Crystal) Mol. Wt. = 308.695

T, °K.	C _p	$\int_0^T \text{cal. mole}^{-1} \text{deg.}^{-1} \text{S}^\circ - (\text{F}^\circ - \text{H}_{298}^\circ)/T$	$\int_0^T \text{kcal. mole}^{-1} \text{deg.}^{-1} \text{H}^\circ - \text{H}_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0						
100						
200						
298	56.350	83.000	83.000	0.00	- 473.000	- 437.064
300						320.361
300	58.440	83.361	83.001	+108	- 472.984	- 436.940
400	60.800	100.614	85.137	6.111	- 474.100	- 424.765
500	63.100	114.431	89.817	12.307	- 473.313	- 412.515
600	65.250	126.128	94.918	18.776	- 472.320	- 400.446
700	67.200	135.235	100.101	25.350	- 471.135	- 388.562
800	68.900	142.167	104.485	32.137	- 469.794	- 376.926
900	70.500	153.642	110.156	39.137	- 468.294	- 365.326
1000	71.850	161.141	114.885	46.256	- 469.199	- 353.787
1100	73.069	168.047	119.408	53.503	- 467.431	- 342.335
1200	74.200	174.434	123.732	60.860	- 465.587	- 330.972
1300	75.250	180.436	127.792	68.331	- 463.672	- 319.677
1400	76.200	186.047	131.493	75.913	- 461.683	- 308.417
1500	77.150	191.337	135.616	83.581	- 459.613	- 297.178
1600	78.000	196.344	139.257	91.339	- 457.439	- 286.728
1700	78.750	201.096	142.436	99.176	- 455.165	- 276.465
1800	79.400	205.626	145.173	107.086	- 452.793	- 266.382
1900	80.025	209.926	147.469	115.058	- 450.321	- 256.469
2000	80.600	214.045	152.500	123.089	- 447.750	- 246.670

Sept. 30, 1963

AlCl_6Na_3

(CRYSTAL)

TRISODIUM HEXACHLOROALUMINATE (Na_3AlCl_6)

MOL. WT. = 308.695

$$\begin{aligned} \Delta H_f^\circ &= \text{Unknown} \\ \Delta H_f^\circ &= [63 \pm 2] \text{ cal. deg.}^{-1} \text{ mole}^{-1} \\ \Delta H_f^\circ &= -473 \pm 1 \text{ kcal. mole}^{-1} \\ T_m &= [780]^\circ\text{K.} \\ \Delta H_m^\circ &= \text{Unknown} \end{aligned}$$

Heat of Formation.

The heat of formation at 298.15°K. was recalculated from the same quantity given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952. The latter value was derived from the enthalpy change for the reaction $\text{Al}_2\text{Cl}_6(\text{c}) + 6\text{NaCl}(\text{c}) = 2\text{Na}_3\text{AlCl}_6(\text{c})$ measured by E. Baud, Ann. Chim. Phys. 1, 8 (1904).

Heat Capacity and Entropy.

Heat capacities and $S_{298.15}^\circ$ were estimated by comparison with the corresponding values of the sum of the constituent halides for $\text{Na}_3\text{AlF}_6(\text{c})$.

Temperature of Melting.

T_m was estimated by comparison with that for $\text{Na}_3\text{AlF}_6(\text{c})$.

AlCl_6Na_3

Aluminum Monofluoride (AlF)

(Ideal Gas)

GFW = 45.9799

ALUMINUM MONOFLUORIDE (AlF)

(IDEAL GAS)

GFW = 45.9799

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	-	-	INFINITE
100	6.900	43.500	63.1374	-	63.1374	-	63.376
200	7.178	48.448	52.081	-	63.134	-	65.293
268	7.632	51.397	47.000	-	63.223	-	67.444
300	7.650	51.469	46.018	-	63.400	-	69.484
400	7.650	51.469	46.018	-	63.400	-	69.484
500	7.650	51.469	46.018	-	63.400	-	69.484
600	7.650	51.469	46.018	-	63.400	-	69.484
700	7.650	51.469	46.018	-	63.400	-	69.484
800	7.650	51.469	46.018	-	63.400	-	69.484
900	7.650	51.469	46.018	-	63.400	-	69.484
1000	7.650	51.469	46.018	-	63.400	-	69.484
1100	7.650	51.469	46.018	-	63.400	-	69.484
1200	7.650	51.469	46.018	-	63.400	-	69.484
1300	7.650	51.469	46.018	-	63.400	-	69.484
1400	7.650	51.469	46.018	-	63.400	-	69.484
1500	7.650	51.469	46.018	-	63.400	-	69.484
1600	7.650	51.469	46.018	-	63.400	-	69.484
1700	7.650	51.469	46.018	-	63.400	-	69.484
1800	7.650	51.469	46.018	-	63.400	-	69.484
1900	7.650	51.469	46.018	-	63.400	-	69.484
2000	7.650	51.469	46.018	-	63.400	-	69.484
2100	7.650	51.469	46.018	-	63.400	-	69.484
2200	7.650	51.469	46.018	-	63.400	-	69.484
2300	7.650	51.469	46.018	-	63.400	-	69.484
2400	7.650	51.469	46.018	-	63.400	-	69.484
2500	7.650	51.469	46.018	-	63.400	-	69.484
2600	7.650	51.469	46.018	-	63.400	-	69.484
2700	7.650	51.469	46.018	-	63.400	-	69.484
2800	7.650	51.469	46.018	-	63.400	-	69.484
2900	7.650	51.469	46.018	-	63.400	-	69.484
3000	7.650	51.469	46.018	-	63.400	-	69.484
3100	7.650	51.469	46.018	-	63.400	-	69.484
3200	7.650	51.469	46.018	-	63.400	-	69.484
3300	7.650	51.469	46.018	-	63.400	-	69.484
3400	7.650	51.469	46.018	-	63.400	-	69.484
3500	7.650	51.469	46.018	-	63.400	-	69.484
3600	7.650	51.469	46.018	-	63.400	-	69.484
3700	7.650	51.469	46.018	-	63.400	-	69.484
3800	7.650	51.469	46.018	-	63.400	-	69.484
3900	7.650	51.469	46.018	-	63.400	-	69.484
4000	7.650	51.469	46.018	-	63.400	-	69.484
4100	7.650	51.469	46.018	-	63.400	-	69.484
4200	7.650	51.469	46.018	-	63.400	-	69.484
4300	7.650	51.469	46.018	-	63.400	-	69.484
4400	7.650	51.469	46.018	-	63.400	-	69.484
4500	7.650	51.469	46.018	-	63.400	-	69.484
4600	7.650	51.469	46.018	-	63.400	-	69.484
4700	7.650	51.469	46.018	-	63.400	-	69.484
4800	7.650	51.469	46.018	-	63.400	-	69.484
4900	7.650	51.469	46.018	-	63.400	-	69.484
5000	7.650	51.469	46.018	-	63.400	-	69.484
5100	7.650	51.469	46.018	-	63.400	-	69.484
5200	7.650	51.469	46.018	-	63.400	-	69.484
5300	7.650	51.469	46.018	-	63.400	-	69.484
5400	7.650	51.469	46.018	-	63.400	-	69.484
5500	7.650	51.469	46.018	-	63.400	-	69.484
5600	7.650	51.469	46.018	-	63.400	-	69.484
5700	7.650	51.469	46.018	-	63.400	-	69.484
5800	7.650	51.469	46.018	-	63.400	-	69.484
5900	7.650	51.469	46.018	-	63.400	-	69.484
6000	7.650	51.469	46.018	-	63.400	-	69.484

Dec. 31, 1960; Sept. 30, 1964; June 30, 1969

Ground State Configuration $1s^2$

$S_{298.15}^\circ = 51.40 \pm 0.01$ gibbs/mol

$\Delta H_{298.15}^\circ = -63.4 \pm 0.8$ kcal/mol

$\Delta H_{298.15}^\circ = -63.4 \pm 0.8$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
43935	2
54251	1

$\omega_e = 801.95$ cm⁻¹

$\sigma = 1$

$\nu_e = 1.6547$ Å

$B_e = 0.55228$ cm⁻¹

$a_e = 0.00483$ cm⁻¹

Heat of Formation

There have been several studies of the interaction of Al with AlF₃ to produce AlF(g) and the results of 2nd and 3rd law analyses are given below.

Ref.	Range, °K	Reaction	Points	$\Delta H_{298.15}^\circ$ kcal/mol	Drift	$\Delta H_{298.15}^\circ$ (AlF, g) kcal/mol
1. [cell 7]	882-931	A	8	162.7 ± 5.8	169.75 ± 0.6	-63.68 ± 0.8
1. [cell 9]	856-932	A	8	171.6 ± 4.1	170.66 ± 0.6	-63.38 ± 0.8
1. [cell 15x]	866-931	A	8	173.4 ± 1.5	170.49 ± 0.2	-63.44 ± 0.6
1. [cell 16x]	867-929	A	7*	171.6 ± 3.7	170.31 ± 0.4	-63.50 ± 0.7
2.		A		58.4	172.8 ± 1.8**	-62.67 ± 1.1
3.	1170-1373	B	5	156.1 ± 1.0	166.50 ± 0.2	-63.39 ± 0.6
4.	1287-1349	B	5	519.5 ± 14.2	176.0 ± 12.8	-60.2 ± 4
5.	1198-1348	C	10	100.8 ± 1.8	98.02 ± 0.5	-62.8 ± 0.9

* 1 point rejected due to statistical test. ** Value given by original author.

A) AlF₃(c) + 2 Al(c) = 3 AlF(g) B) AlF₃(c) + 2 Al(l) = 3 AlF(g) C) AlF₃(g) + 2 Al(l) = 3 AlF(g)

It is apparent that the runs with least drift are in close agreement at -63.4 kcal/mol and we adopt this value. This value is confirmed by Gross et al. (g) who report the heat of reaction A as 172.9 kcal/mol or ΔH_{298}° (AlF, g) = -62.96 kcal/mol. Also the data of Hildenbrand et al. (7) on the reaction $\text{BeF}_2(\text{g}) + \text{Al}(\text{c}) = \text{Be}(\text{c}) + 2 \text{AlF}(\text{g})$ yield ΔH_{298}° = 59.25 ± 0.5 kcal/mol which gives ΔH_{298}° (AlF, g) = -64.12 ± 1.7 kcal/mol. The highest observed levels in the A¹ state of AlF correspond to an absolute minimum of 156.4 kcal for the dissociation energy of AlF. Barrow et al. (g) indicate that normal extrapolation of the levels would yield a dissociation energy of 167.0 kcal. The dissociation energy corresponding to the adopted heat of formation is 159.2 kcal which may indicate a potential hump in the A¹ state.

Heat Capacity and Entropy

The rotational, vibrational constants and electronic levels are from the analyses of Maude and Hugo (g), Barrow et al. (g) and Lide (10).

References

1. D. L. Hildenbrand, L. P. Theard, W. F. Hall, F. Ju, F. S. Laviola and N. D. Potter, Aeronutronic Report U-2055, Ford Motor Company, 15 March 1963.
2. W. P. Witt and R. F. Barrow, Trans. Faraday Soc. **55**, 730 (1959).
3. S. A. Semakovich, Trudy Vsesoyuz. Aiumin.-Magnievyi Inst. No. **14**, 113 (1960).
4. A. V. Baimakov, Trudy Leningradskogo Politekhn. Inst. Elektromet. Tsvetnykh Metal. **188**, 156 (1957).
5. H. C. Ko, M. A. Greenbaum, J. A. Blauer and M. Farber, J. Phys. Chem. **69**, 2311 (1965).
6. P. Gross, C. Hayman and D. L. Levi, "The Physical Chemistry of Process Metallurgy," Met. Soc. Conferences, Interscience Publishers, New York, 1961, Vol. **8**, 903.
7. D. L. Hildenbrand, L. P. Theard and F. Ju, Aeronutronic Report U-2231, Ford Motor Company, 31 July 1963.
8. R. F. Barrow, J. W. C. Johns, and F. J. Smith, Trans. Faraday Soc. **52**, 913 (1956).
9. S. M. Maude and T. M. Hugo, Can. J. Phys. **35**, 64 (1957).
10. D. R. Lide, J. Chem. Phys. **38**, 2077 (1963).

(Ideal Gas) GFW = 45.9794

ALUMINUM MONOFUORIDE UNIPosITIVE ION (AlF⁺) (IDEAL GAS)

GFW = 45.9794

Ground State Configuration [2]

 $\Delta H_f^\circ = 161 \pm 12 \text{ kcal/mol}$ $S_{298.15}^\circ = [52.95 \pm 0.5] \text{ gibbs/mol}$ $\Delta H_f^\circ = 161 \pm 12 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$E_i, \text{ cm}^{-1}$	g_i
0	[2]
[28000]	[4]
[37000]	[2]
[45000]	[2]
$\omega_e x_e = [6] \text{ cm}^{-1}$	$\sigma = 1$
$B_e = [0.5232] \text{ cm}^{-1}$	$\nu_e = [1.7] \text{ \AA}$
$\alpha_e = [0.0063] \text{ cm}^{-1}$	

Heat of Formation

T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964) reported the ionization potential of AlF as $9.7 \pm 0.5 \text{ eV}$ ($224 \pm 12 \text{ kcal}$). The magnitude of the value has been confirmed by R. F. Porter, J. Chem. Phys. 33, 951 (1960) who found it between 9 and 10 eV. Using the above value in conjunction with $\Delta H_f^\circ(\text{AlF}, g) = -62.5 \text{ kcal/mol}$, and the equation $\text{AlF}(g) + \text{AlF}^+(g) + e^-$ yields $\Delta H_f^\circ(\text{AlF}^+, g) = 161 \pm 12 \text{ kcal/mol}$.

Heat Capacity and Entropy

AlF⁺ is isoelectronic with MgF, and the electronic configuration of the ground and excited states we estimate to be those for MgF(g). The vibrational frequency, anharmonicity constant and bond length we estimate by comparison with those for MgF and AlF. The rotational constant is calculated from the bond length and atomic masses, and q_e is calculated from the other constants assuming a Morse potential function.

The enthalpy at 0°K is -2.139 kcal.

June 30, 1968

AlF⁺

Aluminum Oxide Fluoride (AlOF)

(Ideal Gas) Mol. Wt. = 61.98

ALUMINUM OXIDE FLUORIDE (AlOF)

(IDEAL GAS)

MOL. WT. = 61.98

Point Group $C_{\infty v}$ $\Delta H_f^\circ = -139.5 \pm 2.6 \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = [55.986] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^\circ_{298.15} = -140.2 \pm 2.6 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$

[900](1)
 [500](2)
 [750](1)

Bond Distance: O-Al = [1.62] Å

Al-F = [1.65] Å

 $\sigma = 1$

Bond Angle: O-Al-F = [180]°

Rotational Constant: $B_0 = [0.180806] \text{ cm.}^{-1}$

Heat of Formation.

The equilibrium constants (2200-2225°K.) of the chemical reaction $\text{Al}_2\text{O}_3 (c) + \text{AlF}_3 (g) = 3\text{AlOF} (g)$ were measured by M. Farber and H. L. Petersen, Trans. Faraday Soc. 59, 836 (1963). Using this data, the heat of reaction at 298.15°K. was calculated by the third law method to be $266.2 \pm 1.7 \text{ kcal. mole}^{-1}$. The value of ΔH_f° 298.15 for AlOF (g) was then derived.

Heat Capacity and Entropy.

The bond distances of Al-O and Al-F were estimated to be the same as those for AlO (g) and AlF (g), respectively. The point group, ground state quantum weight and vibrational frequencies were obtained from W. H. Evans, J. Hilsenrath and H. W. Woolley, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds," National Bureau of Standards Report 6926, July 1, 1960. The moment of inertia is $1.54800 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C_p°	$-\text{cal. mole}^{-1} \text{ deg.}^{-1}$	$g^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	INFINITE	2.448	-139.461	-139.461	INFINITE
100	7.116	46.705	64.207	1.750	-139.574	-139.968	305.896
200	8.839	52.095	56.908	.963	-139.618	-140.245	153.245
298	10.692	55.986	55.986	0.000	-140.200	-140.347	102.872
300	10.722	56.052	55.986	.020	-140.205	-140.348	102.839
400	12.016	59.328	52.986	1.212	-140.200	-140.343	76.687
500	12.846	62.105	57.290	2.408	-140.550	-140.337	61.338
600	13.381	64.498	58.296	3.721	-140.687	-140.281	51.095
700	13.740	66.590	59.435	5.078	-140.831	-140.202	43.771
800	14.057	68.401	60.460	6.482	-140.982	-139.980	38.595
900	14.337	70.100	61.400	7.892	-141.140	-139.743	34.254
1000	14.599	71.600	62.403	9.297	-141.300	-139.651	30.519
1100	14.839	72.968	63.211	10.732	-141.460	-139.222	27.660
1200	15.077	74.224	64.077	12.176	-141.619	-138.781	25.274
1300	15.287	75.385	64.903	13.627	-141.786	-138.338	23.254
1400	15.467	76.462	65.699	15.082	-141.961	-137.893	21.504
1500	15.627	77.472	66.443	16.544	-142.144	-137.457	20.018
1600	15.659	78.417	67.162	18.009	-142.336	-136.917	18.701
1700	15.687	79.307	67.850	19.476	-142.540	-136.439	17.538
1800	15.713	80.140	68.510	20.948	-142.756	-135.994	16.504
1900	15.730	80.943	69.143	22.418	-142.984	-135.590	15.594
2000	15.746	81.699	69.753	23.892	-143.224	-135.224	14.743
2100	15.761	82.419	70.339	25.367	-143.476	-134.893	13.987
2200	15.773	83.106	70.894	26.844	-143.740	-134.598	13.299
2300	15.783	83.757	71.425	28.324	-144.016	-134.337	12.668
2400	15.794	84.392	71.971	29.801	-144.304	-134.109	12.093
2500	15.803	84.996	72.484	31.281	-144.604	-133.912	11.562
2600	15.810	85.577	72.976	32.761	-144.916	-133.715	11.071
2700	15.817	86.136	73.454	34.252	-145.240	-133.518	10.616
2800	15.823	86.676	73.919	35.753	-145.576	-133.321	10.191
2900	15.829	87.195	74.365	37.267	-145.924	-133.124	9.800
3000	15.834	87.698	74.801	38.690	-146.284	-132.927	9.435
3100	15.838	88.184	75.225	40.174	-146.656	-132.730	9.095
3200	15.842	88.656	75.638	41.658	-147.040	-132.533	8.778
3300	15.846	89.116	76.030	43.151	-147.436	-132.336	8.481
3400	15.849	89.566	76.403	44.657	-147.844	-132.139	8.209
3500	15.852	89.986	76.811	46.112	-148.264	-131.942	7.959
3600	15.855	90.405	77.283	47.598	-148.696	-131.745	7.729
3700	15.858	90.822	77.746	49.103	-149.140	-131.548	7.516
3800	15.861	91.230	78.190	50.633	-149.596	-131.351	7.316
3900	15.864	91.594	78.626	52.055	-150.064	-131.154	7.129
4000	15.866	91.970	78.985	53.542	-150.544	-130.957	6.957
4100	15.868	92.337	79.316	55.028	-151.036	-130.760	6.802
4200	15.869	92.696	79.620	56.515	-151.540	-130.563	6.657
4300	15.871	93.049	79.900	58.006	-152.056	-130.366	6.522
4400	15.871	93.387	79.667	59.499	-152.584	-130.169	6.397
4500	15.873	93.722	80.171	60.976	-153.124	-129.972	6.281
4600	15.874	94.048	80.609	62.443	-153.676	-129.775	6.174
4700	15.874	94.369	80.962	63.901	-154.240	-129.578	6.077
4800	15.874	94.688	81.330	65.349	-154.816	-129.381	5.989
4900	15.878	94.988	81.606	66.786	-155.404	-129.184	5.909
5000	15.879	95.289	81.877	68.215	-156.004	-128.987	5.837
5100	15.880	95.583	82.144	69.635	-156.616	-128.790	5.772
5200	15.882	95.872	82.499	71.046	-157.240	-128.593	5.714
5300	15.882	96.156	82.846	72.450	-157.876	-128.396	5.662
5400	15.882	96.434	83.186	73.846	-158.524	-128.199	5.614
5500	15.883	96.707	83.521	75.235	-159.184	-127.999	5.571
5600	15.884	96.975	83.846	76.615	-159.856	-127.799	5.532
5700	15.885	97.239	84.166	77.985	-160.540	-127.599	5.497
5800	15.885	97.499	84.481	79.346	-161.236	-127.399	5.467
5900	15.886	97.752	84.806	80.696	-161.944	-127.199	5.441
6000	15.887	98.002	85.119	82.046	-162.664	-126.999	5.418

T, °K.	C _v ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-	2.779	-164.575	-164.575	-164.575	INFINITE
100	8.777	52.784	72.387	-1.960	-164.557	-165.601	-165.601	361.906
200	9.204	59.228	64.749	-1.024	-164.763	-166.586	-166.586	182.028
298	10.949	63.381	63.381	0.000	-165.000	-167.434	-167.434	122.727
300	10.967	63.449	63.381	0.020	-165.005	-167.450	-167.450	121.981
400	11.622	66.725	63.622	1.161	-165.231	-168.512	-168.512	73.612
500	12.375	69.424	64.080	2.372	-165.434	-169.654	-169.654	73.606
600	12.761	71.717	65.667	3.630	-165.684	-169.633	-169.633	61.786
700	13.024	73.705	66.676	4.920	-165.932	-170.271	-170.271	53.159
800	13.210	75.457	67.667	6.232	-166.202	-170.874	-170.874	46.678
900	13.345	77.001	68.621	7.580	-166.457	-171.353	-171.353	40.629
1000	13.445	78.432	69.532	8.900	-166.634	-171.787	-171.787	37.242
1100	13.521	79.718	70.401	10.249	-166.557	-172.024	-172.024	34.176
1200	13.580	80.897	71.227	11.604	-166.799	-172.236	-172.236	31.367
1300	13.627	81.986	72.013	12.964	-170.042	-172.430	-172.430	28.087
1400	13.665	82.997	72.762	14.329	-170.264	-172.604	-172.604	25.013
1500	13.695	83.941	73.476	15.697	-170.527	-172.761	-172.761	22.170
1600	13.721	84.825	74.158	17.068	-170.771	-172.901	-172.901	23.616
1700	13.742	85.658	74.811	18.441	-171.016	-173.027	-173.027	22.243
1800	13.760	86.444	75.435	19.816	-171.263	-173.140	-173.140	21.021
1900	13.775	87.186	76.034	21.191	-171.511	-173.241	-173.241	19.936
2000	13.788	87.893	76.610	22.571	-171.759	-173.319	-173.319	18.939
2100	13.799	88.568	77.163	23.950	-172.010	-173.394	-173.394	18.044
2200	13.809	89.210	77.696	25.331	-172.262	-173.452	-173.452	17.230
2300	13.818	89.824	78.210	26.712	-172.516	-173.500	-173.500	16.485
2400	13.826	90.412	78.707	28.094	-172.771	-173.539	-173.539	15.802
2500	13.832	90.977	79.186	29.477	-173.030	-173.565	-173.565	15.172
2600	13.838	91.520	79.650	30.861	-173.289	-173.583	-173.583	14.590
2700	13.843	92.042	80.100	32.245	-173.550	-173.588	-173.588	14.050
2800	13.848	92.546	80.536	33.629	-173.811	-173.594	-173.594	13.419
2900	13.852	93.032	80.958	35.012	-174.072	-173.594	-173.594	12.782
3000	13.856	93.501	81.368	36.399	-174.334	-173.594	-173.594	12.147
3100	13.859	93.956	81.767	37.785	-174.599	-173.594	-173.594	11.573
3200	13.862	94.396	82.155	39.171	-174.868	-173.594	-173.594	11.034
3300	13.865	94.822	82.532	40.558	-175.139	-173.594	-173.594	10.520
3400	13.868	95.236	82.898	41.944	-175.411	-173.594	-173.594	10.031
3500	13.870	95.638	83.258	43.331	-175.684	-173.594	-173.594	9.561
3600	13.872	96.029	83.607	44.718	-175.959	-173.594	-173.594	9.117
3700	13.874	96.409	83.948	46.106	-176.236	-173.594	-173.594	8.775
3800	13.876	96.776	84.281	47.494	-176.515	-173.594	-173.594	8.433
3900	13.877	97.140	84.606	48.883	-176.795	-173.594	-173.594	8.091
4000	13.880	97.491	84.924	50.269	-177.076	-173.594	-173.594	7.769
4100	13.881	97.834	85.235	51.657	-177.358	-173.594	-173.594	7.462
4200	13.883	98.168	85.539	53.045	-177.641	-173.594	-173.594	7.161
4300	13.884	98.495	85.836	54.433	-177.925	-173.594	-173.594	6.866
4400	13.885	98.817	86.126	55.822	-178.210	-173.594	-173.594	6.576
4500	13.886	99.126	86.413	57.210	-178.496	-173.594	-173.594	6.291
4600	13.887	99.431	86.693	58.599	-178.783	-173.594	-173.594	6.019
4700	13.888	99.730	86.967	59.988	-179.071	-173.594	-173.594	5.751
4800	13.889	100.023	87.236	61.377	-179.360	-173.594	-173.594	5.483
4900	13.890	100.310	87.500	62.766	-179.650	-173.594	-173.594	5.224
5000	13.891	100.590	87.759	64.155	-179.941	-173.594	-173.594	5.004
5100	13.892	100.865	88.013	65.544	-180.233	-173.594	-173.594	4.793
5200	13.892	101.134	88.263	66.933	-180.526	-173.594	-173.594	4.590
5300	13.893	101.399	88.508	68.322	-180.820	-173.594	-173.594	4.394
5400	13.894	101.660	88.748	69.711	-181.115	-173.594	-173.594	4.206
5500	13.894	101.914	88.982	71.101	-181.411	-173.594	-173.594	4.023
5600	13.895	102.164	89.219	72.491	-181.708	-173.594	-173.594	3.849
5700	13.895	102.410	89.449	73.880	-182.006	-173.594	-173.594	3.680
5800	13.896	102.652	89.674	75.270	-182.305	-173.594	-173.594	3.516
5900	13.896	102.899	89.896	76.659	-182.605	-173.594	-173.594	3.358
6000	13.897	103.143	90.115	78.049	-182.906	-173.594	-173.594	3.206

Dec. 31, 1960; Sept. 30, 1984

Point Group [C_{2v}].S_{298.15}^o = [63.381] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

$$\frac{\omega}{\text{cm.}^{-1}}$$

[91.7](1)
[236](1)
[750](1)

Bond Distances: Al-F = [1.65] Å

Bond Angle: F-Al-F = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [3.367909 X 10⁻¹¹⁵] g.³ cm.⁶

σ = 2

Heat of Formation.

The selected heat of formation, -185 ± 20 kcal. mole⁻¹ is the weighted average of two estimates (a) [-163 ± 20 kcal. mole⁻¹] and (b) [-175 ± 30 kcal. mole⁻¹]. The first estimate (a) is based upon appearance potentials reported by T. C. Ehlert and J. L. Margrave, J. Am. Chem. Soc. 86, 3901 (1964).

(1) AlF₃(g) → AlF₂⁺(ion) + F(g) 15.2 ± 0.3 e.v.(2) AlF₃⁺(ion) → AlF₂(g) -9 ± 1 e.v.(3) (1) + (2) or AlF₃(g) → AlF₂(g) + F(g) 6.2 ± 1.3 e.v.The second estimate (b) is based upon the average Al-F bond strength of AlF₃(g) and AlF(g). i.e.(4) AlF₃(g) + AlF(g) → 2 AlF₂(g) ΔH_r 298 = 0

Heat Capacity and Entropy.

The bond distance, 1.65 Å, was estimated from a consideration of the Al-F distance 1.63 and 1.65 Å in AlF₃(g) and AlF(g). The bent configuration and bond angle estimates were based on the correlations of A. D. Walsh, J. Chem. Soc., 2266, (1953). From the molecular constants the principal moments of inertia were found to be I_A = 1.7829 X 10⁻³⁹, I_B = 12.8617 X 10⁻³⁹, and I_C = 14.6646 X 10⁻³⁹ g. cm.². The vibrational frequencies were calculated assuming valence forces, [G. Herzberg, "Molecular Spectra and Molecular Structure II", D. Van Nostrand Co., 1945] and using force constants calculated from AlF₃(g).

Aluminum Difluoride Unipositive Ion (AlF₂⁺)

(Ideal Gas) GFW = 64.9778

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ²⁹⁸)/T	H ^o -H ²⁹⁸ ΔH ^o	kcal/mol ΔH ^o	ΔG ^o	Log Kp
100	12.335	57.799	57.799	.000	42.000	39.743	29.132
200	12.355	57.875	57.799	.023	42.007	39.728	29.942
300	13.181	61.553	56.295	1.303	42.415	38.509	21.239
400	13.687	64.533	54.236	2.646	42.819	37.064	16.603
500	14.008	67.079	60.355	4.034	43.211	36.980	13.470
600	14.221	69.255	61.474	5.447	43.584	35.911	11.212
700	14.368	71.164	62.569	6.876	43.927	34.791	9.505
800	14.473	72.663	63.650	8.319	44.229	33.631	8.167
900	14.551	74.392	64.622	9.770	44.554	32.622	7.130
1000	14.609	75.782	65.574	11.228	44.868	31.674	6.293
1200	14.655	77.055	66.479	12.692	45.168	30.698	5.591
1300	14.690	78.230	67.338	14.159	45.457	29.696	4.992
1400	14.719	79.319	68.155	15.629	45.734	28.673	4.466
1500	14.742	80.336	68.934	17.103	46.000	27.628	4.005
1600	14.761	81.288	69.677	18.578	46.258	26.559	3.628
1700	14.777	82.183	70.386	20.055	46.507	25.475	3.275
1800	14.791	83.028	71.065	21.533	46.746	24.372	2.959
1900	14.802	83.828	71.716	23.013	46.975	23.255	2.675
2000	14.812	84.586	72.341	24.493	47.195	22.121	2.417
2100	14.820	85.310	72.941	25.975	47.405	20.970	2.182
2200	14.828	86.000	73.519	27.457	47.607	19.808	1.968
2300	14.834	86.659	74.076	28.941	47.801	18.634	1.771
2400	14.840	87.291	74.614	30.424	47.987	17.444	1.599
2500	14.845	87.897	75.133	31.908	48.167	16.245	1.450
2600	14.849	88.479	75.635	33.393	48.341	15.036	1.264
2700	14.853	89.039	76.122	34.878	48.502	13.816	1.118
2800	14.857	89.580	76.593	36.364	48.651	12.591	1.047
2900	14.860	90.101	77.049	37.850	48.791	11.366	1.106
3000	14.863	90.605	77.493	39.338	48.923	10.141	1.166
3100	14.865	91.092	77.924	40.822	49.048	8.916	1.209
3200	14.868	91.564	78.343	42.309	49.168	7.691	1.254
3300	14.870	92.022	78.750	43.796	49.283	6.466	1.295
3400	14.872	92.466	79.147	45.283	49.393	5.241	1.332
3500	14.873	92.897	79.534	46.770	49.498	4.016	1.367
3600	14.875	93.316	79.911	48.257	49.598	2.791	1.399
3700	14.877	93.723	80.279	49.745	49.693	1.566	1.427
3800	14.878	94.120	80.638	51.233	49.783	3.341	1.454
3900	14.879	94.507	80.999	52.720	49.868	4.116	1.479
4000	14.881	94.883	81.351	54.208	49.948	4.891	1.501
4100	14.882	95.251	81.696	55.697	50.023	5.666	1.522
4200	14.883	95.610	81.994	57.185	50.093	6.441	1.542
4300	14.884	95.960	82.315	58.673	50.158	7.216	1.559
4400	14.885	96.302	82.659	60.162	50.219	7.991	1.576
4500	14.885	96.636	82.936	61.654	50.275	8.766	1.591
4600	14.886	96.964	83.238	63.139	50.327	9.541	1.605
4700	14.887	97.284	83.533	64.627	50.375	10.316	1.617
4800	14.888	97.597	83.823	66.116	50.419	11.091	1.629
4900	14.888	98.104	84.107	67.605	50.459	11.866	1.640
5000	14.889	98.205	84.386	69.094	50.494	12.641	1.650
5100	14.889	98.500	84.660	70.583	50.525	13.416	1.659
5200	14.890	98.789	84.929	72.072	50.552	14.191	1.668
5300	14.890	99.073	85.193	73.561	50.576	14.966	1.675
5400	14.891	99.351	85.453	75.050	50.596	15.741	1.682
5500	14.891	99.624	85.708	76.539	50.612	16.516	1.689
5600	14.892	99.892	85.959	78.028	50.626	17.291	1.695
5700	14.892	100.156	86.206	79.517	50.636	18.066	1.701
5800	14.893	100.415	86.448	81.006	50.642	18.841	1.706
5900	14.893	100.670	86.687	82.495	50.646	19.616	1.710
6000	14.893	100.920	86.920	84.000	50.646	20.391	1.714

June 30, 1968

ALUMINUM DIFLUORIDE UNIPosITIVE ION (AlF₂⁺) (IDEAL GAS)

Point Group [D_{∞h}]

S_{298.15}^o = [57.8 ± 2.0] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
[850] (1)	
[240] (2)	
[500] (1)	

Bond Distance: Al-F = [1.71] Å

Bond Angle: F-Al-F = [180°]

Rotational Constant: B₀ = [0.1535] cm⁻¹

σ = 2

Heat of Formation

T. C. Ehlert, G. D. Blue, J. W. Green and J. L. Margrave, J. Chem. Phys. 41, 2250 (1964) report the appearance potential of AlF₂⁺ from AlF₃ as 15.2 ± 0.3eV. Assuming the reaction to be AlF₃(g) + e⁻ ~ AlF₂⁺ + F + 2e⁻ ΔH = 350.5 ± 7 kcal we calculate ΔH_f^o(AlF₂⁺, g) = 42 ± 10 kcal/mol, or an ionization potential for AlF₂ of 9eV. Due to the neglect of any kinetic energy of the fragments this probably is an upper limit.

Heat Capacity and Entropy

The linear configuration is estimated from the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2268 (1953), however, it should be noted that the isoelectronic MgF₂ is considered to be bent. The vibrational frequencies are estimated to lie between those for AlF₂ and MgF₂. The bond distance is estimated by comparison with AlF and AlF₃.

The enthalpy at 0°K is -2.883 kcal/mol.

Aluminum Difluoride Unipositive Ion (AlF₂⁺) GFW = 64.9778

(IDEAL GAS)

GFW = 64.9778

ΔH_f^o = [42.3 ± 10] kcal/mol

ΔH_f^o = [42 ± 10] kcal/mol

AlF₂⁺

Aluminum Difluoride Uninegative Ion (AlF₂⁻)

(Ideal Gas)

GF_W = 64.9788

ALUMINUM DIFLUORIDE UNINEGATIVE ION (AlF₂⁻)
(IDEAL GAS)

Point Group [C_{2v}]

GF_W = 64.9788

ΔH_{f,0}^o = [-174.5 ± 40] kcal/mol

ΔH_{f,298.15}^o = [-175 ± 40] kcal/mol

S_{298.15}^o = [61.4 ± 0.5] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	
[820] (1)	
[320] (1)	
[900] (1)	

Bond Distance: [1.65] Å

Bond Angle: F-Al-F = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [3.368 × 10⁻¹¹⁵] g³ cm⁶

σ = 2

Heat of Formation

AlF₂⁻ is isoelectronic with SiF₂ and an estimate of its heat of formation may be obtained by assuming the binding energy to be the same; this yields ΔH_{f,298}(AlF₂⁻, g) = -191 kcal/mol, or an electron affinity for AlF₂ of 26 kcal/mol. The binding energy should be close to that of AlF₂ since the extra electron should go into a non-bonding orbital according to the correlation diagrams of A. D. Walsh, J. Chem. Soc. 2266 (1953); using this approach yields ΔH_{f,298}(AlF₂⁻, g) = -177 kcal/mol or an electron affinity for AlF₂ of 12 kcal. Another method of estimation assumes that the heats are identical for the two reactions AlF₃ + AlF₂⁻ + F⁺ and AlF₃ + Al⁺ + F⁺, which yields ΔH_{f,298}(AlF₂⁻, g) = -161 kcal/mol or an electron affinity for AlF₂ of -4 kcal. We adopt a median value for the electron affinity for AlF₂ of 10 ± 20 kcal, which leads to ΔH_{f,298}(AlF₂⁻, g) = -175 ± 40 kcal/mol when combined with ΔH_{f,298}(AlF₂, g) = -165 ± 20 kcal/mol.

Heat Capacity and Entropy

Assumed to lie between those of AlF and AlF₃, the angle is that in AlF₃. The vibrational frequencies are estimated between those for SiF₂ and AlF₂. By analogy with SiF₂, no low electronic levels are expected (G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York 1966). The enthalpy at 0°K is -2.698 kcal/mol.

The individual principal moments of inertia are I_A = 1.783 × 10⁻³⁹ g cm², I_B = 12.882 × 10⁻³⁹ g cm² and I_C = 14.665 × 10⁻³⁹ g cm².

June 30, 1968

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0							
100		61.427	61.427	.000	-175.000	-175.165	12e.546
200							
298	10.702	61.427	61.427	.000	-175.000	-175.165	12e.546
300	10.722	61.493	61.427	.020	-175.014	-175.167	12e.755
400	11.624	64.508	61.427	.080	-175.014	-175.167	12e.755
500	12.245	67.134	61.427	.135	-175.000	-175.169	12e.755
600	12.662	69.646	63.676	3.582	-174.241	-174.857	63.692
700	12.948	71.620	64.673	4.863	-174.992	-174.399	54.450
800	13.150	73.383	65.652	6.169	-176.766	-173.634	47.699
900	13.266	74.951	66.597	7.444	-178.558	-172.341	41.141
1000	13.404	76.326	67.501	8.627	-180.358	-171.229	37.601
1100	13.487	77.609	68.362	10.171	-183.762	-171.118	33.988
1200	13.551	78.786	69.183	11.523	-188.563	-169.834	30.949
1300	13.602	79.872	69.964	12.681	-193.362	-168.481	28.396
1400	13.643	80.882	70.708	14.244	-198.163	-167.167	26.177
1500	13.676	81.824	71.416	15.609	-202.964	-165.997	24.186
1600	13.704	82.708	72.096	16.979	-207.765	-164.873	22.480
1700	13.727	83.539	72.745	18.350	-212.566	-163.999	20.968
1800	13.746	84.325	73.367	19.724	-217.367	-163.170	19.616
1900	13.761	85.067	73.963	21.100	-222.168	-162.381	18.396
2000	13.773	85.775	74.536	22.476	-226.969	-161.631	17.310
2100	13.789	86.447	75.088	23.855	-231.770	-160.920	16.314
2200	13.800	87.089	75.619	25.234	-236.571	-160.249	15.405
2300	13.809	87.702	76.131	26.614	-241.372	-159.617	14.571
2400	13.817	88.290	76.625	27.997	-246.173	-159.024	13.804
2500	13.824	88.854	77.103	29.378	-250.974	-158.467	13.095
2600	13.831	89.397	77.566	30.761	-255.775	-157.946	12.438
2700	13.836	89.919	78.014	32.144	-260.576	-157.455	11.827
2800	13.842	90.422	78.448	33.528	-265.377	-156.994	11.259
2900	13.846	90.908	78.866	34.911	-270.178	-156.562	10.731
3000	13.850	91.377	79.276	36.297	-274.979	-156.159	10.241
3100	13.854	91.832	79.676	37.682	-279.780	-155.784	9.789
3200	13.857	92.272	80.063	39.068	-284.581	-155.437	9.370
3300	13.861	92.698	80.439	40.454	-289.382	-155.116	8.980
3400	13.863	93.112	80.806	41.840	-294.183	-154.819	8.620
3500	13.866	93.514	81.163	43.226	-298.984	-154.544	8.287
3600	13.868	93.904	81.512	44.613	-303.785	-154.291	7.979
3700	13.871	94.284	81.852	46.000	-308.586	-154.059	7.692
3800	13.873	94.654	82.184	47.387	-313.387	-153.846	7.426
3900	13.875	95.015	82.506	48.774	-318.188	-153.652	7.179
4000	13.876	95.366	82.825	50.162	-322.989	-153.477	6.947
4100	13.878	95.709	83.135	51.550	-327.790	-153.320	6.727
4200	13.879	96.043	83.439	52.938	-332.591	-153.181	6.517
4300	13.881	96.370	83.736	54.326	-337.392	-153.059	6.316
4400	13.882	96.669	84.027	55.714	-342.193	-152.954	6.123
4500	13.883	97.001	84.311	57.102	-346.994	-152.865	5.937
4600	13.885	97.306	84.591	58.491	-351.795	-152.791	5.760
4700	13.886	97.605	84.864	59.879	-356.596	-152.731	5.592
4800	13.887	97.897	85.133	61.268	-361.397	-152.684	5.432
4900	13.888	98.183	85.386	62.656	-366.198	-152.649	5.280
5000	13.888	98.464	85.635	64.045	-370.999	-152.624	5.134
5100	13.889	98.739	85.909	65.434	-375.799	-152.609	5.000
5200	13.890	99.009	86.158	66.823	-380.599	-152.604	4.875
5300	13.891	99.273	86.403	68.212	-385.399	-152.609	4.759
5400	13.892	99.533	86.644	69.601	-390.199	-152.624	4.650
5500	13.892	99.788	86.880	70.990	-394.999	-152.639	4.546
5600	13.893	100.038	87.113	72.380	-400.000	-152.654	4.447
5700	13.893	100.284	87.342	73.769	-404.800	-152.669	4.353
5800	13.894	100.526	87.567	75.158	-409.600	-152.684	4.264
5900	13.895	100.763	87.789	76.547	-414.400	-152.699	4.180
6000	13.895	100.997	88.007	77.937	-419.200	-152.714	4.099

AlF₂⁻

Aluminum Trifluoride (AlF₃)

GFW = 83.9767

(Crystal)

ALUMINUM TRIFLUORIDE (AlF₃)

(CRYSTAL)

GFW = 83.9767

AlF₃

$\Delta H_f^\circ = -359.5 \pm 0.3 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -361.0 \pm 0.3 \text{ kcal/mol}$
 $\Delta H_t^\circ = 0.1346 \text{ kcal/mol}$
 $\Delta H_s^\circ_{298.15} = 71.965 \pm 0.6 \text{ kcal/mol monomer}$
 $\Delta H_s^\circ_{298.15} = 92.55 \pm 4 \text{ kcal/mol dimer}$

$S^\circ_{298.15} = 15.89 \pm 0.1 \text{ gibbs/mol}$
 $T_t = 728^\circ\text{K}$
 $T_s = [1549]^\circ\text{K}$

Heat of Formation

The adopted value is from separate calorimetric studies of combustion in fluorine of aluminum (1) and aluminum-Teflon mixtures (2). More extensive auxiliary data (2) for Teflon bring the aluminum-Teflon study into exact agreement with the aluminum study (1). Calorimetric data relating AlF₃ to PbF₂ (1, 2) tend to confirm this value, but PbF₂ is probably more uncertain than is AlF₃.

Solid-state emf data (3) relating AlF₃ to MgF₂ via ThF₄ gave $\Delta G_f^\circ = -305.7 \text{ kcal/mol}$ for AlF₃(c) at 600°C. The adopted negative value indicated by entrainment data (3) for 2/3 AlF₃(c) + 1/3 Al₂O₃(g, c) + 2HF(g) in the range from 849° to 1312°K. Analysis of the equilibrium constants yields $\Delta H_f^\circ_{298.15} = 33.11 \pm 0.2 \text{ kcal/mol}$ (3rd law) and $33.33 \pm 0.22 \text{ kcal/mol}$ (2nd law) with an insignificant entropy difference, $\Delta S_f^\circ(2\text{nd law}) - \Delta S_f^\circ(3\text{rd law}) = 0.2 \pm 0.2 \text{ gibbs/mol}$. It has been suggested (1) that interaction of the condensed phases caused the equilibria to deviate from the standard-state reaction assumed above. An alternative may be that the reaction with water vapor produced Al₂O₃ in a metastable form; such forms require ignition temperatures greater than 1400°K for complete conversion to $\alpha\text{-Al}_2\text{O}_3$ (g).

Heat Capacity and Entropy

C_p° and S°_{298} are taken from Douglas and Dittmars (7), whose tables are based on heat capacity measurements from 54° to 298°K (g) and relative enthalpy measurements from 323° to 1173°K (7). The enthalpy data confirm earlier data (401°-1401°K) of O'Brien and Kelley (9) rather than the adjusted values proposed by Frank (10). Douglas and Dittmars (7) gave a detailed comparison with other data. The entropy is derived from C_p° using the extrapolation $S^\circ_{50} = 0.53 \pm 0.06 \text{ gibbs/mol}$.

Transition Data

T_t and ΔH_t° are from Douglas and Dittmars (7). The values were obtained from extensive enthalpy data for the transition region assuming the presence of a very small amount of impurity in solid solution.

Sublimation Data

T_s is the temperature at which the calculated total pressure (monomer plus dimer) reaches one atm; the mole fraction of dimer is calculated as 0.109 at T_s . Sublimation temperatures of 1533° and 1566°K were obtained in two sublimation-pressure studies (11, 12) at the Technische Hochschule, Breslau. The selected enthalpies of sublimation to AlF₃(g) and Al₂F₆(g) reproduce closely the entrainment data of Krause and Douglas (13). Selection of these values of ΔH_s° and comparisons with other vapor-pressure data are discussed on the gas-phase tables.

References

1. E. Rudzitis, H. M. Feder and W. N. Hubbard, *Inorg. Chem.* **6**, 1716 (1967).
2. E. S. Domalski and G. T. Armstrong, *J. Res. Nat. Bur. Stand.* **71A**, 105 (1967); **69A**, 137 (1965).
3. The JANAF Thermochemical Table for PbF₂(c), June 30, 1959.
4. R. J. Heus and J. J. Egan, *J. Phys. Chem. (Frankfurt)* **70**, 38 (1966).
5. V. P. Mashovets and B. F. Yudin, *Izv. Vysish. Uchab. Zaved.*, Tsvet. Met. **5** (4), 95 (1962).
6. T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.* **68**, 3246 (1964).
7. T. B. Douglas and D. A. Dittmars, *J. Res. Nat. Bur. Stand.* **71A**, 185 (1967).
8. E. G. King, *J. Amer. Chem. Soc.* **79**, 2056 (1957).
9. C. J. O'Brien and K. K. Kelley, *J. Amer. Chem. Soc.* **79**, 5616 (1957).
10. W. B. Frank, *J. Phys. Chem.* **65**, 2081 (1961).
11. O. Ruff and L. LeBoucher, *Z. Anorg. Allg. Chem.* **219**, 376 (1934).
12. W. Olbrich, *Dissertation, Technische Hochschule, Breslau*, 1928.
13. R. F. Krause and T. B. Douglas, *J. Phys. Chem.* **72**, 475 (1968).

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1965; June 30, 1970

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	INFINITE	INFINITE	2.778	-359.519	-359.519	INFINITE
100	5.959	2.882	26.442	2.576	-360.465	-354.484	774.725
200	13.594	9.558	17.403	1.569	-360.951	-348.285	380.987
298	17.957	15.890	15.890	.000	-361.000	-342.053	250.731
300	18.021	16.001	15.490	-.033	-360.999	-341.936	249.100
400	20.623	21.633	16.633	1.979	-360.807	-335.604	183.365
500	22.054	26.349	18.112	4.119	-360.509	-329.338	143.953
600	23.258	30.472	19.636	6.362	-360.153	-323.136	117.029
700	24.246	34.083	21.219	8.924	-359.757	-317.077	93.077
800	25.046	37.183	22.851	11.331	-359.331	-311.093	85.942
900	25.699	40.373	24.511	13.700	-358.888	-304.931	78.047
1000	26.099	42.898	26.401	16.097	-358.426	-298.767	65.296
1100	26.353	45.007	28.371	18.500	-357.946	-292.585	56.123
1200	26.597	46.797	29.844	20.827	-357.446	-286.383	47.125
1300	26.831	48.315	31.285	23.085	-356.928	-280.169	40.106
1400	25.071	51.166	32.640	25.034	-356.394	-274.053	34.782
1500	25.302	52.902	33.733	28.453	-355.834	-267.946	30.040
1600	25.731	54.562	35.170	30.995	-355.244	-261.866	25.769
1700	25.984	57.576	37.404	36.146	-354.628	-255.810	21.945
1800	26.210	58.966	38.756	38.756	-353.985	-249.783	18.528
1900	26.435	60.337	39.842	41.368	-353.312	-243.780	15.441
2000	26.640	61.832	40.659	44.023	-352.621	-237.800	12.646
2100	26.840	63.477	42.590	46.720	-351.913	-231.849	9.219
2200	27.110	64.077	42.590	49.420	-351.193	-225.921	5.203
2300	27.335	65.236	43.510	52.152	-350.467	-220.011	0.700
2400	27.560	66.356	44.401	54.887	-349.735	-214.130	19.499
2500					-348.987	-208.275	18.207

ALUMINUM TRIFLUORIDE (AlF₃)

(IDEAL GAS)

GFN = 83.9767

Point Group D_{3h}
 $S_{288.15}^0 = 66.15 \pm 0.2$ gibbs/mol
 Ground State Quantum Weight = 1

$\Delta H_{298.15}^0 = -288.14 \pm 0.6$ kcal/mol
 $\Delta H_{298.15}^0 = -289.03 \pm 0.6$ kcal/mol

Aluminum Trifluoride (AlF₃)

GFN = 83.9767

(Ideal Gas)

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100	0.000	52.000	INFINITE	-3.368	-288.144	-288.144	INFINITE
200	12.926	60.591	67.457	-1.373	-286.330	-286.330	312.487
298	14.945	66.150	66.150	0.000	-285.073	-285.073	208.564
300	14.977	66.283	66.151	0.028	-285.039	-285.039	207.059
400	15.402	70.760	67.500	1.601	-289.220	-289.220	155.000
500	17.352	74.530	67.945	3.242	-289.510	-289.510	123.306
600	17.945	77.753	69.318	5.061	-289.508	-289.660	102.303
700	18.418	80.560	70.727	6.893	-289.648	-289.407	87.235
800	18.723	83.040	72.115	8.741	-289.806	-277.938	75.928
900	18.943	85.264	73.454	10.624	-289.999	-276.439	67.128
1000	19.107	87.284	74.736	12.557	-292.156	-274.137	60.044
1100	19.232	89.091	75.960	14.445	-292.936	-272.927	54.226
1200	19.329	90.769	77.125	16.373	-293.112	-272.907	49.374
1300	19.406	92.319	78.235	18.310	-293.288	-269.298	45.266
1400	19.468	93.760	79.293	20.254	-293.463	-267.402	41.743
1500	19.516	95.101	80.302	22.203	-293.636	-265.252	38.610
1600	19.560	96.365	81.267	24.157	-293.817	-263.656	36.014
1700	19.594	97.552	82.191	26.115	-293.995	-261.765	33.552
1800	19.624	98.673	83.076	28.076	-294.175	-259.865	31.552
1900	19.649	99.733	83.925	30.039	-294.357	-257.953	29.671
2000	19.670	100.743	84.741	32.005	-294.540	-256.032	27.976
2100	19.688	101.703	85.526	33.973	-294.726	-254.105	26.445
2200	19.704	102.620	86.282	35.943	-294.915	-252.166	25.050
2300	19.718	103.496	87.012	37.914	-295.105	-250.215	23.776
2400	19.731	104.335	87.716	39.866	-295.296	-248.260	22.607
2500	19.742	105.141	88.397	41.860	-295.495	-246.299	21.531
2600	19.751	105.916	89.056	43.835	-295.694	-244.326	20.537
2700	19.760	106.661	89.694	45.810	-295.895	-242.346	19.619
2800	19.768	107.380	90.313	47.787	-296.098	-240.350	18.696
2900	19.775	108.074	90.914	49.764	-296.303	-238.343	17.772
3000	19.781	108.744	91.497	51.742	-296.508	-236.327	16.795
3100	19.787	109.393	92.064	53.720	-296.713	-234.301	15.736
3200	19.792	110.021	92.615	55.699	-296.918	-232.267	14.591
3300	19.797	110.630	93.152	57.678	-297.123	-230.224	13.331
3400	19.801	111.221	93.675	59.658	-297.328	-228.171	11.964
3500	19.805	111.794	94.184	61.639	-297.533	-226.109	10.493
3600	19.809	112.353	94.681	63.619	-297.738	-224.038	8.919
3700	19.812	112.896	95.166	65.600	-297.943	-221.958	7.239
3800	19.815	113.425	95.640	67.582	-298.148	-219.868	5.454
3900	19.818	113.939	96.103	69.563	-298.353	-217.768	3.564
4000	19.821	114.441	96.555	71.545	-298.558	-215.658	1.564
4100	19.823	114.931	96.997	73.527	-298.763	-213.538	0.454
4200	19.825	115.408	97.430	75.510	-298.968	-211.408	0.234
4300	19.827	115.875	97.853	77.492	-299.173	-209.268	0.014
4400	19.829	116.331	98.268	79.475	-299.378	-207.118	0.000
4500	19.831	116.776	98.674	81.458	-299.583	-204.958	0.000
4600	19.833	117.212	99.073	83.442	-299.788	-202.788	0.000
4700	19.835	117.639	99.463	85.425	-299.993	-200.608	0.000
4800	19.836	118.056	99.846	87.408	-300.198	-198.418	0.000
4900	19.838	118.465	100.222	89.392	-300.403	-196.218	0.000
5000	19.839	118.866	100.591	91.376	-300.608	-194.008	0.000
5100	19.841	119.259	100.953	93.360	-300.813	-191.788	0.000
5200	19.843	119.644	101.309	95.344	-301.018	-189.558	0.000
5300	19.844	120.022	101.658	97.328	-301.223	-187.318	0.000
5400	19.846	120.393	102.002	99.312	-301.428	-185.068	0.000
5500	19.848	120.757	102.340	101.297	-301.633	-182.808	0.000
5600	19.849	121.115	102.672	103.281	-301.838	-180.538	0.000
5700	19.850	121.466	102.998	105.266	-302.043	-178.258	0.000
5800	19.851	121.811	103.320	107.251	-302.248	-175.968	0.000
5900	19.852	122.151	103.636	109.235	-302.453	-173.658	0.000
6000	19.853	122.484	103.947	111.220	-302.658	-171.328	0.000

Dec. 31, 1960; Sept. 30, 1963; Sept. 30, 1965; June 30, 1970

Heat of Formation

ΔH^0 is calculated from that of the crystal by use of $\Delta H_{298.15}^0 = 71.965 \pm 0.5$ kcal/mol. Sublimation studies by mass-spectrometric and entrainment techniques suggest the presence of a small amount of dimer in the saturated vapor. These studies are reviewed on the table for Al₂F₆(g). ΔH (monomer) and ΔH (dimer) are selected by adopting (a) the JANAF entropies for crystal, monomer and dimer, (b) the mass spectrometric value of 2 ΔH (monomer) - ΔH (dimer) = -49 kcal/mol at 1000°K, and (c) the entrainment data of Krause and Douglas (1). The resulting calculated pressures deviate by <0.5% from the entrainment data (1), by <0.1 from the mass-spectrometric equation (3) and by <3% from the mass-effusion equation (4).

Further comparisons with experimental data are given below. The adopted values favor the later (11) of two sublimation-point studies (11, 12), both show considerable scatter and similar deviations from the calculated dP/dT . Torsion-effusion data suggest the possibility of more serious discrepancy. Although data of Witt and Barrow (9) are consistent with the JANAF pressures, Hildenbrand et al. (2, 3) noted a trend toward increasing pressure with decreasing orifice area. They concluded (7) that the condensation coefficient <0.06, based on eightfold variation in the product of Clausius factor x orifice area. JANAF predictions for the pressure are 60 to 80% of the adjusted torsion values (7) and the discrepancy corresponds roughly to the ratios used in the adjustment. In contrast, the JANAF predictions agree closely with mass-effusion data of Ko et al. (4), who reported no significant effect from a twofold variation in orifice area.

Comparison of Calculated and Observed Total Pressures over AlF₃(c)

Source	Method	T, °K Range	Mole Fraction Dimer		Difference ^a in dP/dT
			Calc.	Range	
(1) Krause (1968)	Entrainment	1194-1258	0.019-0.029	1.004-0.996	Very small (-)
(2) Maryashkin (1939)	Entrainment	1108-1273	0.010-0.032	0.73-2.22	Uncertain (?)
(3) Erokhin (1967)	Mass Spec. ^b	983-1165	0.003-0.016	1.09-0.91	Small (-)
(4) Ko (1965)	Mass Effusion	1027-1184	0.005-0.018	0.994-0.972	Very small (-)
(5) Blackburn (1965)	Mass Effusion	889-1006	0.001-0.004	1.42-1.66	Uncertain (+)
(6) Evesev (1959)	Mass Effusion	980-1123	0.003-0.012	1.64-0.88	Large (-)
(7) Hildenbrand (1963)	Torsion Effusion ^c				
	Cell 9-22	1004-1114	0.004-0.011	0.67-0.74	Very Small (?)
	Cell 8-7	989-1102	0.004-0.010	0.60-0.81	Medium (+)
	Cell 8-9	977-1088	0.003-0.009	0.63-0.73	Small (+)
	Cell 8-10	977-1088	0.003-0.009	0.60-0.72	Small (+)
	Cell 8-11	977-1088	0.003-0.009	0.60-0.72	Medium (+)
	Cell 8-12	977-1088	0.003-0.009	0.60-0.72	Medium (+)
(8) Hildenbrand (1961)	Torsion Effusion				
	Cell 8-7	992-1101	0.004-0.010	0.89-1.01	Small (+)
	Cell 8-9	989-1080	0.003-0.008	0.94-1.34	Medium (+)
(9) Witt (1959)	Torsion Effusion	956-1063	0.003-0.007	1.11-1.07	Small (-)
(10) Vetyukov (1959)	Dynamic B. P.	1335-1453	0.044-0.076	0.84-1.64	Large (+)
(11) Ruff (1934)	Dynamic B. P.	1367-1524	0.052-0.100	1.33-0.79	Large (-)
(12) Olbrich (1928)	Dynamic B. P.	1371-1567	0.053-0.116	2.70-1.28	Large (-)

^a Magnitude and sign of the difference, calculated minus observed, in dP/dT . ^b Absolute pressures of monomer were obtained by integration of the ion intensity during total sublimation. ^c Based on P calculated from the torsion pressure Pt by the equation given.

Heat Capacity and Entropy

The molecular structure is that derived from electron-diffraction data by Akishin et al. (13). Observed vibrational frequencies are those reported by Büchler et al. (14) from infrared spectra of the vapor at 1000-1200°K. These frequencies are confirmed by infrared spectra of AlF₃ isolated in matrices of neon, argon and krypton (15). The Raman-active fundamental ν_1 is estimated as 650 ± 50 cm⁻¹ by three methods: (a) calculation of the force constant k_1 from ν_3 and ν_4 , (b) comparison of $k_1(XY)/k(XZ)$ for $X = B, Al$ and $Y = F, Cl$ and Br ; and (c) extrapolation of $\nu_1(BF_3)/\nu_1(AlF_3)$ to ν_1 from $Y = Cl, Br$ and I , using recent gas-phase Raman data (16) for AlF₃. Principal moments of inertia are $I_A = 12.572 \times 10^{-38}$ and $I_C = 25.14 \times 10^{-38}$ g cm².

References

1. J. Krause and Th. B. Douglas, *J. Phys. Chem.*, **72**, 475 (1968).
2. I. L. Maryashkin, *Zh. Fiz. Khim.*, **13**, 159 (1939).
3. E. V. Erokhin, N. A. Zhegul'skaya, L. N. Sidorov and P. A. Akishin, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3** (5), 973 (1967).
4. H. C. Ko, H. A. Greenbaum, J. A. Blauer and M. Farber, *J. Phys. Chem.*, **69**, 2311 (1965).
5. P. E. Blackburn, *Oak Ridge Report*, A. D. Little, Inc., May 31, 1965.
6. A. H. Evesev, G. V. Pozharovskaya, An. N. Nesevyanov and Ya. I. Gerasimov, *Zh. Neorg. Khim.*, **4**, 2186 (1959).
7. D. L. Hildenbrand and L. P. Theard, *Contract Non-Proprietary Communication*, July 30, 1963; D. L. Hildenbrand et al., *Aeronautics Rept. No. U-2055*, Contract Non-Proprietary, July 30, 1963.
8. D. L. Hildenbrand and L. P. Theard, *AD 258410*, 24 pp (1961).
9. W. P. Witt and R. F. Barrow, *Trans. Faraday Soc.*, **55**, 730 (1959).
10. M. H. Vetyukov, M. L. Blyustein and V. P. Podymov, *Izv. Vyssh. Ucheb. Zaved.*, **2** (6), 126 (1959).
11. O. Ruff and L. Le Boucher, *Z. Anorg. Allg. Chem.*, **213**, 376 (1934).
12. O. Olbrich, *Abhandlungen der Kaiserlichen Akademie der Wissenschaften, Wien, Math. Naturwiss. Klasse*, **136** (1928).
13. P. A. Akishin, *Abstracts of the International Symposium on Pure and Applied Chemistry*, **136** (1959); English translation, p. 187.
14. A. Büchler, E. P. Harman and J. L. Stauffer, *J. Phys. Chem.*, **72**, 3202 (1967).
15. A. Snelson, *J. Phys. Chem.*, **72**, 3202 (1967).
16. I. R. Beattie and J. R. Hordar, *J. Chem. Soc. A*, **1963**, 2655.

Point Group [C_{2v}] $\Delta H_f^\circ = -441.3 \pm 2 \text{ kcal/mol}$ $\Delta H_f^\circ = -443.0 \pm 2 \text{ kcal/mol}$ $S_{298.15}^\circ = [78.46] \pm 2 \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

Lithium Tetrafluoroaluminate (LiAlF₄)

GFW = 109.9141

(Ideal Gas)

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	INFINITE
100	12.693	58.525	94.759	-4.755	-441.336	INFINITE
200	19.801	69.682	80.545	-3.623	-439.392	960.290
298	24.102	78.463	78.463	-2.173	-436.507	476.992
				-0.000	-433.413	317.700
300	24.163	78.464	78.464	-0.045	-433.355	315.699
400	26.718	85.946	79.446	2.600	-433.210	234.997
500	28.243	92.066	81.377	5.354	-432.102	184.524
600	29.496	97.326	84.410	8.230	-429.278	131.043
700	30.429	101.977	87.000	11.493	-424.720	83.093
800	31.143	105.869	89.154	14.188	-418.549	41.697
900	31.685	109.070	90.927	17.229	-410.713	100.200
1000	32.076	111.702	92.407	20.296	-401.439	69.359
1100	32.349	113.848	94.384	23.383	-390.009	40.648
1200	32.532	115.543	96.272	26.485	-376.722	21.956
1300	32.643	116.935	98.077	29.598	-361.744	6.783
1400	32.685	118.073	100.000	32.712	-345.345	61.404
1500	32.667	119.000	102.000	35.826	-327.667	52.741
1600	32.592	119.732	104.000	38.939	-308.723	37.050
1700	32.457	120.296	106.000	42.052	-288.590	22.440
1800	32.263	120.635	108.000	45.165	-267.243	9.486
1900	32.011	120.773	110.000	48.278	-243.794	4.434
2000	31.708	120.734	112.000	51.391	-218.251	3.565
2100	31.354	119.492	109.831	54.504	-190.611	37.050
2200	30.957	117.960	107.049	57.617	-160.951	34.764
2300	30.519	116.164	103.724	60.730	-130.269	32.677
2400	30.141	114.109	100.000	63.843	-100.573	30.764
2500	31.626	111.400	96.854	66.956	-71.874	29.004
2600	31.638	108.661	93.514	70.069	-43.161	27.380
2700	31.660	105.922	90.172	73.182	-14.451	25.875
2800	31.691	103.183	86.830	76.295	14.254	24.414
2900	31.725	100.444	83.488	79.408	43.504	22.997
3000	31.772	97.705	80.146	82.521	72.754	21.520
3100	31.831	94.966	76.804	85.634	102.004	19.989
3200	31.899	92.227	73.462	88.747	131.254	18.400
3300	31.977	89.488	70.120	91.860	160.504	16.764
3400	32.064	86.749	66.778	94.973	189.754	15.080
3500	32.160	84.010	63.436	98.086	219.004	13.344
3600	32.265	81.271	60.094	101.199	248.254	11.554
3700	32.379	78.532	56.752	104.312	277.504	9.664
3800	32.501	75.793	53.413	107.425	306.754	7.674
3900	32.630	73.054	50.074	110.538	336.004	5.584
4000	32.767	70.315	46.735	113.651	365.254	3.394
4100	32.912	67.576	43.396	116.764	394.504	1.104
4200	33.064	64.837	40.057	119.877	423.754	-1.186
4300	33.223	62.098	36.718	122.990	453.004	-2.476
4400	33.388	59.359	33.379	126.103	482.254	-3.766
4500	33.559	56.620	30.040	129.216	511.504	-5.056
4600	33.735	53.881	26.701	132.329	540.754	-6.346
4700	33.916	51.142	23.362	135.442	570.004	-7.636
4800	34.101	48.403	20.023	138.555	600.254	-8.926
4900	34.290	45.664	16.684	141.668	630.504	-10.216
5000	34.483	42.925	13.345	144.781	660.754	-11.506
5100	34.681	40.186	10.006	147.894	691.004	-12.796
5200	34.883	37.447	6.667	151.007	721.254	-14.086
5300	35.089	34.708	3.328	154.120	751.504	-15.376
5400	35.299	31.969	0.000	157.233	781.754	-16.666
5500	35.513	29.230	-3.339	160.346	812.004	-17.956
5600	35.731	26.491	-6.678	163.459	842.254	-19.246
5700	35.953	23.752	-10.019	166.572	872.504	-20.536
5800	36.179	21.013	-13.360	169.685	902.754	-21.826
5900	36.409	18.274	-16.701	172.798	933.004	-23.116
6000	36.643	15.535	-20.042	175.911	963.254	-24.406

Sept. 30, 1962; Sept. 30, 1963; Dec. 31, 1963; Mar. 31, 1964; June 30, 1970

Vibrational Frequencies and Degeneracies
ω, cm⁻¹ ω, cm⁻¹ ω, cm⁻¹ ω, cm⁻¹800 (1) 1300 (1) 555 (1) 890 (1)
665 (1) 1295 (1) 450 (1) 330 (1)
[580] (1) [180] (1) 240 (1) 285 (1)

Bond Distance: Al-F = [1.69] Å Li-F = [1.8] Å

Bond Angle: F-Al-F = [109.47°]

Product of the Moments of Inertia: I_AI_BI_C = [2.0109 × 10⁻¹¹³] g³ cm⁶

σ = [2]

Heat of Formation

Mass spectrometric studies (1) of the two-phase systems LiF + Li₃AlF₆ and Li₃AlF₆ + AlF₃ suggested that the vapor contains small amounts of Li₂AlF₅ and Li₂(AlF₄)₂, but that LiAlF₄(g) constitutes of the order of 90%. Hildenbrand et al. (2) reported torsion effusion pressures for the compositions 3LiF:AlF₃ and LiF:AlF₃, as a first approximation, these total pressures should correspond to the reactions (A) Li₃AlF₆(c) = LiAlF₄(g) + 2LiF(c), and (B) 1/3 Li₃AlF₆(c) + 2/3 AlF₃(c) = LiAlF₄(g). Porter and Zeller (3) reported mass spectrometric equilibrium constants for the reaction (C) Li₂F₂ + AlF₃(g) = LiF(g) + LiAlF₄(g). Second-order and third-law analyses of these data are summarized below. Kumann and Tillessen (4) reported total vapor pressures over molten LiAlF₄-AlF₃ (0.81 ≤ n ≤ 3), but we have made no attempt to establish the liquid phase activities necessary for use of these data.

The adopted ΔH^o is derived from reaction (B) which exhibits entropy deviations (6S) and orifice area effects which are relatively minor. Data for reaction (A) yield a ΔH^o that is more negative by 1.5 kcal/mol, but the very large entropy deviation suggests the presence of systematic uncertainties. Combination of (B) and (A) into the reaction 3LiF(c) + AlF₃(c) + Li₂AlF₆(c) gives ΔH₂₉₈^o = -3.3 kcal/mol, which is fairly consistent with the calorimetric value (5) of ΔH₂₉₈^o = -5.4 ± 0.5 kcal/mol. Sidorov and Kolosov (6) suggested that the equilibrium constants for reaction (C) should be considered as lower limits since AlF₃ and LiAlF₄ are probably both precursors of AlF₂⁺.

(2)	Hildenbrand (1963)	Source	Reaction	Method	Range T, K	ΔS gibbs/mol	ΔH _{298.15} ^o kcal/mol	ΔH _{298.15} ^o kcal/mol
(2)	Hildenbrand (1963)	A	Torsion effusion, Cell 7	7	987-1058	33 ± 1	103.341.5	69.33
(2)	Hildenbrand (1963)	B	Torsion effusion, Cell 9	9	899-980	74.341.8	74.341.8	-443.122
(3)	Porter (1960)	C	Torsion effusion, Cell 15x	15x	873-976	2.740.5	69.940.5	67.35
(3)	Porter (1960)	C	Mass spectrometry		894-990	2.321.0	69.650.9	67.48
(3)	Porter (1960)	C	Mass spectrometry		1000-1100	4 ± 5	-1 ± 5	-438.426

Heat Capacity and Entropy

The point group and molecular structure are assumed to be similar to those adopted for NaAlF₄. A discussion of the incomplete structural evidence is given on the table for NaAlF₄(g). The adopted structure consists of tetrahedral AlF₄ combined with Li to form a planar ring, AlF₂Li, through coordination with two fluorines. The Al-F distance is assumed to be equal to that observed in NaAlF₄, while the Li-F distance is estimated by comparison of the M-F distances in MF₃(g), M₂F₄(g) (M = Li and Na) with that in NaAlF₄(g). The principal moments of inertia are I_A = 24.026 × 10⁻³⁸ and I_B = I_C = 28.930 × 10⁻³⁹ g cm².

Snelson (7) observed eight fundamentals in the infrared spectra of LiAlF₄ isolated in rare gas matrices. He estimated gas phase fundamentals by assuming a constant shift of about 15 cm⁻¹ from the value in a neon matrix to the value in the gas. McCoy et al. (8) found absorptions near 778 and 866 cm⁻¹ in the infrared spectra of the vapor at high temperatures. We adopt average values of 800 and 890 cm⁻¹ for these two fundamentals and Snelson's values for the other six. The four additional fundamentals necessary for C_{2v} symmetry are estimated by comparison with Li₂F₂, Al₂F₆, AlF₃, and AlCl₃. Sidorov and Kolosov (6), using somewhat different estimates for fundamental frequencies and structural parameters, calculated S₁₀₀₀^o = 114 ± 2 gibbs/mol. The JANAF value is 112.7 ± 2 gibbs/mol.

References

1. A. Büchler and J. Berkowitz-Mattuck, AD 63163, pp 41-3, June, 1967.
2. D. L. Hildenbrand, L. P. Theard, W. F. Hall, F. J. S. Lavioia and N. D. Potter, Aeronutronic Publication No. U-2055, March 15, 1963.
3. R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960).
4. U. Kumann and U. Tillessen, Z. Erzbearbeit Metalluettm. 20, 147 (1967).
5. P. D. Greene, P. Gross and C. Hayman, Trans. Faraday Soc. 54, 633 (1958).
6. L. N. Sidorov and E. N. Kolosov, Russ. J. Phys. Chem. 42, 1382 (1968).
7. A. Snelson, IIT Res. Inst. Report No. IITRI-U6001-13, August 12, 1966.
8. L. D. McCoy, R. C. Paule and J. L. Margrave, J. Phys. Chem. 67, 1086 (1963).

Sodium Tetrafluoroaluminate (NaAlF₄)
(Ideal Gas) GFW = 125.9649

T, °K	C _p ^o	S ^o -(G°-H°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	0.000	INFINITE	-5.158	-484.903	-484.903	INFINITE
100	14.000	60.700	-4.162	-485.723	-482.920	966.101
200	21.613	73.172	-2.321	-486.311	-480.666	320.068
298	25.333	82.566	-1.000	-486.600	-486.600	
300	25.383	82.723	-0.97	-486.604	-486.587	318.049
400	27.524	90.346	2.047	-487.152	-487.152	187.766
500	28.881	96.838	5.523	-487.597	-487.597	
600	29.601	101.963	8.486	-487.714	-487.714	
700	30.127	106.569	10.234	-487.623	-487.623	
800	30.489	110.616	12.534	-487.466	-487.466	
900	30.746	114.223	14.740	-487.259	-487.259	
1000	30.936	117.473	16.860	-486.985	-486.985	
1100	31.079	120.428	18.870	-486.650	-486.650	
1200	31.189	123.138	20.761	-486.275	-486.275	
1300	31.276	125.638	22.591	-485.860	-485.860	
1400	31.345	127.956	24.368	-485.416	-485.416	
1500	31.402	130.123	26.100	-484.942	-484.942	
1600	31.449	132.151	27.789	-484.437	-484.437	
1700	31.487	134.058	29.450	-483.902	-483.902	
1800	31.520	135.859	31.093	-483.336	-483.336	
1900	31.548	137.566	32.721	-482.740	-482.740	
2000	31.572	139.193	34.335	-482.114	-482.114	
2100	31.592	140.724	35.927	-481.467	-481.467	
2200	31.610	142.194	37.500	-480.798	-480.798	
2300	31.625	143.599	39.056	-480.106	-480.106	
2400	31.639	144.948	40.597	-479.392	-479.392	
2500	31.651	146.238	42.127	-478.657	-478.657	
2600	31.662	147.479	43.643	-477.900	-477.900	
2700	31.672	148.674	45.145	-477.122	-477.122	
2800	31.680	149.826	46.634	-476.324	-476.324	
2900	31.686	150.936	48.110	-475.506	-475.506	
3000	31.695	152.012	49.574	-474.668	-474.668	
3100	31.701	153.052	51.027	-473.810	-473.810	
3200	31.707	154.058	52.467	-472.932	-472.932	
3300	31.712	155.034	53.894	-472.034	-472.034	
3400	31.717	155.981	55.308	-471.116	-471.116	
3500	31.721	156.900	56.709	-470.178	-470.178	
3600	31.725	157.794	58.097	-469.220	-469.220	
3700	31.729	158.663	59.474	-468.242	-468.242	
3800	31.732	159.509	60.839	-467.244	-467.244	
3900	31.735	160.334	62.194	-466.226	-466.226	
4000	31.738	161.137	63.539	-465.188	-465.188	
4100	31.741	161.921	64.873	-464.130	-464.130	
4200	31.744	162.686	66.196	-463.052	-463.052	
4300	31.746	163.433	67.509	-461.954	-461.954	
4400	31.748	164.164	68.812	-460.836	-460.836	
4500	31.750	164.876	70.107	-459.698	-459.698	
4600	31.752	165.574	71.393	-458.540	-458.540	
4700	31.754	166.257	72.669	-457.362	-457.362	
4800	31.756	166.926	73.936	-456.164	-456.164	
4900	31.758	167.580	75.194	-454.946	-454.946	
5000	31.759	168.222	76.443	-453.708	-453.708	
5100	31.760	168.851	77.684	-452.450	-452.450	
5200	31.761	169.468	78.916	-451.172	-451.172	
5300	31.763	170.073	80.139	-449.874	-449.874	
5400	31.764	170.666	81.354	-448.556	-448.556	
5500	31.765	171.249	82.561	-447.218	-447.218	
5600	31.766	171.822	83.759	-445.860	-445.860	
5700	31.767	172.384	84.948	-444.482	-444.482	
5800	31.768	172.936	86.129	-443.084	-443.084	
5900	31.769	173.479	87.301	-441.666	-441.666	
6000	31.770	174.013	88.464	-440.228	-440.228	

June 30, 1970

(IDEAL GAS)

SODIUM TETRAFLUOROALUMINATE (NaAlF₄)

Point Group [C_{2v}]

S_{298.15} = [82.571] ± 2 gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies			
ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
800 (1)	[300] (1)	890 (1)	
680 (1)	[160] (1)	340 (1)	320 (1)
[390] (1)	[180] (1)	[190] (1)	[200] (1)

Bond Distance: Al-F = 1.69 ± 0.02 Å Na-F = 2.11 ± 0.02 Å

Bond Angle: F-Al-F = 109.47°

Product of the Moments of Inertia: I_AI_BI_C = 4.79396 × 10⁻¹¹³ g³ cm⁶ σ = [2]

Heat of Formation

ΔH^o is based on ΔH^o_{298.15} = 69.36 kcal/mol for the reaction Na₃AlF₆(c) + 2NaF(c). ΔH^o is calculated by third law analysis of the pressure equation reported for this reaction by Sidorov and Kolosov (1). The second law ΔH^o = 70.5 kcal/mol and the entropy deviation is 1.1 gibbs/mol. Sidorov and Kolosov obtained their pressure equation by combination of the temperature variation of ion intensities with integration of intensities during total sublimation at 931°K (2).

Sidorov et al. (2) concluded that the pressure of the dimer (NaAlF₄)₂ at 931°K is almost half of the monomer pressure over the two-phase system Na₃AlF₆·1/2NaF₃. In contrast, Büchler et al. (3) reported the approximate vapor composition of 97% monomer, 1% dimer, 1% NaAlF₃, and 1% AlF₃ over the same condensed phases at 833°K. The latter composition was obtained from a mass spectrometric study by the twin crucible method.

Vapor pressures over melts in the NaF-AlF₃ system have been measured by the entrainment and boiling point techniques (4-7). We have made no attempt to establish the liquid phase activities necessary for use of these data.

Heat Capacity and Entropy

The adopted structure (C_{2v} symmetry) consists of tetrahedral AlF₄ combined with Na to form a planar ring, AlF₂Na, through coordination with two fluorines. Experimental evidence available for NaAlF₄ and LiAlF₄ does not distinguish conclusively between this structure and the alternatives which have been seriously considered. Alternatives include a C_s structure, in which the ring is non-planar, and two C_{2v} structures, in which Na (or Li) is coordinated to one or three fluorines instead of two.

Electron diffraction data (8) for the vapor gave the adopted bond distances and showed that the AlF₄ group is essentially tetrahedral. Wave error at small scattering angles precluded the calculation of accurate non-bonded distances for Na.

Shelson (9) observed the infrared spectra of LiAlF₄ and NaAlF₄ isolated in matrices of neon and argon. Eight fundamentals were found above 200 cm⁻¹ for LiAlF₄ and six for NaAlF₄. Shelson chose a C_{2v} structure for LiAlF₄ on the basis of Redlich-Teller product-rule calculations for isotopic shifts due to Li.

Neither the infrared data nor the electron-diffraction data are conclusive so we apply these qualitative arguments. Coordination of Na to three fluorines seems less likely, since there are no known examples of this behavior. The C_{2v} structure, as suggested by Büchler and Berkowitz-Mattuck (3), is likely because it is a hybrid between the accepted structures of Na₂F₂ and Al₂F₆. C_{2v} symmetry (σ = 2) is a compromise which has an entropy effect intermediate between the other alternatives. The principal moments of inertia of the C_{2v} structure are I_A = 24.026 × 10⁻³⁹ and I_B = I_C = 44.669 × 10⁻³⁹ g cm².

The fundamental vibrations of 800 and 890 cm⁻¹ are average values from gas phase (10) and matrix (9) spectra. Four other observed values are from the matrix data. Six fundamentals are estimated by comparisons similar to those used for LiAlF₄(g).

References

1. L. N. Sidorov and E. N. Kolosov, Russ. J. Phys. Chem. (English transl.) 42, 1382 (1968); *ibid.*, p. 1384.
2. L. N. Sidorov, E. V. Erokhin, P. A. Akishin and E. N. Kolosov, Dokl. Akad. Nauk. SSSR 173 (2), 370 (1967).
3. A. Büchler, J. L. Stauffer and J. B. Berkowitz-Mattuck, unpublished results (1966), quoted in A. Büchler and J. B. Berkowitz-Mattuck, *AD 653163*, June, 1967.
4. U. Kumann and U. Tillessen, Z. Erzbirgbau Metallhuettenw. 20, 147 (1967).
5. M. Rolin and J. Houriez, Bull. Soc. Chim. Fr. 1964, 891, 897, 900 (1964).
6. A. Vajna and R. Bacchiaga, Met. Ital. 52, 461 (1960).
7. M. M. Vetyukov, M. L. Blyuststein and V. P. Podymov, Izv. Vyssh. Ucheb. Zaved., Tsvet. Met. 2 (6), 126 (1959).
8. V. P. Spiridonov and E. V. Erokhin, Dokl. Akad. Nauk 180 (1), 161 (1968); Proc. Acad. Sci. USSR (English transl.) 180 335 (1968).
9. A. Shelson, IIT Res. Inst. Report No. IITRI-UG6001-13, August 12, 1966.
10. L. D. McCarty, R. C. Paule and J. L. Margrave, J. Phys. Chem. 67, 1086 (1963).

AlF₄Na

Tripotassium Hexafluoroaluminate (K_3AlF_6)

Mol. Wt. = 258.28

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K_p
100					
200					
298	53.250	68.000	0.000	-795.000	554.208
300	53.390	68.001	0.099	-794.903	550.614
400	57.620	84.425	5.704	-786.237	405.692
500	61.020	97.657	11.640	-785.578	318.720
600	63.910	109.046	17.891	-784.657	260.794
700	66.660	119.105	24.420	-783.516	219.472
800	69.230	128.182	31.220	-782.166	188.531
900	71.400	136.472	38.261	-780.637	164.508
1000	73.000	144.081	45.484	-781.503	145.289
1100	74.400	151.106	52.856	-846.418	128.971
1200	75.600	157.633	60.358	-843.798	114.978
1300	76.600	163.725	67.969	-841.087	103.176
1400	77.400	169.432	75.671	-838.287	93.092
1500	78.038	174.794	83.444	-835.448	84.382
1600	78.600	179.849	91.276	-832.552	76.788
1700	79.088	184.629	99.161	-829.615	70.111
1800	79.500	189.161	107.091	-826.645	64.197
1900	79.800	193.468	115.057	-823.651	58.923
2000	80.000	197.567	123.048	-820.641	54.194

AlF_6K_3

MOL. WT. = 258.28

TRIPOTASSIUM HEXAFLUOROALUMINATE (K_3AlF_6)

(CRYSTAL)

$\Delta H_f^\circ =$ Unknown
 $\Delta H_f^\circ 298.15 = [-795 \pm 5] \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ =$ Unknown
 $S_{298.15}^\circ = [68.0 \pm 1.0] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1293^\circ \text{K.}$

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ adopted was calculated based upon $\Delta H_f^\circ = -30.2 \text{ kcal. mole}^{-1}$ for the reaction, $AlF_3(c) + 3KF(c) = K_3AlF_6(c)$, which was estimated by comparison with the values of ΔH_f° of the similar reactions for $Na_3AlF_6(c)$, $Na_3AlCl_6(c)$ and $K_3AlCl_6(c)$.

Heat Capacity and Entropy.

Both C_p and $S_{298.15}^\circ$ were estimated by the addition of a correction term, $3(M_{KF} - M_{NaF})$, to the corresponding values for $Na_3AlF_6(c)$, where M denotes either C_p or $S_{298.15}^\circ$.

Temperature of Melting.

T_m was obtained from P. P. Hall and H. Inaley, J. Am. Ceram. Soc. 21, 113 (1938).

T, K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	-0.000	0.000	INFINITE	7.663	-805.444	-805.444	INFINITE
100	16.965	9.136	79.746	7.061	-807.570	-795.583	1738.744
200	37.338	27.715	49.025	4.262	-808.633	-783.090	655.771
298	48.400	44.907	44.907	0.000	-808.700	-770.517	564.804
300	48.580	45.207	44.908	0.090	-808.496	-770.282	561.150
400	54.940	60.122	46.898	5.289	-804.269	-757.529	413.894
500	59.300	72.874	50.849	11.012	-805.852	-744.692	375.504
600	62.600	83.996	55.466	17.118	-809.040	-731.729	266.539
700	65.000	93.857	60.072	25.070	-805.178	-704.130	192.900
800	67.000	103.457	64.617	34.708	-805.417	-681.585	148.515
1000	73.000	119.624	74.416	45.208	-805.200	-651.255	108.960
1100	75.500	126.699	78.851	52.633	-803.278	-627.315	112.698
1200	77.500	132.717	82.231	60.233	-798.713	-604.336	108.691
1400	83.000	145.775	91.198	76.408	-794.073	-633.633	98.915
1500	85.500	151.586	95.031	84.833	-793.189	-622.130	90.644

Heat Capacity and Entropy

Furukawa et al. (2) measured C_p° (15-370 K) using a sample prepared by fusion of stoichiometric proportions of LiF and AlF_3 in graphite. X-ray diffraction and petrographic examination of separate portions of the sample indicated a single phase identified as $\beta\text{-Li}_3\text{AlF}_6$. The authors tabulated values of C_p° and S° based on their data and the extrapolation $S_{15}^\circ = 0.042$ gibbs/mol. These values are adopted.

Douglas and Neuffer (3) reported relative enthalpy data (323-973 K) for part of the same sample used in measurement of C_p° (2). Their study was made prior to discovery of the five crystalline phases, and their drop-calorimetric data reveal only the transition near 748 K. Reinterpretation of the data above 748 K is complicated by the proximity of the furnace temperatures to the transition temperatures and by the tendency of high-temperature forms to revert to both α - and β -forms under different conditions of cooling. Björge and Jørgensen (4) and Rolin et al. (5) also reported crystalline enthalpy data, but these are relatively imprecise and include similar uncertainties in the final state after the drop. These difficulties preclude the derivation of accurate heat capacities for the high-temperature forms.

C_p° for the β -form is adopted from (2, 3), since the two methods are in good agreement. The curve is extrapolated linearly above 748 K to obtain C_p° for the high-temperature forms. Obvious differences in C_p° are not apparent in the observed data for the different forms, so this should be an adequate approximation.

Transition Data

Existence of five polymorphic forms was shown by high-temperature X-ray diffraction (1, 5, 7) and differential thermal analysis (5, 7). Both α - and β -forms persisted at room temperature, but the α -form appeared only on quenching of high-temperature forms (1). The α -form transformed to β near 490 K (1, 6), but the reverse transformation was not observed. Single-crystal X-ray diffraction showed the α -form to be orthorhombic (5).

The adopted values of T_t are the lowest temperatures at which the high-temperature form was observed growing at the expense of the low-temperature form (1). DTA data (5, 7) were higher by roughly 30° for T_{t1} and 25° for T_{t2} . Combination of the observed enthalpies (3) with the adopted C_p° yields $\Delta H_{t1}^\circ = 0.76$ and $\Delta H_{t2}^\circ = 0.03$ or 0.15 kcal/mol; however, we prefer to adopt ΔH_{t1}° values (0.5 and 0.3 kcal/mol) which are more consistent with the areas of peaks in the DTA curve (7). Evidence suggests that ΔH_{t2}° is small, so we estimate 0.1 kcal/mol.

Melting Data

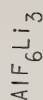
See the table for the liquid.

References

1. P. D. Greens, P. Gross and C. Hayman, Trans. Faraday Soc. **64**, 633 (1968).
2. G. T. Furukawa, W. G. Saba and J. C. Ford, Nat. Bur. Stand. Report 10074, p. 47, issued July 1, 1969.
3. T. B. Douglas and J. E. Neuffer, Nat. Bur. Stand. Report 8186, p. 68, issued January 1, 1964.
4. B. Björge and B. Jørgensen, Acta Chem. Scand. **22**, 1347 (1968).
5. M. Rolin, H. Lartrille and H. Phan, Bull. Soc. Chim. Fr. **1969** (7), 2271.
6. G. Garton and B. M. Wanklyn, J. Inorg. Nucl. Chem. **27**, 2466 (1965).
7. J. L. Holm, Acta Chem. Scand. **20**, 1167 (1966).
8. J. H. Burns, A. C. Tennissen and G. D. Brunton, Acta Cryst. **B24**, 225 (1968).

Trilithium Hexafluoroaluminate (Li_3AlF_6)
(Liquid) GFW = 161.7889

T, °K	C_p^0	$\frac{\text{gibbs/mol}}{S^0}$	$-(G^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	$\frac{\text{kcal/mol}}{\Delta H^0}$	ΔG^0	Log Kp
0							
100	46.400	58.759	58.759	.000	-792.935	-758.882	556.275
200	46.550	59.058	58.759	.090	-792.931	-758.673	552.692
300	54.940	73.973	60.750	5.289	-792.504	-747.304	408.308
400	59.300	86.725	64.701	11.012	-798.087	-735.852	321.641
500	62.680	97.848	69.318	17.416	-793.275	-728.275	243.817
600	65.500	107.728	74.112	23.531	-792.200	-712.558	222.544
700	66.000	119.212	79.048	32.131	-788.991	-701.746	191.708
800	66.000	129.341	84.084	40.731	-785.854	-691.028	167.605
900	66.000	136.402	89.071	46.331	-785.312	-680.475	148.716
1000	66.000	146.599	93.934	57.931	-782.211	-670.142	133.115
1100	66.000	154.082	98.639	66.531	-776.125	-660.091	120.210
1200	66.000	160.966	103.172	75.131	-776.050	-650.295	109.324
1300	66.000	167.339	107.531	83.731	-772.985	-640.735	100.023
1400	66.000	173.272	111.718	92.331	-769.926	-631.395	91.994
1500	66.000	178.853	115.761	100.931	-766.967	-622.259	84.997
1600	66.000	184.036	119.604	109.531	-764.967	-602.330	78.335
1700	66.000	188.952	123.323	118.131	-763.382	-594.159	72.141
1800	66.000	193.602	126.901	126.731	-761.804	-578.186	66.622
1900	66.000	198.013	130.347	135.331	-758.238	-564.404	61.675
2000	66.000	202.209	133.670	143.931	-754.484	-549.408	57.219
2100	66.000	206.210	136.877	152.531	-751.482	-535.370	53.184
2200	66.000	210.032	139.975	161.131	-747.605	-521.093	49.515
2300	66.000	213.683	142.971	169.731	-744.087	-506.975	46.166
2400	66.000	217.203	145.871	178.331	-740.581	-493.001	43.098
2500	66.000	220.576	148.680	186.931	-737.087	-479.149	40.278
2600	66.000	223.822	151.403	195.531	-733.408	-465.468	37.677
2700	66.000	226.949	154.045	204.131	-729.551	-451.968	35.207
2800	66.000	229.967	156.612	212.731	-725.546	-438.112	32.791
2900	66.000	232.883	159.106	221.331	-721.556	-424.292	30.545
3000	66.000						



TRILITHIUM HEXAFLUOROALUMINATE (Li_3AlF_6) (LIQUID)
 $S^0_{298.15} = 58.758$ gibbs/mol
 $T_m = 1058 \pm 3$ K
 $\Delta H^0_{298.15} = -792.935$ kcal/mol
 $\Delta H_m^0 = 20.6 \pm 1.0$ kcal/mol
 GFW = 161.7889

Heat of Formation
 $\Delta H^0_{298.15}$ is calculated from that of the crystal by addition of ΔH_m^0 and the difference of $(H^0_{1058} - H^0_{298.15})$ for the crystal and liquid.

Heat Capacity and Entropy

Relative enthalpy data were measured by Björge and Jensen (1) from 1065 to 1088 K and by Rolin et al. (2) from about 1075 to 1145 K. The data are consistent with liquid heat capacities in the range from roughly 82 to 92 gibbs/mol. We adopt the mean value of 86 gibbs/mol and extrapolate this to higher and lower temperatures. A glass transition is assumed at 700 K and C_p^0 at lower temperatures is taken to be the same as that of $\beta\text{-Li}_3\text{AlF}_6$. S^0_{298} is calculated in a manner analogous to that of the heat of formation.

Melting Data

T_m was observed at 780°C (3), 782°C (2, 4), 783°C (5, 8) and 785°C (1). The last and highest value is adopted for this table. Combination of the observed liquid enthalpies with the adopted crystal enthalpies yields values for ΔH_m^0 of 19.7 kcal/mol (1), authors gave 20.2 \pm 1.0 and 21.5 \pm 0.3 kcal/mol (2, authors gave 21.5). We adopt the mean value of 20.6 kcal/mol which is confirmed by values of 20.7 (8), 20.8 (4), 22.2 (4), 20.1 (4) and 22.0 (2) derived from crystal-liquid phase data for binary systems. The agreement among values for ΔH_m^0 seemingly excludes the possibility of large discrepancies in the enthalpies due to formation of the α -phase instead of β during drop-calorimetry from high temperatures.

Vaporization Data

Li_3AlF_6 vaporizes mainly to $\text{LiAlF}_4(\text{g})$ with small contributions from species such as $\text{Li}_2\text{AlF}_5(\text{g})$, $\text{Li}_2\text{F}_2(\text{g})$ and $\text{LiF}(\text{g})$ (5, 7).

References

1. B. Björge and B. Jensen, Acta Chem. Scand. 22, 1347 (1968).
2. R. Rolin, H. Latreille and H. Pham, Bull. Soc. Chim. Fr. 1969 (7), 2271.
3. J. L. Holm, Acta Chem. Scand. 20, 1187 (1967).
4. M. Malinovsky, Chem. Zvesti 21, 783 (1967); ibid., p. 794.
5. G. Garton and B. Wanklyn, J. Inorg. Nucl. Chem. 27, 2466 (1965).
6. A. Büchler and J. Berkowitz-Hattuck, AD 653163, pp 41-3, June, 1967.
7. R. F. Porter and E. E. Zeller, J. Chem. Phys. 33, 858 (1960).
8. T. Matsushima, Denki Kagaku Oyobi Kogyo Butsuri Kagaku (Electrochemistry and Industrial Physical Chemistry) 37, 778 (1969).



T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	0.000	-786.056	-786.056	INFINITE
100	23.910	14.864	46.214	9.105	-786.056	-786.056	18.278
200	42.559	26.214	46.214	4.178	-791.685	-791.685	835.542
298	51.559	36.990	56.990	1.000	-791.685	-791.685	835.542
300	51.674	37.309	56.991	1.009	-790.994	-751.395	547.391
400	56.077	72.866	59.079	5.507	-792.523	-735.099	403.278
500	59.191	85.657	63.154	11.271	-792.038	-724.540	316.699
600	62.577	96.779	67.854	17.355	-791.268	-711.115	259.023
700	66.519	106.715	72.707	23.605	-790.174	-697.839	217.875
800	70.941	115.882	77.538	30.675	-788.704	-684.745	187.064
900	77.400	126.378	82.428	39.555	-785.284	-671.988	163.101
1000	87.400	133.479	87.184	46.895	-786.602	-657.283	144.066
1100	97.400	139.903	91.689	53.035	-785.385	-646.616	126.471
1200	107.000	146.518	95.972	60.491	-782.999	-632.699	115.230
1300	116.000	153.351	100.128	68.191	-780.457	-614.483	103.304
1400	124.000	159.651	104.157	77.691	-777.928	-596.541	93.124
1500	131.000	165.515	108.054	86.191	-775.411	-578.649	84.338
1600	137.000	171.001	111.819	94.691	-773.906	-561.394	76.683
1700	142.000	176.154	115.453	103.191	-772.407	-544.183	69.956
1800	146.000	181.012	118.962	111.691	-770.922	-527.125	64.002
1900	150.000	185.608	122.350	120.191	-769.444	-510.283	58.496
2000	153.000	189.968	125.622	128.691	-767.978	-493.620	53.941

Sept. 30, 1961; Sept. 30, 1963; Dec. 31, 1963; Dec. 31, 1965; Dec. 31, 1968

$\Delta H_f^\circ = -788 \pm 1$ kcal/mol
 $\Delta H_f^\circ = -791 \pm 1$ kcal/mol
 $\Delta H^\circ(\alpha + \beta) = 1.97 \pm 0.40$ kcal/mol
 $\Delta H^\circ(\beta + \gamma) = 0.09 \pm 0.10$ kcal/mol
 $\Delta H_m^\circ = 25.64$ kcal/mol

$S_{298.15}^\circ = 56.99 \pm 0.40$ gibbs/mol
 $T_f(\alpha + \beta) = 838^\circ K$
 $T_f(\beta + \gamma) = 1153^\circ K$
 $T_m = 1285^\circ K$

Heat of Formation

The heats of solution of Al(c), NaCl(c), and Na₃AlF₆(c) in 4.36 M HCl acid solution were determined at 303.15°K by Coughlin (1). The enthalpy change for the reaction $Al(c) + 2.96 NaCl(c) + 5.96 (HF+5.716 H_2O) + 3.617 H_2O(l) = Na_2.96AlF_6(aq) + 2.96 (HCl+12.731 H_2O) + 3/2 H_2(g)$ was derived as $\Delta H_{298.15}^\circ = -153.22 \pm 0.14$ kcal/mol. Using the ΔH_{298}° data on H₂O(l), HCl and HF solution from (2, 3) and NaCl from JANAF Table (5), we calculate the value $\Delta H_{298}^\circ = -791.2 \pm 0.7$ kcal/mol for Na₃AlF₆(c). Baud (5) reported $\Delta H^\circ = -40.7$ kcal/mol for the reaction $2AlF_3(c) + 6NaF(c) = 2Na_3AlF_6(c)$. Based on JANAF ΔH_{298}° values for AlF₃(c) and NaF(c), we obtain $\Delta H_{298}^\circ(Na_3AlF_6, c) = -793.7 \pm 2$ kcal/mol.

Hashovets and Yudin (6) determined the equilibrium constants in the temperature range 1101-1238°K for the reaction $2/3 Na_3AlF_6(c) + H_2O(g) = 1/3 Al_2O_3(c) + 2HF(g) + 2NaF(c)$, using the transpiration method. Based on the reported Kp values, we evaluate $\Delta H_{298}^\circ = 48.1 \pm 0.8$ and 46.6 kcal/mol by the second and third law methods, respectively. From the third law ΔH_{298}° value, we calculate $\Delta H_{298}^\circ(Na_3AlF_6, c) = -791.3$ kcal/mol.

The equilibrium pressures of sodium vapor in the reaction $2NaF(c) + 1/3 Al(c) = Na(g) + 1/3 Na_3AlF_6(c)$ at temperatures 1020 - 1150°K were determined by Ono et al. (7), employing differential thermal analysis and X-ray analysis. Since the reported vapor pressures are the total pressures of Na(g) and Na₂(g), we calculate the partial pressures of Na(g) by use of the equilibrium constants for the reaction $Na_2(g) = 2Na(g)$ derived from JANAF functions for Na₂(g) and Na(g). Based on the calculated Na(g) pressures we evaluate the enthalpy change of the above reaction by the third law method to be 109.2 kcal/mol, yielding $\Delta H_{298}^\circ(Na_3AlF_6, c) = -791.1$ kcal/mol.

The amounts of sodium over the mixtures of cryolite and aluminum were measured in the temperature range 1023 - 1373°K by the ultraviolet absorption method by Stokes and Frank (8). The enthalpy change for the reaction $6NaF(c) + Al(c) = 3Na(g) + Na_3AlF_6(c)$ is not evaluated due to lack of appropriate data on the activities of NaF(c) and Na₃AlF₆(c).

The heat of formation (298°K) for cryolite(c) is adopted as -791 ± 1 kcal/mol.

Heat Capacity and Entropy

The low temperature heat capacities, $53.66 - 296.00^\circ K$, were measured by King (9). The values of Cp below $53.66^\circ K$ are extrapolated using the Cp equation given by King. S_{298}° is derived based on the adopted low temperature heat capacities.

The high temperature enthalpies, $401.3 - 1370.5^\circ K$, determined by O'Brien and Kelley (10), are adopted to derive the heat capacities which join smoothly at $298^\circ K$ with the low temperature Cp's. The heat capacity of Na₃AlF₆(γ) is estimated such that the calculated enthalpy at $1200.5^\circ K$ is consistent with the measured value reported by O'Brien and Kelley. The heat capacity above the melting point is obtained by linear extrapolation.

Frank (21) commented that the enthalpies reported by O'Brien and Kelley were incorrect due to an apparent error in temperature measurement. However, his reported corrected enthalpy values are not used here (see NaF(c) table for details). The high temperature enthalpies have also been measured by the following investigators: Joly, $284.5 - 373.3^\circ K$ (11); Baud, $289 - 328^\circ K$ (12); Roth and Bertram, $369 - 1371^\circ K$ (13); Krestonikov and Karetnikov, $573 - 1273^\circ K$ (14); Lyshenko, $290 - 1217^\circ K$ (15); and Albright, $350.0 - 1311.8^\circ K$ (16). Their data are not used for evaluation due to inconsistencies among the reported values.

Transition Data

Landon and Ubbelohde (17) determined the electrical conductance (σ) of crystals and melt of cryolite, and observed two transition temperatures from a plot of log σ vs 1/T, i.e., $T_f(\alpha + \beta) = 838^\circ K$ and $T_f(\beta + \gamma) = 1153^\circ K$, which are adopted here. Other values of $T_f(\alpha + \beta)$ reported are ($^\circ K$): 823 (18), 833 (18), 834 (18), 835 (20), and 838 (13).

The values of $\Delta H^\circ(\alpha + \beta)$ and $\Delta H^\circ(\beta + \gamma)$ are calculated as the difference between the adopted enthalpies for α and β at $838^\circ K$ and β and γ at $1153^\circ K$, respectively. The value of $\Delta H^\circ(\alpha + \beta)$ has also been reported as (kcal/mol): 1.24 (13), 2.16 (10), 2.24 (20), and 2.38 (16). Landon and Ubbelohde (17) estimated that $\Delta H^\circ(\beta + \gamma) = 0.01 \times \Delta H_m = 0.2$ kcal/mol.

The cause of the discrepancies among the reported values for T_f , ΔH° and the high temperature enthalpies may be due to differences in the sample composition.

Melting Data

See the Na₃AlF₆(c) table for details.

References

1. T. P. Coughlin, J. Am. Chem. Soc. **80**, 1802 (1958).
2. U. S. National Bureau of Standards, NBS Monograph No. 270-3, 1963.
3. ΔH_{298}° (HF+5.716 H₂O) is recalculated based on JANAF ΔH_{298}° (HF, g) value.
4. JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, Sept. 30, 1964.
5. E. Baud, Ann. Chim. Phys. **1**, 8 (1904).
6. V. P. Hashovets and B. F. Yudin, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. **5**, 95 (1962).
7. K. Ono, T. Matsushima, and T. Ito, Nippon Kinzoku Gakkaishi **23**, 501 (1965).
8. J. J. Stokes, Jr. and W. B. Frank, "Extractive Metallurgy of Aluminum," Vol. II, Interscience Publishers, 1963, p. 3.
9. E. G. King, J. Am. Chem. Soc. **79**, 2056 (1957).
10. O. Brien and K. R. Kelley, J. Res. Nat. Bur. Stand. **72**, 569 (1968).
11. J. Joly, Proc. Acad. Sci. Paris, **20** (1886).
12. M. E. Baud, J. Phys. Radium Ser. **4**, 2, 569 (1903).
13. W. A. Roth and Bertram, Z. Elektrochem. **35**, 297 (1929).
14. A. N. Krestonikov and G. A. Karetnikov, Legkie Metal. **3**, 29 (1934).
15. V. S. Lyshenko, Metallurg. **10**, 85 (1935).
16. U. S. National Bureau of Standards, NBS Monograph No. 270-3, 1963.
17. L. D. Landon and J. H. Ubbelohde, J. Res. Nat. Bur. Stand. **70A**, 160 (1957).
18. C. J. Byners, J. Phys. Chem. **66**, 160 (1962).
19. F. C. Kracek, Handbook of Physical Constants, Geological Society of America, Special Paper No. 8, 495 (1960).
20. A. J. Hajundar and R. Roy, J. Inorg. Nucl. Chem. **27**, 1961 (1965).
21. W. B. Frank, J. Phys. Chem. **65**, 2081 (1961).

CRYOLITE (Na₃AlF₆)

(LIQUID)

CRYOLITE (Na₃AlF₆)

Cryolite (Na₃AlF₆)

(Liquid) GFW = 209.9413

S^{298.15} = 68.544 gibbs/mol

ΔH_f^{298.15} = -774.052 kcal/mol

T_m = 1285°K

ΔH_m^{*} = 25.64 kcal/mol

T, °K	C _p ^a	S ^b - (C _p ^a - H ₂₉₈)/T	gibbs/mol	ΔH _f ^c	kcal/mol	ΔG ^d	Log K _p
0							
100							
200							
298	51.559	68.544	68.544	.000	-774.052	-736.137	541.069
300	51.674	68.663	68.545	.005	-774.046	-737.913	537.569
400	56.077	84.400	70.633	5.507	-775.575	-785.773	396.544
500	59.191	97.250	74.708	11.271	-775.086	-713.375	311.616
600	62.577	108.333	79.408	17.355	-774.320	-701.099	255.375
700	66.519	118.269	84.261	23.605	-773.226	-686.979	215.109
800	94.700	127.436	89.091	30.676	-771.755	-677.040	184.959
900	94.700	136.590	93.884	40.146	-767.785	-665.481	161.591
1000	94.700	146.568	98.952	49.616	-766.333	-654.103	142.954
1100	94.700	157.593	103.879	59.086	-762.384	-643.077	127.767
1200	94.700	165.633	108.704	66.556	-758.184	-631.029	114.926
1300	94.700	173.414	113.394	76.026	-753.674	-614.781	104.354
1400	94.700	180.432	117.935	87.496	-749.175	-596.682	93.490
1500	94.700	186.965	122.321	96.966	-744.688	-583.302	84.967
1600	94.700	193.077	126.555	104.436	-740.213	-568.023	77.588
1700	94.700	198.618	130.638	115.906	-735.744	-553.019	71.095
1800	94.700	204.231	134.578	125.376	-731.289	-538.286	65.357
1900	94.700	209.351	138.360	134.646	-726.841	-523.793	60.250
2000	94.700	214.209	142.051	144.316	-722.405	-509.537	55.680
2100	94.700	218.829	145.598	153.786	-717.975	-495.511	51.568
2200	94.700	223.235	149.027	163.856	-713.557	-481.686	47.651
2300	94.700	227.444	152.366	172.726	-709.144	-468.060	44.076
2400	94.700	231.475	155.560	182.196	-704.744	-454.626	41.399
2500	94.700	235.340	158.674	191.666	-700.353	-441.387	38.566
2600	94.700	239.055	161.695	201.136	-695.974	-428.309	36.003
2700	94.700	242.629	164.626	210.606	-691.604	-415.406	33.625
2800	94.700	246.073	167.474	220.076	-687.256	-402.639	31.365
2900	94.700	249.396	170.242	229.546	-682.948	-389.737	29.145
3000	94.700	252.606	172.934	239.016	-678.686	-371.615	27.087

Heat of Formation
The ΔH_f²⁹⁸(*l*) is obtained from ΔH_f²⁹⁸(*c*) by adding ΔH_m^{*} and the difference between H₂₉₈²⁹⁸ - H₂₉₈²⁹⁸ for crystal and liquid. Yudin and Mashovets (1) studied the dissociation of cryolite and reported K₁₃₀₀ = 2.43x10⁻⁵ for the reaction Na₃AlF₆(*l*) = 3NaF(*l*) + AlF₃(*c*). Based on this K₁₃₀₀ value, we evaluated the enthalpy change by the third law method as 24.3 kcal/mol. Using ΔH_f²⁹⁸ = -360.8 and -130.6 kcal/mol for AlF₃(*c*) and NaF(*l*), respectively, we obtain ΔH_f²⁹⁸ = -776.7 ± 3 kcal/mol for Na₃AlF₆(*l*).

Heat Capacity and Entropy

The high temperature enthalpies, 1285.5 - 1370.5°K, were measured by O'Brien and Kelley (2). Using their data we derive a constant Cp, 94.7 gibbs/mol, for Na₃AlF₆(*l*). A glass transition temperature is assumed at 800°K., and the heat capacities below 800°K are taken to be the same as those of the Na₃AlF₆(*c*). The Cp values above 1370.5°K are obtained by linear extrapolation. The entropy, S₂₉₈, is calculated in a manner analogous to that of the heat of formation.

Albright (3) measured the high temperature enthalpies of Na₃AlF₆(*l*) in the temperature range 1298.1 - 1311.8°K. However, his data are systematically higher (about 4.9%) than the values determined by O'Brien and Kelley (2), which is also true for the other sets of enthalpy data measured using this calorimeter. Therefore Albright's enthalpy data is not used for evaluation.

Melting Data

The melting point of cryolite has been reported as (°K): 1273 (4), 1279 (3), 1281 (5), 1282 (6, 7), 1293 (9), and 1300 (2). The value of Tm adopted is that determined by Landon and Ubbelohde (9). This value is corrected from the original measured value 1286°K, due to the thermocouple standardization against the freezing points of assay gold giving a gold point of 1064.2 ± 0.15°C compared with the fixed value of 1063.0°C.

The value of ΔH_m^{*} is calculated as the difference between the enthalpies at Tm for crystal and liquid. Other reported values of ΔH_m^{*} are (in kcal/mol): 16.64 (4), 26.6 (10), 27.64 (2), and 27.91 (3).

References

1. B. F. Yudin and V. P. Mashovets, *J. Appl. Chem.*, **36**, 1132 (1963).
2. C. J. O'Brien and K. K. Kelley, *J. Am. Chem. Soc.*, **79**, 5616 (1957).
3. D. M. Albright, Ph.D. Thesis, Carnegie Institute of Technology, 1956.
4. W. A. Roth and W. Bertram, *Z. Elektrochem.*, **35**, 297 (1929).
5. J. Brynestadt, K. Grjotheim, and S. Urnes, *Metallurgia Ital.*, **52**, No. 8, 495 (1960).
6. M. Rolin, *Bull. Soc. Chim. France*, **1960**, 671 (1960).
7. N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, *J. Electrochem. Soc.*, **102**, 690 (1955).
8. G. J. Landon and A. R. Ubbelohde, *Proc. Roy. Soc. (London)*, **240A**, 160 (1957).
9. F. C. Kracek, *Handbook of Physical Constants*, Geological Society of America, Special Papers No. 36, 140, 1942.
10. M. Rolin and M. Bernard, *Bull. Soc. Chim. France*, **1962**, 423 (1962).

Aluminum Monohydride (AIH)

(Ideal Gas) Mol. Wt. = 27.988

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF ^o	Log K _p
0	0.000	INFINITE	- 2.071	62.034	INFINITE	
100	6.961	37.259	1.382	62.034	62.034	INFINITE
200	6.968	42.066	4.515	62.034	59.897	- 130.808
298	7.020	44.875	0.000	62.000	57.540	- 62.874
300	7.022	44.918	0.013	61.995	55.291	- 40.527
400	7.180	46.958	4.512	61.761	55.249	- 40.247
500	7.408	48.584	1.451	61.513	53.036	- 28.076
600	7.650	49.956	46.282	61.260	50.882	- 22.240
700	7.865	51.121	40.604	61.010	48.780	- 17.767
800	8.053	52.117	35.798	60.727	46.609	- 13.216
900	8.232	53.177	46.073	60.459	44.469	- 10.372
1000	8.370	54.051	48.628	57.639	42.713	- 10.372
1100	8.486	54.855	49.158	57.419	40.944	- 8.948
1200	8.585	55.588	49.664	57.205	39.285	- 7.805
1300	8.672	56.259	50.148	56.996	37.665	- 6.856
1400	8.742	56.893	50.609	56.790	36.089	- 6.056
1500	8.806	57.539	51.051	56.584	34.419	- 5.373
1600	8.863	58.109	51.475	56.379	32.822	- 4.769
1700	8.913	58.698	51.891	56.180	31.252	- 4.269
1800	8.959	59.258	52.297	55.986	29.713	- 3.816
1900	9.001	59.644	52.647	55.764	28.135	- 3.410
2000	9.039	60.107	53.008	55.559	26.595	- 3.059
2100	9.074	60.549	53.357	55.382	25.065	- 2.739
2200	9.107	60.977	53.697	55.142	23.545	- 2.450
2300	9.138	61.377	54.019	54.938	22.036	- 2.189
2400	9.168	61.767	54.333	54.730	20.539	- 1.951
2500	9.196	62.141	54.638	54.521	19.044	- 1.734
2600	9.222	62.503	54.934	54.312	17.561	- 1.535
2700	9.248	62.851	55.221	54.102	16.086	- 1.352
2800	9.272	63.186	55.497	53.896	14.619	- 1.183
2900	9.296	63.514	55.770	53.690	13.168	- 1.030
3000	9.319	63.829	56.033	53.487	11.733	- 0.890
3100	9.341	64.135	56.290	53.280	10.313	- 0.762
3200	9.363	64.422	56.540	53.076	8.913	- 0.646
3300	9.385	64.699	56.786	52.876	7.536	- 0.541
3400	9.406	64.960	57.021	52.680	6.183	- 0.446
3500	9.426	65.274	57.253	52.476	4.856	- 0.360
3600	9.446	65.540	57.479	52.268	3.559	- 0.283
3700	9.465	65.759	57.701	52.056	2.291	- 0.214
3800	9.483	65.933	57.919	51.840	1.056	- 0.151
3900	9.504	66.298	58.129	51.620	0.000	0.000
4000	9.523	66.539	58.311	51.396		
4100	9.542	66.774	58.539	51.168		
4200	9.571	67.004	58.738	50.932		
4300	9.597	67.450	59.124	50.688		
4400	9.615	67.666	59.311	50.442		
4500	9.635	67.877	59.495	50.196		
4600	9.653	68.085	59.676	49.950		
4700	9.671	68.285	59.853	49.704		
4800	9.687	68.488	60.027	49.458		
4900	9.704	68.684	60.198	49.212		
5000	9.722	68.876	60.367	48.966		
5100	9.739	69.065	60.532	48.720		
5200	9.756	69.250	60.695	48.474		
5300	9.773	69.433	60.855	48.228		
5400	9.791	69.613	61.013	47.982		
5500	9.808	69.789	61.168	47.736		
5600	9.825	69.963	61.321	47.490		
5700	9.842	70.134	61.473	47.244		
5800	9.859	70.302	61.619	46.998		
5900	9.876	70.468	61.765	46.752		
6000	9.876	70.468	61.765	46.506		

Dec. 31, 1960; June 30, 1963

Ground State Configuration 1s²
 $S_{298.15}^o = 44.875 \text{ cal deg}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 62.0 \pm 5.0 \text{ kcal mole}^{-1}$
 $\Delta H_f^o = 62.0 \pm 5.0 \text{ kcal mole}^{-1}$
 $\Delta H_f^o = 62.0 \pm 5.0 \text{ kcal mole}^{-1}$

Electronic Levels and Multiplicities
 $\frac{E_{el} \text{ cm}^{-1}}{0}$
 $\frac{g_i}{1}$

$\omega_e = 1682.56 \text{ cm}^{-1}$
 $\sigma = 1$
 $B_e = 6.3907 \text{ cm}^{-1}$
 $\alpha_e = 0.1858 \text{ cm}^{-1}$
 $r_e = 1.6477 \text{ \AA}$

Heat of Formation

A. G. Gaydon, "Dissociation Energies", 2nd Ed., Chapman Hall, Ltd., London (1953), extrapolated the available $X^2\Sigma$ vibrational levels and also considered predissociation in the $A^1\Pi$ state and concluded that the best value of D_0^o was $2.9 \pm 0.2 \text{ e.v.}$. The linear Birge-Sponer extrapolation gave a value of 3.05 e.v. while the predissociation limit was 3.07 e.v. Gaydon's recommended value is adopted here and leads to a value of $\Delta H_f^o = 62.16 \pm 5.0 \text{ kcal mole}^{-1}$ using JANAF auxiliary data.

Heat Capacity and Entropy

P. B. Zeeman and G. J. Ritter, Can. J. Phys. 32, 555 (1954) examined the UV band system of AIH under high resolution and reported the molecular constants adopted above.

Aluminum Oxide Hydride (HA10)
(Ideal Gas) Mol. Wt. = 43.988

AlHO

ALUMINUM OXIDE HYDRIDE (HA10) (IDEAL GAS) MOL. WT. = 43.988

Point Group [C_{2v}]

$\Delta H_f^\circ = [9 \pm 20] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [51.464] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [8 \pm 20] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	[900] (1)	[1000] (2)	[1800] (1)
------------------------------	-----------	------------	------------

Bond Distance: Al-O = [1.62] Å Al-H = [1.64] Å

Bond Angle: H-Al-O = [180°] $\sigma = 1$

B₀ = [0.5271] cm.⁻¹

Heat of Formation.

The heat of formation was estimated by summing the constituent bond energies. The Al-O was taken as that in AlO(g) and the Al-H bond was taken as that in AlH(g), this gave a heat of atomization of 182 kcal.

Heat Capacity and Entropy.

Vibrational frequencies, bond lengths and angles and point group were taken from National Bureau of Standards Report 6297, Jan. 1, 1959, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine".

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	-	8.988	8.988	INFINITE
100	6.957	43.532	2.155	8.988	8.988	-17.370
200	7.242	48.400	5.135	8.988	8.988	-7.836
298	7.464	51.464	7.56	8.988	8.988	-4.861
300	8.285	51.515	7.991	8.988	8.988	-4.825
400	9.541	54.072	1.807	8.988	8.988	-3.404
500	10.634	56.323	1.918	8.988	8.988	-2.593
600	11.495	58.341	2.026	8.988	8.988	-2.074
700	12.184	60.115	2.121	8.988	8.988	-1.758
800	12.656	61.622	2.206	8.988	8.988	-1.459
900	13.042	63.336	2.283	8.988	8.988	-1.265
1000	13.342	64.726	2.359	8.988	8.988	-1.155
1100	13.578	65.009	2.431	8.988	8.988	-1.086
1200	13.767	65.199	2.497	8.988	8.988	-1.050
1300	13.919	65.307	2.556	8.988	8.988	-1.026
1400	14.043	65.344	2.606	8.988	8.988	-1.004
1500	14.146	65.316	2.654	8.988	8.988	-0.977
1600	14.232	65.232	2.699	8.988	8.988	-0.951
1700	14.304	65.093	2.741	8.988	8.988	-0.926
1800	14.366	64.916	2.778	8.988	8.988	-0.902
1900	14.418	64.695	2.810	8.988	8.988	-0.879
2000	14.464	64.435	2.837	8.988	8.988	-0.857
2100	14.503	64.142	2.859	8.988	8.988	-0.834
2200	14.538	63.816	2.877	8.988	8.988	-0.812
2300	14.568	63.461	2.892	8.988	8.988	-0.790
2400	14.594	63.085	2.904	8.988	8.988	-0.767
2500	14.618	62.691	2.913	8.988	8.988	-0.745
2600	14.639	62.285	2.919	8.988	8.988	-0.723
2700	14.658	61.864	2.923	8.988	8.988	-0.701
2800	14.675	61.431	2.926	8.988	8.988	-0.679
2900	14.690	60.986	2.928	8.988	8.988	-0.657
3000	14.704	60.535	2.929	8.988	8.988	-0.635
3100	14.716	60.077	2.929	8.988	8.988	-0.613
3200	14.728	59.613	2.929	8.988	8.988	-0.591
3300	14.738	59.145	2.929	8.988	8.988	-0.569
3400	14.748	58.673	2.929	8.988	8.988	-0.547
3500	14.756	58.200	2.929	8.988	8.988	-0.525
3600	14.764	57.725	2.929	8.988	8.988	-0.503
3700	14.772	57.249	2.929	8.988	8.988	-0.481
3800	14.779	56.773	2.929	8.988	8.988	-0.459
3900	14.785	56.297	2.929	8.988	8.988	-0.437
4000	14.791	55.821	2.929	8.988	8.988	-0.415
4100	14.796	55.345	2.929	8.988	8.988	-0.393
4200	14.801	54.869	2.929	8.988	8.988	-0.371
4300	14.806	54.393	2.929	8.988	8.988	-0.349
4400	14.810	53.917	2.929	8.988	8.988	-0.327
4500	14.814	53.441	2.929	8.988	8.988	-0.305
4600	14.818	52.965	2.929	8.988	8.988	-0.283
4700	14.822	52.489	2.929	8.988	8.988	-0.261
4800	14.825	52.013	2.929	8.988	8.988	-0.239
4900	14.828	51.537	2.929	8.988	8.988	-0.217
5000	14.831	51.061	2.929	8.988	8.988	-0.195
5100	14.834	50.585	2.929	8.988	8.988	-0.173
5200	14.837	50.109	2.929	8.988	8.988	-0.151
5300	14.839	49.633	2.929	8.988	8.988	-0.129
5400	14.842	49.157	2.929	8.988	8.988	-0.107
5500	14.844	48.681	2.929	8.988	8.988	-0.085
5600	14.846	48.205	2.929	8.988	8.988	-0.063
5700	14.848	47.729	2.929	8.988	8.988	-0.041
5800	14.850	47.253	2.929	8.988	8.988	-0.019
5900	14.852	46.777	2.929	8.988	8.988	0.003
6000	14.854	46.301	2.929	8.988	8.988	0.025

Dec. 31, 1960; Mar. 31, 1961

AlHO

Aluminum Monohydroxide (AlOH)

(Ideal Gas) GFW = 43.9889

ALUMINUM MONOHYDROXIDE (AlOH)

(IDEAL GAS)

GFW = 43.9889

Point Group [C_{2v}]

$\Delta H_f^\circ = [-42 \pm 3] \text{ kcal/mol}$

S[°]_{298.15} = [51.7 ± 0.5] gibbs/mol

$\Delta H_f^\circ = [-43 \pm 3] \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	
[1000] (1)	
[1300] (2)	
[3600] (1)	

Bond Distance: Al-O = [1.87] Å
Bond Angle: Al-O-H = [180°]
Rotational Constant: B₀ = [0.4256] cm⁻¹

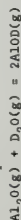
σ = 1

Heat of Formation

From a mass-spectrometric investigation of the equilibrium



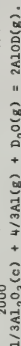
H. Farber et al. (1) report second law heats of reaction of 56.7 ± 0.6 kcal at 1800°K, 57.1 ± 2.8 kcal at 2060°K and 62.7 ± 1.4 kcal at 2000°K. Using JANAF auxiliary data, assuming AlOD to be AlOH, we obtain ΔH_f° ₂₉₈(AlOD, g) = -44.6 ± 1, -44.0 ± 3.2 and -38.6 ± 1.8 kcal/mol. A second equilibrium in the same investigation was



for which second law heats of reaction of 6.3 ± 2.1 kcal at 2060°K and 5.7 ± 0.8 kcal at 2000°K were reported. Farber et al. also measured the heat of reaction



at the same temperatures as -10.7 ± 2.8 kcal at 2060° and -10.3 ± 10.2 kcal at 2000°K. Combining these reactions and eliminating Al₂O(g) yields ΔH_f° ₂₀₆₀ = -4.4 ± 5.0 kcal and ΔH_f° ₂₀₀₀ = -5 ± 11 kcal for the reaction



Using auxiliary JANAF values for Al₂O₃(c) and Al(g), ΔH_f° ₂₉₈(D₂O, g) = -59.56 kcal/mol (2), and functions for D₂O(g) from Friedman and Haar (3) we obtain ΔH_f° ₂₉₈(AlOD, g) = -43.9 ± 6 kcal/mol and -43.4 ± 3 kcal/mol. From all the above results we adopt a value of ΔH_f° ₂₉₈(AlOD, g) = -44 ± 3 kcal/mol, assuming that AlOH is less stable than AlOD by 1 kcal/mol as is the case for H₂O, HDO and D₂O. We obtain ΔH_f° ₂₉₈(AlOH, g) = -43 ± 3 kcal/mol.

Farber et al. (1) also performed weight loss experiments under molecular flow conditions by allowing hydrogen to flow over Al₂O₃(c). The products assumed were AlOH(g), Al(g), Al₂O(g), H(g) and H₂O(g) and the equilibrium amounts of H(g), Al(g) and Al₂O(g) were assumed to be those predicted by the free energies from the JANAF tables. A 3rd law analysis of the equilibrium constants given by Farber for the reaction 2H₂(g) + Al₂O₃(c) = 2AlOH(g) + H₂O(g) yields ΔH_f° ₂₉₈ = 238 ± 12 kcal/mol and ΔH_f° ₂₉₈(AlOH, g) = -52 ± 6 kcal/mol. However, the assumed equilibria involving Al₂O(g) and Al(g) may be significantly in error and thus the ΔH_f° ₂₉₈ should be considered as simply confirming the magnitude determined mass-spectrometrically.

References

1. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Final Report, under USAF contract F04611-67-C-0010, AFPL-TR-67-244, November 1967.
2. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
3. A. S. Friedman and L. Haar, J. Chem. Phys. 22, 2051 (1954).

Heat Capacity and Entropy

The vibrational frequencies are estimated by using the AlO(g) fundamental as approximately the Al-O stretch; the O-H stretch is that in H₂O(g); and the bending frequency is approximately the OH bend in CH₃OH(g) reported by T. Shimanouchi, U. S. Natl. Bur. Std. NBS-RS-NBS 6, 1967.

The AlO bond length was taken from U. S. Natl. Bur. Std. Report No. 5297, Jan. 1, 1959, and the OH bond length is assumed to be that in H₂O(g). The bond angle is assumed to be 180° using the prediction of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAB" molecules with less than 11 valence electrons. Confirmation of this prediction is scanty for molecules having a more electronegative than B; however, R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966), have confirmed the linearity of KOH and CsOH which have 8 valence electrons.

Mar. 31, 1964; Dec. 31, 1967

T, °K	Cp [°]	S [°]	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH [°]	ΔG [°]	Log Kp
0	6.000	INFINITE	INFINITE	2.110	- 61.947	-	INFINITE
100	41.955	58.106	1.1019	- 42.104	- 43.046	- 41.947	94.076
200	7.053	48.752	52.377	- 7.717	- 42.498	- 43.868	47.936
250	7.628	51.701	1.701	- 43.000	- 44.439	- 45.375	32.575
300	7.643	51.748	1.701	- 43.010	- 44.480	- 45.426	32.480
400	6.566	54.052	1.718	- 43.953	- 45.135	- 46.151	23.500
500	6.366	56.032	1.728	- 43.953	- 45.135	- 46.151	19.729
600	10.110	57.840	53.349	2.694	- 44.364	- 45.333	16.513
700	10.659	59.444	54.107	3.736	- 44.747	- 45.664	14.194
800	11.151	60.905	54.867	4.530	- 45.122	- 46.046	12.111
900	11.599	62.285	55.534	5.145	- 45.495	- 46.419	10.250
1000	11.929	63.485	56.130	5.615	- 45.837	- 46.751	8.516
1100	12.227	64.636	57.042	6.354	- 46.770	- 47.684	6.951
1200	12.487	65.712	57.720	9.590	- 49.084	- 49.698	6.141
1300	12.715	66.720	58.374	10.650	- 49.383	- 49.970	5.451
1400	12.913	67.667	58.999	11.550	- 49.645	- 50.202	4.851
1500	13.089	68.567	59.612	13.432	- 49.946	- 50.499	4.338
1600	13.251	69.418	60.199	14.750	- 50.215	- 50.766	3.882
1700	13.390	70.225	60.765	16.082	- 50.476	- 51.017	3.477
1800	13.515	70.994	61.312	17.326	- 50.728	- 51.260	3.121
1900	13.628	71.728	61.841	18.484	- 50.970	- 51.495	2.804
2000	13.725	72.429	62.353	20.152	- 51.233	- 51.758	2.516
2100	13.813	73.101	62.849	21.529	- 51.480	- 52.044	2.230
2200	13.893	73.746	63.330	22.914	- 51.725	- 52.323	1.966
2300	13.965	74.365	63.796	24.307	- 51.966	- 52.592	1.723
2400	14.030	74.968	64.246	25.700	- 52.203	- 52.851	1.497
2500	14.089	75.534	64.689	27.113	- 52.456	- 53.103	1.285
2600	14.142	76.088	65.117	28.525	- 52.699	- 53.356	1.086
2700	14.190	76.623	65.533	29.941	- 52.944	- 53.609	0.899
2800	14.235	77.140	65.939	31.368	- 53.183	- 53.862	0.724
2900	14.276	77.640	66.334	32.798	- 53.416	- 54.115	0.561
3000	14.312	78.124	66.719	34.217	- 53.645	- 54.368	0.409
3100	14.346	78.594	67.094	35.650	- 53.870	- 54.619	0.266
3200	14.377	79.050	67.461	37.086	- 54.092	- 54.869	0.131
3300	14.406	79.493	67.819	38.526	- 54.312	- 55.117	0.004
3400	14.433	79.924	68.168	39.969	- 54.530	- 55.364	- 0.127
3500	14.457	80.342	68.510	41.412	- 54.746	- 55.610	- 0.266
3600	14.479	80.750	68.844	42.859	- 54.959	- 55.856	- 0.409
3700	14.500	81.147	69.172	44.308	- 55.169	- 56.102	- 0.557
3800	14.518	81.534	69.480	45.759	- 55.376	- 56.348	- 0.709
3900	14.534	81.911	69.776	47.212	- 55.580	- 56.594	- 0.865
4000	14.555	82.279	70.113	48.666	- 55.782	- 56.840	- 1.026
4100	14.571	82.639	70.414	50.123	- 55.982	- 57.086	- 1.191
4200	14.586	82.990	70.709	51.580	- 56.180	- 57.332	- 1.360
4300	14.599	83.334	70.999	53.040	- 56.376	- 57.578	- 1.533
4400	14.612	83.674	71.288	54.500	- 56.570	- 57.824	- 1.710
4500	14.625	83.998	71.582	55.962	- 56.762	- 58.070	- 1.891
4600	14.636	84.320	71.836	57.425	- 56.952	- 58.316	- 2.076
4700	14.647	84.634	72.105	58.889	- 57.140	- 58.562	- 2.266
4800	14.657	84.943	72.369	60.355	- 57.326	- 58.808	- 2.460
4900	14.666	85.248	72.618	61.824	- 57.510	- 59.054	- 2.659
5000	14.675	85.542	72.864	63.288	- 57.692	- 59.300	- 2.862
5100	14.684	85.832	73.135	64.756	- 57.872	- 59.546	- 3.069
5200	14.692	86.118	73.382	66.225	- 58.050	- 59.792	- 3.280
5300	14.700	86.397	73.625	67.694	- 58.226	- 60.038	- 3.494
5400	14.707	86.671	73.861	69.163	- 58.400	- 60.284	- 3.711
5500	14.714	86.942	74.099	70.633	- 58.572	- 60.530	- 3.930
5600	14.720	87.207	74.331	72.107	- 58.742	- 60.776	- 4.151
5700	14.726	87.466	74.559	73.580	- 58.910	- 61.022	- 4.375
5800	14.732	87.724	74.784	75.053	- 59.076	- 61.268	- 4.601
5900	14.738	87.980	75.000	76.524	- 59.240	- 61.514	- 4.828
6000	14.743	88.224	75.224	78.000	- 59.402	- 61.760	- 5.056

Aluminum Monohydroxide Unipositive Ion (AlOH⁺)

GFW = 43.98832

(Ideal Gas)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	8.015	54.432	54.432	.000	130.000	126.200	- 92.507
300	8.034	54.482	54.432	.015	130.000	126.176	- 91.919
400	9.079	57.138	54.960	.871	130.052	124.596	- 86.456
500	9.962	59.262	55.613	1.825	130.136	123.596	- 84.024
600	10.643	61.142	56.381	2.857	130.299	122.270	- 84.537
700	11.167	62.823	57.183	3.948	130.461	120.919	- 87.753
800	11.566	64.343	57.984	5.087	130.628	119.545	- 32.658
900	11.953	65.728	58.769	6.263	130.776	118.151	- 26.551
1000	12.229	67.001	59.529	7.472	130.916	116.724	- 25.554
1100	12.487	68.179	60.263	8.708	128.568	115.770	- 23.001
1200	12.713	69.275	60.969	9.948	126.775	114.598	- 20.871
1300	12.913	70.301	61.648	11.249	125.954	113.406	- 19.065
1400	13.090	71.264	62.300	12.550	125.223	112.250	- 17.515
1500	13.246	72.173	62.929	13.867	124.468	111.175	- 16.109
1600	13.389	73.033	63.533	15.199	123.702	109.734	- 14.989
1700	13.514	73.848	64.116	16.544	122.951	108.480	- 13.946
1800	13.626	74.626	64.679	17.903	122.203	107.209	- 13.017
1900	13.728	75.358	65.222	19.276	121.466	105.916	- 12.181
2000	13.816	76.050	65.777	20.646	120.716	104.627	- 11.433
2100	13.897	76.746	66.255	22.032	120.975	103.314	- 10.752
2200	13.970	77.394	66.745	23.429	131.295	101.991	- 10.132
2300	14.036	78.017	67.223	24.826	131.496	100.657	- 9.565
2400	14.095	78.619	67.595	26.219	131.666	99.312	- 9.046
2500	14.149	79.192	67.955	27.644	132.014	97.952	- 8.563
2600	14.198	79.748	68.570	29.062	132.274	96.586	- 8.119
2700	14.242	80.284	68.994	30.484	132.531	95.209	- 7.707
2800	14.283	80.803	69.406	31.910	132.786	93.821	- 7.367
2900	14.321	81.306	69.806	33.338	133.038	92.424	- 7.051
3000	14.354	81.791	70.200	34.774	133.286	91.018	- 6.755
3100	14.386	82.262	70.581	36.211	133.529	89.603	- 6.480
3200	14.414	82.719	70.953	37.651	133.765	88.178	- 6.224
3300	14.441	83.163	71.317	39.094	133.994	86.746	- 5.980
3400	14.465	83.593	71.671	40.538	134.218	85.300	- 5.746
3500	14.486	84.014	72.018	41.989	134.438	83.842	- 5.521
3600	14.509	84.423	72.357	43.437	134.652	82.373	- 5.306
3700	14.528	84.821	72.689	44.889	134.862	80.895	- 5.100
3800	14.547	85.208	73.013	46.342	135.068	79.407	- 4.903
3900	14.564	85.585	73.331	47.796	135.270	77.910	- 4.715
4000	14.579	85.955	73.641	49.255	135.468	76.405	- 4.536
4100	14.594	86.315	73.946	50.714	135.662	74.890	- 4.364
4200	14.608	86.667	74.245	52.174	135.852	73.365	- 4.200
4300	14.620	87.017	74.538	53.635	136.038	71.831	- 4.043
4400	14.631	87.361	74.824	55.096	136.220	70.288	- 3.894
4500	14.644	87.676	75.107	56.562	136.398	68.736	- 3.751
4600	14.654	87.998	75.384	58.027	136.572	67.175	- 3.614
4700	14.664	88.314	75.656	59.493	136.742	65.605	- 3.482
4800	14.674	88.623	75.923	60.959	136.908	64.027	- 3.354
4900	14.684	88.927	76.186	62.426	137.070	62.440	- 3.231
5000	14.691	89.222	76.443	63.896	137.228	60.844	- 3.113
5100	14.699	89.513	76.696	65.366	137.382	59.239	- 3.000
5200	14.707	89.798	76.945	66.836	137.532	57.625	- 2.892
5300	14.714	90.079	77.190	68.307	137.678	56.002	- 2.789
5400	14.721	90.354	77.429	69.779	137.820	54.371	- 2.691
5500	14.727	90.624	77.659	71.251	137.958	52.732	- 2.597
5600	14.733	90.889	77.903	72.724	138.092	51.086	- 2.507
5700	14.739	91.150	78.133	74.197	138.222	49.433	- 2.421
5800	14.744	91.406	78.360	75.672	138.348	47.772	- 2.338
5900	14.749	91.658	78.584	77.146	138.470	46.105	- 2.258
6000	14.754	91.906	78.803	78.621	138.588	44.433	- 2.180

ALUMINUM MONOHYDROXIDE UNIPOSITIVE ION (AlOH⁺)

(IDEAL GAS)

GFW = 43.98832

Point Group [C_{∞v}]

ΔHf° = [131 ± 26] kcal/mol

S°_{298.15} = [54.6 ± 0.5] gibbs/mol

ΔHf°_{298.15} = [130 ± 26] kcal/mol

Ground State Quantum Weight = [4]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[800] (1)
[1100] (2)
[3600] (1)

O-H = [0.86] Å

Bond Angle: Al-O = [1.90] Å

Bond Angle: Al-O-H = [180°]

Rotational Constant: B₀ = [0.413] cm⁻¹

Heat of Formation

The heat of formation is obtained from ΔHf°₂₉₈(AlOH, g) and its ionization potential, which is estimated to be 7.5 ± 1 eV (173 ± 23 kcal). The ionization potential is estimated from a reported value of 7.5 eV for the appearance potential of AlOH⁺, presumably from the parent AlOH, by M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, Space Sciences, Inc., Final Report under USAF contract F04611-67-C-0010, AFRL-TR-67-244, November, 1967.

Heat Capacity and Entropy

According to the correlation diagram given by A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAg" molecules, a compound with 9 valence electrons would have the three outermost electrons in an unfilled π orbital. Thus, it would be a ²Π state since the molecule ought to be linear if it has less than 11 valence electrons. The outermost orbital is a bonding orbital and thus the loss of an electron from it would weaken the bonding. The vibrational frequencies are estimated from those for AlOH(g) with somewhat lower frequencies due to the weaker bonding. Similarly, the Al-O bond length is slightly increased over that in AlOH(g). The enthalpy at 0°K is -2.138 kcal/mol.

Point Group [C_s]
 $S_{298.15}^{\circ} = [57.3 \pm 0.5]$ gibbs/mol
 Ground State Quantum Weight = [2]

$\Delta H_f^{\circ} = [-54.33 \pm 23]$ kcal/mol

$\Delta H_f^{\circ} = [-55 \pm 23]$ kcal/mol

Vibrational Frequencies and Degeneracies

ω_e , cm⁻¹
 [900] (1)
 [1100] (1)
 [3600] (1)

Bond Distance: Al-O = [1.90] Å
 Bond Angle: Al-O-H = [120°]
 Product of the moments of Inertia: $I_{A'B'C} = [4.554 \times 10^{-117}]$ g³ cm⁶ $\sigma = 1$

Heat of Formation

The heat of formation is obtained from ΔH_f° (AlOH, g) and its electron affinity, which is estimated to be 0.5 ± 0.9 eV (12 ± 20 kcal). The electron affinity is estimated to be small, or even negative, since the additional electron must go into an antibonding orbital, according to the correlation diagram of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

Heat Capacity and Entropy

Since the molecule now has 11 valence electrons, the Walsh correlation diagram predicts a bent molecule. The extra electron is antibonding thus making the bonds weaker than in AlOH(g). Thus the vibrational frequencies and bond lengths are taken to be the same as in AlOH⁺(g), which is also less strongly bound than AlOH(g). The bond angle is arbitrarily chosen as 120°. The principal moments of inertia are $I_A = 6.536 \times 10^{-39}$ g cm², $I_B = 0.105 \times 10^{-39}$ g cm² and $I_C = 6.641 \times 10^{-39}$ g cm². The enthalpy at 0 K is -2.419 kcal/mol.

T, °K	C _p ^o	S ^o	gibbs/mol	-(G ^o -H ^o sub)/T	H ^o -H ^o sub	kcal/mol	ΔH ^o	ΔG ^o	Log Kp
0									
100									
200									
298	6.729	57.304	57.304		.000		-55.000	-56.622	41.505
300									
350	6.742	57.358	57.304	.016			-55.017	-56.632	41.257
400	6.754	57.372	57.655	.927			-55.905	-57.036	31.163
500	10.040	62.147	58.342	1.903			-56.772	-57.218	25.010
600	10.489	64.019	59.136	2.930			-57.628	-57.227	20.845
700	10.441	65.694	59.723	3.956			-59.352	-56.835	17.527
800	11.181	66.456	61.543	4.222			-60.285	-56.467	13.712
900	11.603	69.667	62.296	7.371			-63.688	-55.814	12.198
1000									
1100	11.803	70.783	63.017	8.542			-64.566	-54.985	10.925
1200	11.984	71.815	63.708	9.726			-65.321	-54.096	9.294
1300	12.156	72.761	64.369	10.924			-66.061	-53.167	8.226
1400	12.319	73.629	65.003	12.140			-66.781	-52.050	6.825
1500	12.429	74.489	65.611	13.387			-67.492	-50.945	5.123
1600	12.550	75.348	66.195	14.666			-68.197	-49.785	4.000
1700	12.688	76.196	66.746	15.986			-68.887	-48.591	3.240
1800	12.844	77.039	67.276	17.347			-69.563	-47.368	2.744
1900	12.944	77.831	67.614	18.657			-70.233	-46.102	2.472
2000	12.923	78.192	68.319	19.746			-71.269	-44.652	2.073
2100									
2200	12.995	78.824	68.804	21.042			-72.094	-43.258	1.698
2300	13.119	80.012	69.728	23.653			-74.567	-40.355	1.347
2400	13.172	80.571	70.168	24.968			-75.393	-38.850	1.074
2500	13.220	81.110	70.595	26.288			-76.220	-37.314	.835
2600	13.265	81.629	71.009	27.612			-77.048	-35.739	.624
2700	13.302	82.115	71.402	30.273			-78.870	-34.120	.437
2800	13.375	83.064	72.185	31.609			-80.690	-32.471	.285
2900	13.406	83.538	72.555	32.948			-82.516	-30.792	.161
3000									
3100	13.435	83.978	72.917	34.290			-84.342	-29.103	.074
3200	13.463	84.420	73.263	35.642			-86.167	-27.394	.020
3300	13.491	84.820	73.613	36.982			-88.000	-25.674	.004
3400	13.507	85.223	73.949	38.331			-89.841	-23.946	.000
3500	13.528	85.614	74.276	39.683			-91.690	-22.211	.000
3600									
3700	13.547	85.996	74.597	41.037			-93.546	-20.476	.000
3800	13.565	86.379	74.916	43.750			-95.410	-18.741	.000
3900	13.597	87.082	75.516	45.109			-97.282	-16.996	.000
4000	13.611	87.427	75.809	46.469			-99.162	-15.251	.000
4100									
4200	13.625	87.763	76.097	47.831			-101.052	-13.506	.000
4300	13.649	88.112	76.454	50.559			-102.964	-11.761	.000
4400	13.660	88.726	76.925	51.924			-104.899	-10.016	.000
4500	13.671	89.033	77.191	53.291			-106.849	-8.271	.000
4600									
4700	13.680	89.334	77.452	54.659			-108.806	-6.526	.000
4800	13.698	89.827	77.959	57.956			-110.782	-4.781	.000
4900	13.706	90.199	78.206	58.766			-112.768	-3.036	.000
5000	13.714	90.476	78.449	60.137			-114.764	-1.291	.000
5100									
5200	13.721	90.748	78.687	61.509			-116.780	.454	.000
5300	13.726	91.074	78.922	62.955			-118.816	2.209	.000
5400	13.741	91.533	79.379	65.638			-120.874	3.964	.000
5500	13.747	91.785	79.602	67.003			-122.944	5.719	.000
5600									
5700	13.752	92.032	79.822	68.378			-125.026	7.474	.000
5800	13.759	92.275	80.255	71.129			-127.121	9.229	.000
5900	13.767	92.751	80.461	73.506			-129.230	10.984	.000
6000	13.772	92.682	80.668	73.863			-129.563	10.953	.000

Aluminum Dioxide (AlO₂H)
(Ideal Gas) GFW = 59.9827

ALUMINUM DIOXYDRIDE (AlO₂H)

(IDEAL GAS)

GFW = 59.9827

Point Group [C_s]

$\Delta H_f^\circ = [-109 \pm 15] \text{ kcal/mol}$

$S_{298.15}^\circ [60.8 \pm 1.5] \text{ gibbs/mol}$

$\Delta H_f^\circ = [-110 \pm 15] \text{ kcal/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\frac{\omega}{\text{cm}^{-1}}$	$\frac{\omega}{\text{cm}^{-1}}$
[3400] (1)	[700] (1)
[1200] (1)	[500] (1)
[1100] (1)	[400] (1)

Bond Distances: Al-O = [1.62] Å Al-O = [1.87] Å O-H = [0.94] Å

$\sigma = 1$

Bond Angles: O-Al-O = [180°] Al-O-H = [105°]

Product of the Moments of Inertia: $I_A I_B I_C = [37.349 \times 10^{-117}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

The hydroxyl group can often be considered as intermediate between F and Cl as is illustrated by the following examples of bond energies from these tables.

D(F-H) = 136 kcal, D(Cl-H) = 103 kcal and D(HO-H) = 119 kcal; also

D(F-BO) = 163 kcal, D(Cl-BO) = 105 kcal and D(HO-BO) = 143 kcal. Thus from

D(F-ALO) = 181 kcal and D(Cl-ALO) = 134 kcal we estimate D(HO-ALO) = 158 ± 20 kcal. This yields ΔH_f° (HOALO, g) = -127 ± 20 kcal/mol.

Consider also D(FB-O) = 175 kcal and D(CIB-O) = 169 kcal; and D(FAL-O) = 138 kcal and D(CIAL-O) = 132 kcal; it is evident that the substituent F or Cl has little effect on the B-O and Al-O bonds. Thus, we assume that D(HOAl-O) = 135 ± 10 kcal/mol which leads to ΔH_f° (HOALO, g) = -119 ± 10 kcal/mol.

M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, "Investigation of the Thermodynamic Properties of Rocket Combustion Products," AFRL-TR-67-244, Nov. 1967, found no evidence for the ion DOAlO⁺ when reacting D₂O(g) + Al₂O₃(c). From estimates of the pressure needed to ensure detection of DOAlO and a knowledge of the D₂O pressure, they calculated the most negative value of ΔH_f° (HOALO, g) = -104 ± 10 kcal/mol. The absence of DOAlO⁺ may be caused by fragmentation by the ionizing electrons and thus the value quoted may not be a real limit.

We adopt ΔH_f° (HOALO, g) = -110 ± 15 kcal/mol which encompasses all the values.

Heat Capacity and Entropy

Vibrational frequencies, bond distances, bond angles, and the product of the moments of inertia were taken from "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and Their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine," National Bureau of Standards Report No. 6297, January 1, 1959. The individual moments of inertia are: $I_A = 0.13 \times 10^{-39} \text{ g cm}^2$, $I_B = 16.9 \times 10^{-39} \text{ g cm}^2$, and $I_C = 17.0 \times 10^{-39} \text{ g cm}^2$.

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log K _p
0	8.000	INFINITE	-	2.861	-108.620	-108.620	INFINITE
100	10.137	56.367	61.809	1.086	-107.526	-107.526	237.100
200	11.983	60.770	60.770	1.000	-106.838	-106.838	177.787
300	12.914	60.844	60.770	1.022	-110.008	-106.818	77.617
400	13.483	64.512	61.260	1.761	-110.393	-105.495	37.733
500	14.386	67.643	62.231	2.766	-110.693	-104.185	25.670
600	15.360	70.773	63.366	4.204	-110.959	-103.219	37.597
700	15.961	72.788	64.543	5.771	-111.206	-101.908	31.617
800	16.436	74.951	65.711	7.392	-111.453	-100.564	27.873
900	16.825	76.910	66.848	9.056	-111.721	-99.187	24.086
1000	17.154	78.700	67.945	10.755	-112.051	-97.759	21.329
1100	17.436	80.349	68.999	12.485	-112.472	-95.890	19.052
1200	17.681	81.877	70.009	14.241	-112.990	-94.164	17.150
1300	17.894	83.300	70.977	16.020	-113.598	-92.420	15.537
1400	18.081	84.634	71.906	17.819	-114.295	-90.660	14.053
1500	18.246	85.887	72.796	19.636	-115.085	-88.886	12.651
1600	18.391	87.069	73.652	21.468	-115.968	-87.100	11.897
1700	18.519	88.188	74.474	23.313	-116.937	-85.300	10.966
1800	18.632	89.250	75.266	25.171	-117.991	-83.489	10.137
1900	18.733	90.250	76.029	27.039	-119.134	-81.669	9.314
2000	18.823	91.183	76.764	28.917	-120.362	-79.840	8.418
2100	18.904	92.043	77.475	30.804	-121.673	-78.000	7.565
2200	18.976	92.825	78.162	32.698	-123.068	-76.152	6.755
2300	19.041	93.570	78.827	34.599	-124.549	-74.293	6.000
2400	19.099	94.281	79.468	36.506	-126.114	-72.425	5.300
2500	19.151	94.962	80.095	38.418	-127.767	-70.555	4.646
2600	19.199	95.614	80.700	40.336	-129.509	-68.678	4.024
2700	19.242	96.239	81.288	42.258	-131.336	-66.781	3.453
2800	19.282	96.840	81.860	44.184	-133.251	-64.852	2.918
2900	19.316	97.417	82.416	46.114	-135.256	-62.900	2.418
3000	19.351	97.973	82.957	48.048	-137.350	-60.935	1.943
3100	19.381	98.508	83.484	49.984	-139.534	-58.958	1.496
3200	19.408	99.023	83.997	51.924	-141.808	-56.968	1.073
3300	19.434	99.521	84.498	53.866	-144.172	-54.965	0.673
3400	19.457	100.000	84.987	55.810	-146.626	-52.948	0.296
3500	19.479	100.466	85.464	57.757	-149.170	-50.918	-0.158
3600	19.499	100.915	85.930	59.706	-151.804	-48.875	-0.583
3700	19.518	101.349	86.385	61.657	-154.528	-46.819	-1.000
3800	19.535	101.770	86.831	63.610	-157.342	-44.752	-1.413
3900	19.551	102.176	87.266	65.564	-160.246	-42.675	-1.821
4000	19.566	102.573	87.693	67.520	-163.240	-40.588	-2.225
4100	19.580	102.956	88.111	69.477	-166.324	-38.491	-2.625
4200	19.593	103.328	88.520	71.436	-169.498	-36.384	-3.021
4300	19.605	103.689	88.921	73.396	-172.762	-34.268	-3.413
4400	19.617	104.040	89.311	75.357	-176.116	-32.143	-3.801
4500	19.627	104.381	89.689	77.319	-179.560	-30.008	-4.185
4600	19.637	104.713	90.077	79.282	-183.094	-27.863	-4.565
4700	19.647	105.039	90.449	81.246	-186.718	-25.708	-4.940
4800	19.656	105.360	90.813	83.211	-190.432	-23.543	-5.311
4900	19.665	105.676	91.177	85.177	-194.236	-21.368	-5.678
5000	19.672	105.985	91.523	87.144	-198.130	-19.184	-6.041
5100	19.679	106.288	91.861	89.112	-202.114	-16.991	-6.399
5200	19.687	106.583	92.208	91.080	-206.188	-14.788	-6.753
5300	19.693	106.872	92.542	93.049	-210.352	-12.575	-7.103
5400	19.699	107.156	92.871	95.019	-214.606	-10.353	-7.448
5500	19.700	107.434	93.194	96.989	-218.950	-8.122	-7.788
5600	19.711	107.708	93.512	98.960	-223.384	-5.882	-8.123
5700	19.717	107.978	93.825	100.931	-227.908	-3.633	-8.453
5800	19.722	108.244	94.133	102.903	-232.522	-1.378	-8.779
5900	19.727	108.507	94.436	104.876	-237.226	+0.982	-9.100
6000	19.731	108.766	94.736	106.849	-242.020	+2.922	-9.418

Lithium Tetrahydroaluminate (LiAlH₄)

(Crystal) Mol. Wt. = 37.952

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹ S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
200						
298	20.650	21.000	4.000	-28.000	-11.560	0.474
300						
400	20.780	21.128	4.098	-28.010	-11.459	0.547
500	21.400	21.582	4.250	-28.040	-11.215	0.715
600	22.200	22.370	4.464	-28.083	-10.953	
700	23.550	23.309	4.716	-28.106	-10.685	
800	25.000	24.451	5.004	-28.128	-10.418	
900	26.600	25.841	5.322	-28.150	-10.151	
1000	28.317	27.479	5.671	-28.171	-9.884	
1100	30.150	29.317	6.046	-28.190	-9.617	
1200	32.100	31.366	6.446	-28.208	-9.350	
1300	34.160	33.626	6.871	-28.225	-9.083	
1400	36.330	36.096	7.321	-28.240	-8.816	
1500	38.610	38.777	7.796	-28.253	-8.549	
1600	41.000	41.666	8.296	-28.264	-8.282	
1700	43.500	44.771	8.821	-28.273	-8.015	
1800	46.100	48.096	9.371	-28.280	-7.748	
1900	48.800	51.641	9.946	-28.285	-7.481	
2000	51.600	55.406	10.546	-28.288	-7.214	

June 30, 1963; Mar. 31, 1964

LITHIUM TETRAHYDROALUMINATE (LiAlH₄)

(CRYSTAL)

MOL. WT. = 37.952

ΔH_f^o 0 = Unknown

ΔH_f^o 298.15 = -28.0 ± 2.0 kcal. mole⁻¹

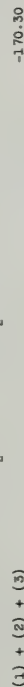
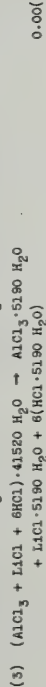
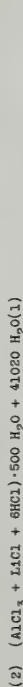
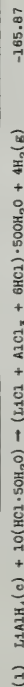
S_{298.15}^o = [21.0 ± 2.0]

T_d = [410 ± 10]*K.

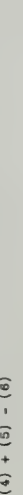
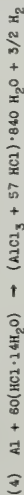
Heat of Formation.

The heats of solution of LiAlH₄(c) in HCl(aq.) were measured calorimetrically by the following investigators: W. D. Davis, L. S. Mason and G. Stegemann, J. Am. Chem. Soc. 71, 2775 (1949), L. G. Fasolino, et al., "Heat of Formation of Lithium Aluminum Hydride," Special Report, National Research Corporation, Ma., April 26, 1963, and M. B. Smith and G. E. Bues, Jr., J. Chem. Eng. Data, 6, 342 (1963). The results are given in the following table. Investigator

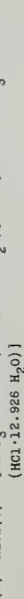
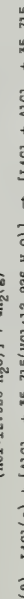
Davis, et al.



Fasolino, et al.



Smith and Bues



Incorporating appropriate auxiliary thermal data, the heats of formation (ΔH_f^o 298.15) for LiAlH₄(c) were derived as -28.51 (recalculated value, by Smith and Bues, loc. cit.), -24.67 ± 1.31 and -28.4 ± 1.5 kcal. mole⁻¹, resp. The adopted value, -28.0 ± 2.0 kcal. mole⁻¹, is the weighted average of the above three values.

Heat Capacity and Entropy.

Heat capacities were estimated by comparison with those for LiBH₄(c), LiBO₂(c) and LiAlO₂(c). The entropy value (S_{298.15}^o) was calculated from that for LiBH₄(c) by the substitution of the entropy contribution of B atom by that of Al atom in the LiAlH₄(c) molecule. The entropy values of the constituent B and Al atoms in crystalline compounds were taken from O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.

Temperature of Decomposition.

T_d was reported by A. E. Pinholt, R. C. Bond, Jr. and H. I. Schlesinger, J. Am. Chem. Soc. 69, 1199 (1947). The decomposition products are aluminum, hydrogen, and lithium hydride. This reaction is apparently kinetically controlled since the free energy for the decomposition is negative even at room temperature.

AlH₄Li

Aluminum Moniodide (AlI)

(Ideal Gas) Mol. Wt. = 153.89

T. °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.412	50.408	66.655	1.625	14.641	14.641	∞
200	8.245	59.858	74.074	1.625	14.641	14.641	∞
298	8.634	59.843	74.074	1.625	14.641	14.641	∞
300	8.638	59.297	74.074	1.625	14.641	14.641	∞
400	8.789	61.805	74.074	1.625	14.641	14.641	∞
500	8.870	63.776	74.074	1.625	14.641	14.641	∞
600	8.921	65.398	74.074	1.625	14.641	14.641	∞
700	8.957	66.776	74.074	1.625	14.641	14.641	∞
800	8.985	67.974	74.074	1.625	14.641	14.641	∞
900	9.007	69.033	74.074	1.625	14.641	14.641	∞
1000	9.027	69.983	74.074	1.625	14.641	14.641	∞
1100	9.045	70.845	74.074	1.625	14.641	14.641	∞
1200	9.061	71.632	74.074	1.625	14.641	14.641	∞
1300	9.076	72.358	74.074	1.625	14.641	14.641	∞
1400	9.091	73.031	74.074	1.625	14.641	14.641	∞
1500	9.105	73.659	74.074	1.625	14.641	14.641	∞
1600	9.119	74.247	74.074	1.625	14.641	14.641	∞
1700	9.132	74.800	74.074	1.625	14.641	14.641	∞
1800	9.145	75.323	74.074	1.625	14.641	14.641	∞
1900	9.158	75.817	74.074	1.625	14.641	14.641	∞
2000	9.171	76.288	74.074	1.625	14.641	14.641	∞
2100	9.183	76.735	74.074	1.625	14.641	14.641	∞
2200	9.196	77.163	74.074	1.625	14.641	14.641	∞
2300	9.208	77.572	74.074	1.625	14.641	14.641	∞
2400	9.221	77.964	74.074	1.625	14.641	14.641	∞
2500	9.233	78.341	74.074	1.625	14.641	14.641	∞
2600	9.245	78.703	74.074	1.625	14.641	14.641	∞
2700	9.257	79.052	74.074	1.625	14.641	14.641	∞
2800	9.269	79.389	74.074	1.625	14.641	14.641	∞
2900	9.282	79.715	74.074	1.625	14.641	14.641	∞
3000	9.294	80.029	74.074	1.625	14.641	14.641	∞
3100	9.306	80.334	74.074	1.625	14.641	14.641	∞
3200	9.318	80.630	74.074	1.625	14.641	14.641	∞
3300	9.330	80.917	74.074	1.625	14.641	14.641	∞
3400	9.342	81.196	74.074	1.625	14.641	14.641	∞
3500	9.354	81.467	74.074	1.625	14.641	14.641	∞
3600	9.366	81.730	74.074	1.625	14.641	14.641	∞
3700	9.378	81.987	74.074	1.625	14.641	14.641	∞
3800	9.390	82.237	74.074	1.625	14.641	14.641	∞
3900	9.402	82.481	74.074	1.625	14.641	14.641	∞
4000	9.414	82.720	74.074	1.625	14.641	14.641	∞
4100	9.426	82.952	74.074	1.625	14.641	14.641	∞
4200	9.438	83.179	74.074	1.625	14.641	14.641	∞
4300	9.449	83.402	74.074	1.625	14.641	14.641	∞
4400	9.461	83.619	74.074	1.625	14.641	14.641	∞
4500	9.473	83.832	74.074	1.625	14.641	14.641	∞
4600	9.485	84.040	74.074	1.625	14.641	14.641	∞
4700	9.497	84.244	74.074	1.625	14.641	14.641	∞
4800	9.509	84.444	74.074	1.625	14.641	14.641	∞
4900	9.521	84.640	74.074	1.625	14.641	14.641	∞
5000	9.533	84.835	74.074	1.625	14.641	14.641	∞
5100	9.545	85.022	74.074	1.625	14.641	14.641	∞
5200	9.556	85.207	74.074	1.625	14.641	14.641	∞
5300	9.568	85.389	74.074	1.625	14.641	14.641	∞
5400	9.580	85.568	74.074	1.625	14.641	14.641	∞
5500	9.592	85.744	74.074	1.625	14.641	14.641	∞
5600	9.604	85.917	74.074	1.625	14.641	14.641	∞
5700	9.616	86.087	74.074	1.625	14.641	14.641	∞
5800	9.628	86.255	74.074	1.625	14.641	14.641	∞
5900	9.640	86.419	74.074	1.625	14.641	14.641	∞
6000	9.651	86.581	74.074	1.625	14.641	14.641	∞

Dec. 31, 1961; Sept. 30, 1964

ALUMINUM MONIODIDE (AlI)

(IDEAL GAS)

MOL. WT. = 153.89

Ground State Configuration $1\sum^+$

$\Delta H_f^o = 14.6 \pm 2.0$ kcal. mole⁻¹

$S_{298.15}^o = [59.243]$ cal. deg.⁻¹ mole⁻¹

$\Delta H_f^o = 14.3 \pm 2.0$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

$$\frac{E_i}{\text{e.v. cm.}^{-1}} = \frac{g_i}{1}$$

$\omega_e = 316.1$ cm.⁻¹

$\sigma = 1$

$\omega_e x_e = 1.0$ cm.⁻¹

$r_e = [2.56] \text{ \AA}$

$\alpha_e = [0.000492]$ cm.⁻¹

Heat of Formation.

The dissociation energy (D_0^o) of AlI(g) was reported by A. G. Gaydon¹, R. F. Barrow², and G. Herzberg³, respectively. Hence the corresponding values of ΔH_f^o 298.15 for AlI(g) were derived. The results are given as follows.

Investigator	e.v.	D ₀ ^o	kcal. mole ⁻¹	ΔH _f ^o 298.15 kcal. mole ⁻¹
Gaydon 1	3.92	90.4	12.7	
Barrow 2	—	87.0	16.0	
Herzberg 3	2.9	66.9	36.2	

1 A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall Ltd., London, 1953.

2 R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960).

3 G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950.

The adopted value of ΔH_f^o 298.15 for AlI(g) is the average of the first two ΔH_f^o 298.15 values listed in the above table.

Heat Capacity and Entropy.

The spectroscopic constants, ω_e and $\omega_e x_e$, and ground state configuration were taken from G. Herzberg, loc. cit. The values of B_e and α_e were estimated. The bond length (r_e) was estimated by comparison with those for Al₂I₆(g) reported by K. J. Palmer and N. Elliott, J. Am. Chem. Soc. 80, 1852 (1958).

Aluminum Triiodide (AlI₃)
(Crystal) Mol. Wt. = 407.71

T, °K.	cal. mole ⁻¹ deg. ⁻¹		- (F° - H° ₂₉₈)/T		H° - H° ₂₉₈		kcal. mole ⁻¹		Log K _p
	C _p	S°	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	ΔH _f °	ΔF _f °	
0									
100	23.640	45.300	45.300	0.000	-73.900	-72.974	53.489		
200	23.680	45.446	45.300	0.044	-73.903	-72.968	53.155		
300	23.720	45.592	45.300	0.088	-73.906	-72.963	52.821		
400	23.760	45.738	45.300	0.132	-73.909	-72.958	52.487		
500	23.800	45.884	45.300	0.176	-73.912	-72.953	52.153		
600	29.158	63.797	50.321	8.086	-94.129	-64.079	23.340		
700	29.899	68.353	52.578	11.042	-93.208	-59.143	18.464		
800	30.335	72.376	54.806	14.055	-92.263	-54.340	14.844		
900	30.524	75.964	56.962	17.102	-91.319	-49.652	12.056		
1000	30.700	79.192	59.026	20.166	-90.384	-44.982	9.611		
1100	30.799	82.123	60.995	23.242	-89.459	-40.143	7.074		
1200	30.870	84.806	62.869	26.325	-88.540	-35.485	6.402		
1300	30.908	87.279	64.653	29.414	-87.624	-30.913	5.197		
1400	30.921	89.541	66.352	32.506	-86.711	-26.424	4.364		
1500	31.000	91.708	67.972	35.605	-85.801	-22.001	3.205		

Dec. 31, 1961; June 30, 1964

ALUMINUM TRIIODIDE (AlI₃) (CRYSTAL)

MOL. WT. = 407.71

ΔH_f° = Unknown
ΔH_f° 298.15 = -73.9 ± 1.5 kcal. mole⁻¹
ΔH_m° = 3.8 kcal. mole⁻¹
ΔH_g° 298.15 (to dimer) = 28.8 ± 1.8 kcal. mole⁻¹

S° 298.15 = {46.3 ± 2.0} cal. deg.⁻¹ mole⁻¹
T_m = 464.15°K.

Heat of Formation.

J. D. Corbett and N. W. Gregory, J. Am. Chem. Soc. 76, 1446 (1954) reported the free energy change, ΔF° 298.15 = -8.7 ± 0.2 kcal. mole⁻¹, for the reaction AlI₃(c) + 3HCl(g) → AlCl₃(c) + 3HI(g). By the relationship ΔH = ΔF + TΔS the value of ΔH° 298.15 was derived as -10.1 ± 0.2 kcal. mole⁻¹. The heat of formation (ΔH_f° 298.15) for AlI₃(c) was evaluated to be -73.66 ± 0.30 kcal. mole⁻¹. The heat of solution of AlI₃(c) in water was measured by D. J. A. Dear and D. D. Riley, J. Chem. Soc., 4684 (1954). From the value, ΔH_f° 298.15 = -91.4 ± 1.5 kcal. mole⁻¹ for the reaction AlI₃(c) → Al³⁺(aq.) + 3I⁻(aq.), the heat of formation for AlI₃(c) was calculated to be -74.1 ± 1.5 kcal. mole⁻¹. The adopted value of ΔH_f° 298.15 for AlI₃(c) is the average of the above two values.

Heat Capacity and Entropy.

The heat capacities, 298.15-464°K., were taken from K. K. Kelley, U. S. Bur. Mines Bull. 594 (1960). They were derived from the enthalpy data measured by W. Fischer, Z. anorg. Chem. 200, 332 (1931). Above 464°K. the C_p values were obtained by graphical extrapolation. The entropy, S° 298.15, for AlI₃(c) was calculated from S° 298.15 for AlI₃(l) by subtracting ΔS° and the difference between S° 298.15-298.15 for crystal and liquid.

Melting Data.

Temperature and heat of melting were reported by W. Fischer, loc. cit.

Heat of Sublimation.

Heat of sublimation was calculated from vapor pressure data reported by W. Fischer, O. Rehfs, and B. Benze, Z. anorg. allgem. Chemie, 205, 1 (1932), by both the second and third law methods. See Al₂I₆(g) table for details.

Aluminum Triiodide (AlI₃)

(Liquid) Mol. Wt. = 407.71

T, °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$-(F^\circ - H^\circ_{298})/T$ kcal. mole ⁻¹	$H^\circ - H^\circ_{298}$ kcal. mole ⁻¹	ΔF°_f kcal. mole ⁻¹	Log K _p
0						
100						
200						
298	29.000	52.450	52.450	0.000	- 70.770	- 71.976
300	29.000	52.450	52.450	0.000	- 70.763	- 71.983
350	29.000	52.629	52.629	0.179	- 70.584	- 71.799
400	29.000	53.088	53.088	0.638	- 70.126	- 71.341
450	29.000	54.443	54.443	2.000	- 68.765	- 69.980
500	29.000	56.731	56.731	4.288	- 66.487	- 67.702
600	29.000	62.161	62.161	9.754	- 61.031	- 62.246
700	29.000	69.553	69.553	17.624	- 53.161	- 54.316
800	29.000	78.821	78.821	28.054	- 42.731	- 43.886
900	29.000	89.889	89.889	40.084	- 30.661	- 31.816
1000	29.000	102.711	102.711	53.754	- 16.991	- 18.186
1100	29.000	117.329	117.329	69.169	- 1.576	- 1.771
1200	29.000	133.801	133.801	86.281	13.544	14.694
1300	29.000	152.173	152.173	105.053	33.316	34.566
1400	29.000	171.401	171.401	125.281	58.544	59.794
1500	29.000	191.443	191.443	146.924	89.184	90.434
1600	29.000	212.253	212.253	169.974	125.234	126.484
1700	29.000	233.793	233.793	205.424	166.684	167.934
1800	29.000	255.923	255.923	253.274	213.534	214.484
1900	29.000	278.513	278.513	313.524	265.784	266.984
2000	29.000	301.523	301.523	386.074	323.334	324.534

ALUMINUM TRIIODIDE (AlI₃)

(LIQUID)

MOL. WT. = 407.71

S_{298.15} = [52.45] cal. deg.⁻¹ mole⁻¹

ΔH_f^o 298.15 = -70.77 ± 1.5 kcal. mole⁻¹

ΔH_m^o = 3.8 kcal. mole⁻¹

T_m = 464.15°K.

Heat of Formation.

ΔH_f^o 298.15(1) was obtained from ΔH_f^o 298.15(c) by adding ΔH_m^o and the difference between H_{464.15}^o-H_{298.15}^o for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity, 464-500°K., was obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960). It was derived based on the enthalpy data measured by W. Fischer, Z. anorg. Chem. 200, 332 (1931). The C_p values above 500°K. were assumed to be the same as that at 500°K. The entropy, S_{298.15}^o, was estimated so that the values of ΔH_f^o calculated from vapor pressure data by the second and third law methods were in reasonable agreement.

Melting Data.

T_m and ΔH_m^o were reported by W. Fischer, loc. cit.

Aluminum Triiodide (AlI₃)

(Ideal Gas) Mol. Wt. = 407.71

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞
100	13.828	69.035	102.015	-47.535	INFINITE
200	16.950	79.725	88.414	-52.224	114.130
298	18.281	86.776	86.776	-56.543	61.784
300	18.298	86.890	86.777	-56.440	44.502
300	18.298	86.890	86.777	-56.511	44.502
400	16.917	92.249	87.403	-55.504	34.084
500	15.238	96.508	88.693	-54.643	28.254
600	14.422	100.033	90.464	-53.265	23.043
700	13.654	102.951	92.001	-51.697	18.518
800	12.924	105.295	93.285	-50.047	14.538
900	12.221	107.064	94.362	-48.250	11.067
1000	11.540	108.298	95.268	-46.350	8.250
1100	10.884	109.018	96.048	-44.390	5.970
1200	10.248	109.218	96.719	-42.400	4.213
1300	9.632	108.998	97.285	-40.420	2.900
1400	9.034	108.358	97.759	-38.480	1.970
1500	8.452	107.308	98.142	-36.590	1.360
1600	7.884	105.858	98.442	-34.760	1.000
1700	7.330	104.008	98.662	-32.980	0.750
1800	6.790	101.758	98.802	-31.260	0.590
1900	6.262	99.108	98.862	-29.600	0.420
2000	5.746	96.058	98.842	-28.000	0.300
2100	5.242	92.608	98.742	-26.460	0.220
2200	4.750	88.758	98.562	-24.980	0.160
2300	4.270	84.508	98.302	-23.560	0.110
2400	3.800	79.858	97.862	-22.200	0.070
2500	3.340	74.808	97.262	-20.900	0.040
2600	2.890	69.358	96.502	-19.660	0.020
2700	2.450	63.508	95.582	-18.480	0.010
2800	2.020	57.258	94.502	-17.360	0.005
2900	1.600	50.608	93.262	-16.300	0.002
3000	1.190	43.558	91.862	-15.300	0.001
3100	0.790	36.108	90.302	-14.360	0.000
3200	0.400	28.258	88.582	-13.480	0.000
3300	0.020	20.008	86.702	-12.660	0.000
3400	-0.360	11.358	84.662	-11.900	0.000
3500	-0.740	2.308	82.462	-11.200	0.000
3600	-1.120	-6.842	80.102	-10.560	0.000
3700	-1.500	-15.992	77.582	-10.000	0.000
3800	-1.880	-25.242	74.902	-9.500	0.000
3900	-2.260	-34.592	72.062	-9.060	0.000
4000	-2.640	-44.042	69.062	-8.680	0.000
4100	-3.020	-53.492	65.902	-8.360	0.000
4200	-3.400	-62.942	62.582	-8.100	0.000
4300	-3.780	-72.392	59.102	-7.900	0.000
4400	-4.160	-81.842	55.562	-7.760	0.000
4500	-4.540	-91.292	51.862	-7.680	0.000
4600	-4.920	-100.742	48.102	-7.660	0.000
4700	-5.300	-110.192	44.282	-7.700	0.000
4800	-5.680	-119.642	40.402	-7.800	0.000
4900	-6.060	-129.092	36.462	-7.960	0.000
5000	-6.440	-138.542	32.462	-8.180	0.000
5100	-6.820	-147.992	28.402	-8.460	0.000
5200	-7.200	-157.442	24.282	-8.800	0.000
5300	-7.580	-166.892	20.102	-9.200	0.000
5400	-7.960	-176.342	15.862	-9.660	0.000
5500	-8.340	-185.792	11.562	-10.180	0.000
5600	-8.720	-195.242	7.202	-10.760	0.000
5700	-9.100	-204.692	2.782	-11.400	0.000
5800	-9.480	-214.142	-1.618	-12.100	0.000
5900	-9.860	-223.592	-5.858	-12.860	0.000
6000	-10.240	-233.042	-10.098	-13.680	0.000

Dec. 31, 1961, June 30, 1964

ALUMINUM TRIIODIDE (AlI₃) (IDEAL GAS) MOL. WT. = 407.71

Point Group [D_{3h}]
 $\Delta H_f^\circ 0 = -47.5 \pm 1.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [86.776] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -49.0 \pm 1.6 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

λ , cm ⁻¹	λ , cm ⁻¹
[210] (1)	[95] (1)
[170] (1)	[450] (2)

Bond Distance: Al-I = $2.44 \pm 0.02 \text{ \AA}$
 Bond Angle: I-Al-I = $[120]^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 1.33213 \times 10^{-110} \text{ g. cm.}^2$

Heat of Formation: $\Delta H_f^\circ 298.15 = -49.0 \pm 1.6 \text{ kcal. mole}^{-1}$

Heat of Formation

The equilibrium pressures of the reaction $\text{Al}_2\text{I}_6(\text{g}) \rightarrow 2\text{AlI}_3(\text{g})$ at several temperatures were determined by W. Fischer, O. Rehfs and B. Benze, Z. anorg. allgem. Chem. 205, 1 (1932). The heats of dissociation of $\text{Al}_2\text{I}_6(\text{g})$ were calculated by both second and third law methods. The heats of vaporization, i.e. $\text{AlI}_3(\text{l}) \rightarrow \text{AlI}_3(\text{g})$, were also evaluated using the calculated partial pressure of $\text{AlI}_3(\text{g})$ over $\text{AlI}_3(\text{l})$. See $\text{Al}_2\text{I}_6(\text{g})$ table for detail. The results obtained are summarized as follows:

Chemical Reaction or Process	Temperature Range (°K.)	Second Law Value	Third Law Value	Kcal. Mole ⁻¹
$\text{Al}_2\text{I}_6(\text{g}) \rightarrow 2\text{AlI}_3(\text{g})$	614 - 744	25.18	23.34	-47.9
$\text{Al}_2\text{I}_6(\text{g}) \rightarrow 2\text{AlI}_3(\text{g})$	482.8 - 578.0	23.07	23.34	-49.0
$\text{AlI}_3(\text{l}) \rightarrow \text{AlI}_3(\text{g})$	493.6 - 645.2	21.45	22.69	-49.2

The three $\Delta H_f^\circ 298.15(\text{AlI}_3, \text{g})$ values were calculated using the respective second law values of $\Delta H_f^\circ 298.15$. The adopted value, $\Delta H_f^\circ 298.15 = -49.0 \pm 1.6 \text{ kcal. mole}^{-1}$, is the weighted average of the above three values.

Heat Capacity and Entropy

The molecular structure, bond angles and angles were obtained from P. A. Akishin, N. G. Rambidi, and E. L. Zosorin, Kristallografiya, 4, 186 (1959). The vibrational frequencies were estimated such that the values of ΔH_f° obtained by the third law method are in reasonable agreement with the corresponding values calculated by the second law method. The three principal moments of inertia are: $I_A = I_B = 1.8815 \times 10^{-37}$ and $I_C = 3.7630 \times 10^{-37} \text{ g. cm.}^2$.

Lithium Aluminate (LiAlO₂)
(Crystal) Mol. Wt. = 65.92

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	4.000	INFINITE	0.000	INFINITE	2.723	-282.779	-282.779	INFINITE
100	4.293	1.532	1.532	2.727	2.179	-283.175	-278.574	9.959
200	11.491	12.751	12.751	12.749	1.001	-284.339	-269.429	197.487
300	16.283	12.651	12.749	12.749	.031	-284.334	-269.337	196.203
400	19.490	18.012	13.432	13.432	1.832	-284.462	-264.312	144.406
500	21.130	22.567	15.614	15.614	3.876	-285.194	-259.179	113.290
600	22.153	26.514	16.442	16.442	6.043	-285.151	-254.003	92.516
700	22.683	29.986	16.136	16.136	8.297	-285.062	-248.819	77.681
800	23.462	33.082	15.613	15.613	10.613	-284.950	-243.650	66.559
900	23.949	35.875	21.445	21.445	12.987	-284.830	-238.493	57.911
1000	24.360	38.421	23.017	23.017	15.403	-287.203	-233.166	50.756
1100	24.774	40.763	24.525	24.525	17.861	-286.972	-227.774	45.252
1200	25.143	42.935	25.970	25.970	20.357	-286.712	-222.404	40.503
1300	25.495	44.961	27.354	27.354	22.889	-286.423	-217.057	36.469
1400	25.834	46.883	28.680	28.680	25.456	-286.105	-211.733	33.076
1500	26.163	48.657	29.953	29.953	28.056	-285.759	-206.432	30.076
1600	26.485	50.355	31.175	31.175	30.698	-285.385	-201.155	27.475
1700	26.802	51.971	32.351	32.351	33.383	-285.009	-195.875	25.013
1800	27.115	53.511	33.484	33.484	36.049	-284.619	-190.574	22.730
1900	27.425	54.986	34.577	34.577	38.776	-284.214	-185.242	20.690
2000	27.733	56.400	35.633	35.633	41.534	-283.784	-179.882	18.859
2100	28.040	57.761	36.655	36.655	44.322	-283.332	-174.506	17.206
2200	28.340	59.065	37.644	37.644	47.126	-282.858	-169.104	15.705
2300	28.640	60.312	38.603	38.603	49.930	-282.360	-163.676	14.339
2400	28.940	61.505	39.532	39.532	52.734	-281.838	-158.222	13.089
2500	29.240	62.650	40.434	40.434	55.538	-281.292	-152.742	11.941
2600	29.540	63.749	41.310	41.310	58.342	-280.722	-147.236	10.885
2700	29.840	64.808	42.161	42.161	61.146	-280.128	-141.704	9.908
2800	30.140	65.827	42.988	42.988	63.950	-279.510	-136.146	9.074
2900	30.440	66.811	43.793	43.793	66.754	-278.868	-130.562	8.343
3000	30.740	67.762	44.576	44.576	69.558	-278.202	-124.954	7.684

LITHIUM ALUMINATE (LiAlO₂)

(CRYSTAL)

MOL. WT. = 65.92



ΔH_f^o = -282.78 kcal. mole⁻¹
 ΔH_f^o 298.15 = -284.33 ± .20 kcal. mole⁻¹
 S_{298.15} = 12.75 cal. deg.⁻¹ mole⁻¹
 T_m = 1863°K
 ΔH_m = [5000] cal. mole⁻¹

Heat of Formation.

ΔH_f 298.15 was measured by J. P. Coughlin, J. Am. Chem. Soc. 79, 2397 (1957).

Heat Capacity and Extrapolation.

Thermodynamic functions are based on the low temperature heat capacity data of E. O. King, J. Am. Chem. Soc. 77, 3189 (1955), and on the high temperature heat content results of A. O. Christensen, K. O. Conway, and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 5565 (1960).

Melting.

R. Ballo and E. Dittler, Z. anorg. u. allgem. Chem. 75, 39 (1912), list the melting point as between 1900° to 2000°K. More recently, K. H. Kim and P. A. Hummel, J. Am. Ceram. Soc. 43, 611 (1960), determined the melting point as 1863° ± 15°K. by rapidly heating a small sample on a Pt-Rh strip furnace. The value, which was used in this report, was derived from an average of ten measurements by Kim and Hummel.

H. Prophet, The Dow Chemical Company, private communication March 9, 1961, using an arc-image furnace reports the melting point to be about 1975°K. After seven successive runs on the same sample the melting point approached that of Al₂O₃ at 2308°K. The sample, therefore is decomposed upon fusion to Li₂O vapor and Al₂O₃(c). See O. N. Salmon and L. Marcus J. Am. Ceram. Soc. 43, 549 (1960), and P. A. Hummel, B. S. R. Sastry and D. Watring, Ibid., 41, 88 (1958).



INTERIM TABLE

T, °K.	C _p	S° -(F°-H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈)/T	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	21,000	19,200	19,200	.000	-273.301	-240.323	190.613
300	21,000	19,330	19,200	.039	-273.297	-240.344	189.578
400	21,000	25,371	20,024	2,139	-273.126	-255.920	139.621
500	21,000	30,037	21,550	4,239	-273.402	-251.553	109.948
600	21,000	33,886	23,321	6,339	-273.826	-247.101	90.002
700	21,000	37,123	25,068	8,439	-273.891	-242.843	75.753
800	21,000	40,401	26,576	10,539	-273.891	-238.143	63.944
900	21,000	43,613	28,158	12,639	-273.891	-233.143	53.944
1000	21,000	46,613	29,675	14,739	-276.638	-228.995	50.044
1100	21,000	46,613	31,307	16,839	-276.665	-224.205	44.543
1200	21,000	48,442	32,660	18,939	-277.101	-219.403	39.057
1300	21,000	51,179	34,131	21,039	-277.101	-214.603	33.566
1400	21,000	51,179	35,131	23,139	-277.593	-209.744	32.744
1500	21,000	53,128	36,302	25,239	-277.547	-204.928	29.657
1600	21,000	54,483	37,397	27,339	-277.705	-200.080	27.320
1700	21,000	55,757	38,440	29,439	-312.518	-193.896	24.926
1800	21,000	57,052	39,439	31,539	-312.592	-188.691	22.691
1900	21,000	58,095	40,388	33,639	-312.592	-183.486	20.456
2000	21,000	59,169	41,300	35,739	-312.890	-178.281	18.221
2100	21,000	60,184	42,175	37,839	-312.894	-173.076	15.986
2200	21,000	61,171	43,017	39,939	-312.906	-167.871	13.751
2300	21,000	62,138	43,827	42,039	-312.918	-162.666	11.516
2400	21,000	62,998	44,607	44,139	-312.947	-157.461	9.281
2500	21,000	63,855	45,360	46,239	-312.979	-152.256	7.046
2600	21,000	64,679	46,087	48,339	-313.017	-147.051	4.811
2700	21,000	65,472	46,790	50,439	-313.064	-141.846	2.576
2800	21,000	66,242	47,471	52,539	-313.121	-136.641	0.341
2900	21,000	66,982	48,131	54,639	-313.188	-131.436	-1.904
3000	21,000	67,684	48,771	56,739	-313.401	-126.231	-4.169

September 30, 1961

Lithium Aluminate (LiAlO₂) (Liquid)

Mol. Wt. = 65.92

ΔH_f^o 298.15 = [-273.3] kcal. mole⁻¹

S_{298.15}^o = [19.2] cal. deg.⁻¹ mole⁻¹

T_m = 1883°K

ΔH_m = [6000] cal. mole⁻¹

Heat capacity, entropy, and ΔH_m are all estimated.

Aluminum Nitride (AlN) (Crystal) Mol. Wt. = 40.988

ALUMINUM NITRIDE (AlN) (CRYSTAL) MOL. WT. = 40.988

T, °K	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	0.000	INFINITE	-0.925	-74.785	-74.795	INFINITE
100	1.360	5.519	9.388	-887	-75.205	-75.205	-73.187	159.942
200	4.813	2.495	5.399	-590	-75.701	-75.701	-70.979	77.558
298	7.221	4.816	4.000	-400	-76.000	-76.000	-68.595	50.279
300	7.225	4.861	4.816	-401	-76.004	-76.004	-68.549	49.035
400	8.700	7.155	5.119	-814	-76.149	-76.149	-66.038	36.080
500	9.701	9.210	5.736	-1.737	-76.204	-76.204	-63.503	27.756
600	10.439	11.048	6.471	2.767	-76.207	-76.207	-60.962	22.204
700	10.915	12.696	7.245	3.616	-76.188	-76.188	-58.423	18.240
800	11.255	14.177	8.020	4.926	-76.166	-76.166	-55.887	15.267
900	11.495	15.518	8.780	6.064	-76.155	-76.155	-53.352	12.955
1000	11.660	16.738	9.516	7.222	-76.055	-76.055	-50.634	11.065
1100	11.769	17.855	10.224	8.394	-76.577	-76.577	-47.835	9.504
1200	11.836	18.882	10.803	9.575	-78.497	-78.497	-45.044	8.203
1300	11.876	19.831	11.554	10.760	-78.417	-78.417	-42.260	7.104
1400	11.901	20.712	12.177	11.949	-78.339	-78.339	-39.482	6.163
1500	11.923	21.534	12.774	13.140	-78.262	-78.262	-36.709	5.348
1600	11.955	22.304	13.345	14.336	-78.186	-78.186	-33.940	4.636
1700	12.000	23.030	13.894	15.532	-78.110	-78.110	-31.178	4.008
1800	12.023	23.717	14.421	16.733	-78.033	-78.033	-28.420	3.450
1900	12.035	24.367	14.927	17.936	-77.957	-77.957	-25.664	2.952
2000	12.065	24.985	15.415	19.141	-77.881	-77.881	-22.914	2.504
2100	12.092	25.575	15.885	20.349	-77.804	-77.804	-20.169	2.099
2200	12.115	26.138	16.338	21.559	-77.727	-77.727	-17.415	1.731
2300	12.135	26.677	16.776	22.772	-77.649	-77.649	-14.667	1.396
2400	12.152	27.194	17.199	23.986	-77.570	-77.570	-11.951	1.088
2500	12.165	27.690	17.609	25.202	-77.491	-77.491	-9.218	0.806
2600	12.183	28.167	18.006	26.420	-77.412	-77.412	-6.490	0.545
2700	12.198	28.628	18.391	27.639	-77.333	-77.333	-3.763	0.305
2800	12.215	29.072	18.765	28.859	-77.254	-77.254	-1.033	0.086
2900	12.231	29.500	19.127	30.082	-77.175	-77.175	1.702	0.445
3000	12.245	29.915	19.480	31.305	-77.096	-77.096	4.436	0.816

$\Delta H_f^0 = -74.8 \pm 0.3 \text{ kcal. mole}^{-1}$
 $T_D = [2790^\circ \text{K}]$
 $\Delta H_f^{298.15} = -76.0 \pm 0.3 \text{ kcal. mole}^{-1}$
 $S^{298.15} = 4.816 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Heat of Formation.

The selected heat of formation is the average of two independent calorimetric determinations. The heat of formation was reported to be $-76.5 \pm 0.2 \text{ kcal. mole}^{-1}$ and $-75.6 \pm 0.4 \text{ kcal. mole}^{-1}$. The former value was reported by C. A. Neugebauer and J. L. Margrave, *Z. Anorg. Allgem. Chem.* **280**, 82 (1957). The later value was reported by A. D. Mah, E. G. King, W. N. Weller, and A. V. Christensen, *U. S. Bureau of Mines Report of Investigations* **5716** (1961).

Vapor pressure measurements agree with the selected heat of formation. For instance $\Delta H_f^{298.15} = -75.5 \text{ kcal. mole}^{-1}$ for AlN(c) was calculated from the heat for the reaction $2\text{AlN(c)} \rightarrow 2\text{Al(g)} + \text{N}_2(\text{g})$ and the heat of sublimation, $78.0 \text{ kcal. mole}^{-1}$, for Al(c). This heat of reaction was obtained from a third law calculation using JANAF values for the free energy functions and torsion effusion pressures measured by D. L. Hildenbrand and L. P. Theard, *Aeronutronic Technical Report U-1497* (1961). Vapor pressure measurements with a microbalance in a vacuum system by L. H. Dreger, V. V. Dedape, and J. L. Margrave, *J. Phys. Chem.* **66**, 1556 (1962) agree with the selected $\Delta H_f^{298.15}$. When recalculated with the sublimation coefficient ($\alpha = 2.2 \times 10^{-5}$) reported by Hildenbrand and Theard, some of the Knudsen cell measurements by M. Hoch and D. White, "The Vaporization of Boron Nitride and Aluminum Nitride," *ASTIA Unclassified Report 142616*, October 29, 1956, agree with the selected heat of formation.

Earlier determinations of the heat of formation which apparently are in error are summarized by C. A. Neugebauer and J. L. Margrave (*loc. cit.*) and by L. H. Dreger et al. (*loc. cit.*).

Heat Capacity and Entropy.

The heat capacity and entropy were reported by A. D. Mah et al. (*loc. cit.*). They measured the low temperature (51-298.15°K) and high temperature (298.15-1800°K) heat capacities and extrapolated the heat capacity from 0 to 51°K using the T^3 law. A smooth extrapolation of the heat capacity was made from 1800° to 3000°K. The heat content of AlN(c) was recently determined from 300 to 1200°K by R. Mezaki, "Heat Contents of Inorganic Substances at High Temperatures," M. S. Thesis, University of Wisconsin (1961). The enthalpies reported by Mezaki are about 1% greater than those of Mah et al.

Decomposition Data.

P. O. Schissel and W. S. Williams, *Bull. Am. Phys. Soc. II*, **4**, 139 (1959) studied the vaporization of AlN with the mass spectrometer and detected only the gaseous species Al and N_2 . The temperature at which the ΔH_f^0 of AlN(c) and Al(g) were equal, 2768.9°K, was taken as the temperature of decomposition.

(Ideal Gas)

GFW = 40.9882

ALUMINUM NITRIDE (AlN)

(IDEAL GAS)

OPW = 40.9882

Ground State Configuration $[1\sum^+]$ $\Delta H_f^\circ = 104 \pm 20$ kcal/mol
 $S_{298.15}^\circ = [50.573]$ gibbs/mol $\Delta H_f^\circ = 104 \pm 20$ kcal/mol
 $S_{298.15}^\circ = 104 \pm 20$ kcal/mol

Electronic Levels and Quantum Weights

$$\frac{e_j, \text{ cm}^{-1}}{0} \frac{g_j}{1}$$

$w_e = [930] \text{ cm}^{-1}$ $w_e x_e = [6.9] \text{ cm}^{-1}$ $\sigma = 1$
 $B_e = [0.6748] \text{ cm}^{-1}$ $\alpha_e = [0.0064] \text{ cm}^{-1}$ $r_e = [1.65] \text{ \AA}$

Heat of Formation.

The heat of formation is calculated from the estimated w_e and $w_e x_e$, using $D_0 = w_e^2/\omega_e x_e$, as 89 kcal/mol.
J. L. Margrave and P. Staphitanonda, J. Phys. Chem. 59, 1231 (1955) estimated values of the bond length as $1.23 - 1.65 \text{ \AA}$ and calculated from an ionic model D_0 values of $137 - 82$ kcal/mol. Using an estimated bond length of 1.65 \AA and a $D_0 = 87$ kcal/mol leads to $\Delta H_f^\circ = 104$ kcal/mol.

Heat Capacity and Entropy.

The bond length is estimated as 1.65 \AA from a comparison with the bond lengths of SO, PO, SiO, AlO, MgO, S₂, SIS, AlS, PN, SiN, and the sum of covalent radii. This bond length is then used with Guggenheimer's Relation [K. M. Guggenheimer, Proc. Phys. Soc. (London), 59, 456 (1946)] to calculate a value for ω_e . By analogy with SiN(g) it is taken to closely approach the multiple bonding case, which gives $\omega_e = 960 \text{ cm}^{-1}$. The anharmonicity correction x_e is calculated by assuming the product $x_e \mu^{1/2}$ equal to that for AlO(g). The value of α_e is calculated using the relation:

$$\alpha_e = 6(w_e x_e B_e)^{1/2} / w_e$$

Dec. 31, 1960; Mar. 31, 1964; Mar. 31, 1967

Sodium Aluminate (NaAlO₂)

(Crystal) Mol. Wt. = 81.971

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.000	INFINITE	INFINITE	-	2.864	-268.974	-	INFINITE
100	4.784	3.589	20.155	-	2.597	-265.864	-265.338	570.869
200	13.011	10.983	18.323	-	1.548	-270.526	-250.537	284.687
298	17.610	16.826	16.826	0.000	0.000	-270.840	-255.561	187.322
300	17.660	16.935	16.826	0.033	-	-270.843	-255.466	186.098
400	16.936	22.347	17.549	1.919	-	-271.659	-250.805	107.032
500	21.608	20.868	18.982	3.993	-	-271.654	-244.937	107.032
600	22.531	30.973	20.654	6.191	-	-271.568	-239.591	87.267
700	23.592	34.520	22.386	8.494	-	-271.436	-234.272	73.140
800	23.602	38.085	24.136	11.159	-	-270.980	-228.999	62.557
900	24.026	40.889	25.844	13.560	-	-270.850	-223.718	54.378
1000	24.050	43.442	27.478	15.904	-	-273.215	-218.357	47.117
1100	24.874	45.792	29.037	18.430	-	-272.984	-212.873	42.592
1200	25.598	47.975	30.526	20.939	-	-295.963	-206.462	37.691
1300	25.722	50.017	31.947	23.400	-	-295.476	-199.566	33.548
1400	26.146	51.938	33.307	26.083	-	-284.934	-192.269	30.004
1500	26.370	53.757	34.610	28.719	-	-284.566	-184.891	26.937
1600	26.994	55.485	35.862	31.397	-	-293.762	-177.611	24.259
1700	27.426	57.135	37.065	34.119	-	-293.118	-170.371	21.902
1800	27.842	58.714	38.224	36.882	-	-282.441	-163.170	19.611
1900	28.241	60.230	39.344	39.590	-	-281.723	-156.002	17.476
2000	28.624	61.688	40.424	42.230	-	-280.983	-148.884	15.409
2100	28.990	63.094	41.470	45.411	-	-290.204	-141.799	13.4757
2200	29.340	64.451	42.484	48.377	-	-289.398	-134.750	13.386
2300	29.604	65.761	43.447	51.275	-	-288.564	-127.741	12.138
2400	29.853	67.026	44.323	54.248	-	-287.712	-120.764	10.997
2500	30.084	68.249	45.152	57.245	-	-286.842	-113.828	9.950
2600	30.300	69.434	46.255	60.264	-	-285.956	-106.924	8.987
2700	30.499	70.581	47.135	63.304	-	-285.056	-100.037	8.099
2800	30.683	71.693	47.992	66.363	-	-354.698	-91.569	7.147
2900	30.849	72.763	48.828	69.444	-	-354.698	-83.147	6.147
3000	31.000	73.822	49.644	72.533	-	-354.698	-74.680	5.107

SODIUM ALUMINATE (NaAlO₂)

(CRYSTAL)

MOL. WT. = 81.971



$$\Delta H_f^0 = -268.97 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^{298.15} = -270.84 \pm 0.17 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 0.310 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = \text{Unknown}$$

$$S_f^{298.15} = 16.826 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_c = 740^\circ\text{K.}$$

$$T_m = \text{above } 1923^\circ\text{K.}$$

Heat of Formation.

$\Delta H_f^{298.15}$ was reported by J. P. Coughlin, J. Am. Chem. Soc. **79**, 2397 (1957). The value was calculated from the measured heat of solution of NaAlO₂(c) at 303.15°K. in 4.36M hydrochloric acid solution.

Heat Capacity and Entropy.

The low temperature heat capacities, below 350°K., were measured by E. F. Westrum, University of Michigan, Ann Arbor, Michigan, private communication, May 19, 1960. Heat capacities above 350°K., 399.4 — 1698.6°K., were measured by A. U. Christensen, K. C. Conway, and K. K. Kelley, U. S. Bur. Mines Rept. Invest. 5565 (1960).

These two sets of C_p data were plotted graphically and joined smoothly at 350°K. Low temperature heat capacities $S_f^{298.15}$ were also determined by E. G. King, J. Am. Chem. Soc. **77**, 3189 (1955), which agree very well with those reported by E. F. Westrum, loc. cit. $S_f^{298.15}$ was reported by E. F. Westrum, loc. cit., using $S_f^{298.15}(\text{extrap.}) = 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_c and ΔH_c^0 were obtained from A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit.

Temperature of Melting.

T_m was taken from K. Kammermeyer and A. B. Peck, J. Am. Ceram. Soc. **16**, 363 (1933).

ALUMINIUM MONOXIDE (A10)

(IDEAL GAS)

GFW = 42.9809

Aluminum Monoxide (A10)

(Ideal Gas) GFW = 42.9809

Symmetry Number = 1

 $\Delta H_f^\circ = 20 \pm 4 \text{ kcal/mol}$ $S_{298.15}^\circ = 52.169 \pm 0.01 \text{ gibbs/mol}$ $\Delta H_f^\circ = 20 \pm 4 \text{ kcal/mol}$

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	6.000	0.000	INFINITE	2.100	20.031	20.031	INFINITE
100	6.937	44.459	56.513	1.405	20.273	18.462	39.456
200	7.082	44.462	52.169	1.000	20.000	18.462	39.456
298	7.391	52.169	52.169	0.000	20.000	13.769	10.093
300	7.388	52.214	52.169	0.014	19.996	13.730	10.003
400	7.765	54.392	52.463	0.772	19.800	11.672	6.377
500	8.066	56.159	53.031	1.564	19.596	9.863	4.224
600	8.290	57.651	53.690	2.362	19.377	7.697	2.804
700	8.459	58.942	54.331	3.220	19.141	5.769	1.801
800	8.601	60.081	54.949	4.073	18.878	4.073	1.059
900	8.738	61.102	55.612	4.940	18.576	2.618	0.490
1000	8.862	62.030	56.208	5.821	18.241	1.360	0.093
1100	9.044	62.884	56.777	6.717	17.884	0.226	0.026
1200	9.224	63.678	57.319	7.631	17.509	0.235	0.040
1300	9.420	64.424	57.837	8.563	17.114	0.260	0.050
1400	9.628	65.130	58.333	9.515	16.695	0.288	0.060
1500	9.840	65.801	58.809	10.488	16.254	0.317	0.070
1600	10.051	66.443	59.266	11.483	15.791	0.346	0.080
1700	10.254	67.058	59.707	12.498	15.307	0.375	0.090
1800	10.445	67.650	60.132	13.533	14.801	0.404	0.100
1900	10.619	68.220	60.542	14.587	14.274	0.433	0.110
2000	10.774	68.768	60.940	15.656	13.727	0.462	0.120
2100	10.909	69.297	61.325	16.741	13.160	0.491	0.130
2200	11.022	69.807	61.699	17.837	12.574	0.520	0.140
2300	11.116	70.299	62.063	18.944	11.970	0.549	0.150
2400	11.190	70.774	62.416	20.060	11.348	0.578	0.160
2500	11.246	71.232	62.759	21.182	10.707	0.607	0.170
2600	11.286	71.674	63.094	22.309	10.049	0.636	0.180
2700	11.311	72.101	63.420	23.439	9.376	0.665	0.190
2800	11.323	72.512	63.737	24.570	8.690	0.694	0.200
2900	11.325	72.910	64.046	25.703	7.990	0.723	0.210
3000	11.317	73.293	64.348	26.835	7.276	0.752	0.220
3100	11.302	73.664	64.630	27.965	6.552	0.781	0.230
3200	11.281	74.023	64.930	29.095	5.819	0.810	0.240
3300	11.255	74.370	65.211	30.222	5.076	0.839	0.250
3400	11.225	74.705	65.486	31.346	4.324	0.868	0.260
3500	11.193	75.030	65.754	32.467	3.561	0.897	0.270
3600	11.158	75.345	66.016	33.585	2.786	0.926	0.280
3700	11.123	75.650	66.272	34.699	1.999	0.955	0.290
3800	11.086	75.946	66.523	35.809	1.200	0.984	0.300
3900	11.050	76.234	66.768	36.916	0.390	1.013	0.310
4000	11.014	76.513	67.008	38.019	-0.420	1.042	0.320
4100	10.979	76.785	67.243	39.115	-1.220	1.071	0.330
4200	10.945	77.049	67.474	40.215	-2.000	1.100	0.340
4300	10.912	77.306	67.699	41.308	-2.770	1.129	0.350
4400	10.880	77.556	67.921	42.398	-3.540	1.158	0.360
4500	10.850	77.801	68.137	43.484	-4.300	1.187	0.370
4600	10.822	78.039	68.350	44.568	-5.050	1.216	0.380
4700	10.795	78.271	68.559	45.648	-5.790	1.245	0.390
4800	10.770	78.498	68.763	46.727	-6.520	1.274	0.400
4900	10.746	78.720	68.964	47.802	-7.250	1.303	0.410
5000	10.724	78.937	69.162	48.876	-7.980	1.332	0.420
5100	10.704	79.149	69.355	49.947	-8.710	1.361	0.430
5200	10.685	79.357	69.546	51.017	-9.440	1.390	0.440
5300	10.669	79.560	69.733	52.084	-10.170	1.419	0.450
5400	10.653	79.759	69.917	53.151	-10.900	1.448	0.460
5500	10.640	79.955	70.097	54.215	-11.630	1.477	0.470
5600	10.628	80.146	70.275	55.270	-12.360	1.506	0.480
5700	10.617	80.334	70.450	56.321	-13.090	1.535	0.490
5800	10.608	80.519	70.622	57.362	-13.820	1.564	0.500
5900	10.601	80.700	70.791	58.402	-14.550	1.593	0.510
6000	10.594	80.878	70.958	59.437	-15.280	1.622	0.520

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1962; Sept. 30, 1965; June 30, 1970

Electronic Levels and Molecular Constants

State	ϵ_i , cm ⁻¹	g_i	r_0 , Å	B_0 , cm ⁻¹	a_0 , cm ⁻¹	ω_e , cm ⁻¹	$\omega_e x_e$, cm ⁻¹
$X^2\Sigma^+$	0	2	1.6176	0.64136	0.0058	979.23	6.97
$A^2\Pi$	5282	2	1.7748	0.5328	[0.0050]	728.5	4.15
	5411	2					
E_2^+	20635.2	2	1.6668	0.60408	0.00447	870.05	3.52
$C^2\Pi$	33082.5	4	[1.730]	[0.5605]		855.4	6.0
D_2^+	40187.2	2	1.7304	0.5605	[0.0056]	819.6	5.8
E_2^-	45260	4	1.849	0.4910	[0.0050]	[520]	[2.5]

Heat of Formation

The vibrational quanta of the ground and first excited states can be linearly extrapolated to obtain approximate dissociation energies of 98.3 and 106.5 kcal/mol. Both these states can correlate with ground state atoms and we assume, with a high degree of confidence, that these are the products of the dissociation. Hildenbrand (1) has shown that improved values from ground state extrapolations can be obtained by correcting the extrapolation for the ionicity of the state. The corrected value is obtained from $D_0 = D(\text{linear extrapolation})[0.365(r_0/r_e)^{4.0448}]$ eV where $r_e = 14.4/(\text{IP-EA})$ and IP-EA is the difference, in eV, between the ionization potential of the electropositive element and EA is the electron affinity of the more electronegative element. This approach yields a corrected value of 114.7 kcal for the ground state dissociation energy. The second and higher excited states all have extrapolations of the same magnitude as the ground state but involve excited products, thus, they do not add materially to the knowledge of the dissociation energy.

Drowart et al. (2) have determined the partial pressures of Al(g), O(g) and AlO(g) over Al_2O_3 , by mass-spectrometry in the temperature range 2000-2500°K. A similar experiment has also been reported by Efimenko (3) over a mixture of Be and Al_2O_3 . An analysis of this data for the reaction $\text{AlO(g)} \rightarrow \text{Al(g)} + \text{O(g)}$ by the 2nd and 3rd law methods is given below.

Reference	Points	Range °K	ΔH_{298}° , kcal/mol	2nd law	3rd law	Drift	$\Delta H_{298}^\circ(\text{AlO}, \text{g})$, kcal/mol
2. Mo cell	15	2036-2468	114.7 ± 7.0	116.0 ± 2.6	0.4 ± 3.1	21.6	
2. W cell	15*	2188-2614	122.1 ± 5.0	114.7 ± 1.9	-3.2 ± 2.2	22.9	
3. W cell	10*	1511-1743	68.4 ± 7.3	75.2 ± 1.9	3.7 ± 4.4	62.4	
*2 or 3 points rejected due to failure of a statistical test.							

In addition Tyte (4) has obtained a value for the onset of continuous absorption, which he interprets as the dissociation of AlO, of 3630 cm⁻¹ or 104.73 kcal. However, McDonald and Innes (5) conclude that Tyte was seeing continuous absorption from the $A^2\Pi$ state, since bands of two systems terminating in this state were seen by Tyte. On this basis they conclude that the best value of the dissociation energy should be 4192 cm⁻¹ or 119.83 kcal/mol, which corresponds to $\Delta H_{298}^\circ(\text{AlO}, \text{g}) = 16.57$ kcal/mol. Many other values have been reported for $\Delta H_{298}^\circ(\text{AlO}, \text{g})$, including 9.3 kcal/mol (6), -0.7 kcal/mol (7), 48.7 kcal/mol (8) and 20.3 ± 3 kcal/mol (9).

The situation is not clearly resolved, and so a median value of $D_0^\circ = 116.3 \pm 4$ kcal is adopted which corresponds to $\Delta H_{298}^\circ(\text{AlO}, \text{g}) = 20 \pm 4$ kcal/mol.

Heat Capacity and Entropy

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states. The ground and B state constants were obtained from Lagerqvist et al. (10), the A and E state constants from McDonald and Innes (5), the C state constants from McDonald et al. (11), and the D state constants are from Krishnamachari et al. (12). Estimated quantities are obtained by comparison with other states and from combination of references (5) and (13) for ω_e of the E state. Several other sets of data exist but are no longer considered significant to the analysis. References to them may be found in the adopted studies.

References

1. D. L. Hildenbrand, OPTA Publication No. 146 Vol. 1, p. 63 (1967).
2. J. Drowart, G. Delaunay, R. F. Bur, Rept. 8905, 1 July 1968, AFOSR 68-1924.
3. J. Efimenko, Natl. Bur. Std. Rept. 8905, 1 July 1968, AFOSR 68-1924.
4. D. C. Tyte, Proc. Phys. Soc. (London) 92, 1134 (1967).
5. J. K. McDonald and K. K. Innes, J. Mol. Spectry, 32, 501 (1968).
6. L. Brewer and A. W. Seary, J. Amer. Chem. Soc. 73, 5308 (1951).
7. F. P. Dalt, Bull. Acad. Sci. USSR, Div. Chem. Sci., Ser. Phys. 22, 673 (1958).
8. R. P. Burns, J. Chem. Phys. 48, 3307 (1968).
9. A. Lagerqvist, N. E. L. Nilsson and R. F. Barrow, Arkiv Fysik, 12, 543 (1957).
10. J. K. McDonald, K. K. Innes, W. Goodlett and T. W. Tolbert, J. Mol. Spectry, 32, 511 (1968).
11. S. N. G. Krishnamachari, N. A. Narasimham, and M. Singh, Can. J. Phys. 44, 2613 (1966).
12. H. Singh and N. A. Narasimham, Proc. Phys. Soc. (At. Mol. Phys.) 2, (1969).

ALUMINUM MONOXIDE UNIPosITIVE ION (AlO⁺) (IDEAL GAS) GFW = 42.9804

ΔHf₀^o = 239 ± 15 kcal/mol

ΔHf_{298.15}^o = 239 ± 15 kcal/mol

Ground State Configuration [1s²]

S_{298.15}^o = [51.1 ± 3] gibbs/mol

Electronic Levels and Degeneracies

ϵ_i , cm ⁻¹	g_i
0	[1]
[2300]	[6]
[2300]	[3]
[3600]	[2]
[20000]	[1]

$\omega_e = [850]$ cm⁻¹
 $B_e = [0.581]$ cm⁻¹
 $\alpha_e \omega_e = [6.0]$ cm⁻¹
 $\alpha_e B_e = [0.0053]$ cm⁻¹
 $\sigma = 1$
 $r_e = [1.7]$ Å

Heat of Formation

The ionization potential of AlO has been reported as 9.5 ± 0.5 eV (219 kcal) by J. Drowart, G. DeMaria, R. P. Burns, and M. G. Inghram, J. Chem. Phys. 32, 1366 (1960), and by G. DeMaria, J. Drowart and M. G. Inghram, J. Chem. Phys. 30, 318 (1959). Using this value in conjunction with ΔHf₀^o(AlO, g) = 20 ± 4 kcal/mol, we obtain ΔHf₂₉₈^o(AlO⁺) = 239 ± 15 kcal/mol.

Heat Capacity and Entropy

AlO⁺ is isoelectronic with MgO and we estimated the electronic ground state and excited states by comparison with those for MgO as reported by W. G. Richards, G. Verhaegen and C. H. Moser, J. Chem. Phys. 45, 3226 (1966). The bond length is estimated to be longer than that in AlO since the dissociation energy of AlO⁺ is less than that of AlO. The vibrational frequency and anharmonicity are estimated between those for MgO and AlO and the rotational constant, α_e, is derived from the above quantities assuming a Morse potential function. The enthalpy at 0°K is -2.118 kcal/mol.

Aluminum Monoxide Unipositive Ion (AlO⁺)

GFW = 42.9804

(Ideal Gas)

T, °K	Cp ^o	S ^o -(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔHf ^o	ΔGf ^o	Log Kp
0						
100						
200						
298	7.591	51.064	0.000	239.000	231.612	-169.776
300	7.601	51.064	0.018	239.006	231.565	-168.495
400	8.271	51.330	1.605	239.339	229.037	-125.140
500	9.275	55.330	5.970	239.714	226.419	-98.967
600	10.523	57.129	12.669	240.164	223.716	-81.489
700	11.596	58.494	20.783	240.706	220.976	-68.579
800	12.458	59.480	30.000	241.400	218.200	-58.241
900	13.088	61.083	40.998	242.228	215.432	-52.241
1000	13.441	63.365	55.767	243.187	212.708	-46.400
1100	12.984	64.612	69.006	240.601	209.510	-41.626
1200	12.659	65.730	80.891	241.200	206.956	-37.637
1300	12.425	66.761	91.461	241.811	204.956	-34.254
1400	12.258	67.733	100.859	242.428	203.462	-31.348
1500	12.145	68.648	109.222	242.763	202.413	-28.824
1600	12.071	69.519	116.690	243.216	199.822	-26.611
1700	12.029	70.347	123.373	243.635	197.785	-24.556
1800	12.009	71.130	129.309	244.016	196.262	-22.654
1900	12.006	71.880	134.556	244.363	195.242	-20.894
2000	12.014	72.603	139.161	244.739	194.739	-19.347
2100	12.033	72.132	142.424	245.068	194.420	-18.072
2200	12.063	72.611	145.309	245.350	194.266	-17.012
2300	12.104	73.039	147.784	245.587	194.262	-16.124
2400	12.154	73.494	149.899	245.686	194.482	-15.476
2500	12.217	73.903	151.624	245.674	194.907	-15.022
2600	12.293	74.293	153.008	245.568	195.629	-14.752
2700	12.377	74.666	154.066	245.380	196.625	-13.754
2800	12.466	75.024	154.831	245.135	197.833	-12.966
2900	12.557	75.368	155.250	244.866	199.242	-12.384
3000	12.649	75.698	155.369	244.508	200.854	-11.956
3100	12.741	76.017	155.229	244.088	202.673	-11.680
3200	12.832	76.325	154.860	243.635	204.700	-11.540
3300	12.921	76.621	154.196	243.161	206.933	-11.540
3400	13.008	76.904	153.264	242.683	209.374	-11.672
3500	13.093	77.170	152.088	242.208	212.022	-11.940
3600	13.176	77.421	150.674	241.739	214.873	-12.352
3700	13.257	77.656	149.039	241.268	217.922	-12.912
3800	13.336	77.875	147.196	240.796	221.167	-13.622
3900	13.412	78.079	145.166	240.324	224.704	-14.482
4000	13.486	78.268	142.959	239.852	228.529	-15.502
4100	13.558	78.441	140.596	239.380	232.649	-16.692
4200	13.628	78.599	138.096	238.908	237.072	-18.062
4300	13.696	78.743	135.474	238.436	241.807	-19.622
4400	13.761	78.871	132.746	237.964	246.854	-21.382
4500	13.824	78.984	129.924	237.492	252.222	-23.362
4600	13.885	79.092	126.924	237.020	257.929	-25.592
4700	13.944	79.186	123.766	236.548	263.974	-28.092
4800	14.001	79.275	120.474	236.076	270.367	-30.892
4900	14.056	79.359	117.066	235.604	277.112	-33.992
5000	14.109	79.438	113.566	235.132	284.222	-37.492
5100	14.161	79.512	110.000	234.660	291.707	-41.392
5200	14.212	79.581	106.388	234.188	299.577	-45.742
5300	14.262	79.646	102.750	233.716	307.842	-50.592
5400	14.311	79.707	99.000	233.244	316.512	-55.992
5500	14.359	79.764	95.150	232.772	325.597	-61.992
5600	14.406	79.817	91.210	232.300	335.107	-68.592
5700	14.452	79.866	87.180	231.828	345.052	-75.792
5800	14.497	79.911	83.066	231.356	355.442	-83.592
5900	14.541	79.952	78.874	230.884	366.287	-92.092
6000	14.584	79.989	74.600	230.412	377.597	-101.392

Aluminum Dioxide (AlO₂)

(Ideal Gas)

GFW = 58.9803

ALUMINUM DIOXIDE (AlO₂)

(IDEAL GAS)

GFW = 58.9803

Point Group [D_{∞h}]S_{298.15} = [58.7 ± 4] gibbs/mol $\Delta H_f^\circ = [-44 \pm 20]$ kcal/mol $\Delta H_f^\circ_{298.15} = [-44 \pm 20]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[20000]	[4]
[25000]	[2]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	
[680] (1)	
[295] (2)	
[1005] (1)	

 $\sigma = 2$

Bond Distance: Al-O = [1.86] Å

Bond Angle: O-Al-O = [180°]

Rotational Constant: B₀ = [0.1912] cm⁻¹

Heat of Formation

The OH bond strength in H₂O is 119 kcal and in HOBO it is 118 kcal. Thus, it appears very reasonable to assume 118 kcal for the value in HOAlO. This assumption leads to $\Delta H_f^\circ(\text{AlO}_2, g) = -44 \pm 20$ kcal/mol, using the JANAF $\Delta H_f^\circ(\text{HOAlO}, g) = -110$ kcal/mol. This value is consistent with the independently estimated $\Delta H_f^\circ_{298}(\text{AlO}_2, g) = -130 \pm 15$ kcal/mol, since it yields an electron affinity for AlO₂ of 46 kcal in good agreement with the value 98 kcal for BO₂.

Heat Capacity and Entropy

The electronic ground and excited states and molecular configuration are estimated to be similar to those for BO₂. The AlO bond length is assumed to be equal to that in Al₂O. The vibrational frequencies are estimated from a valence force field treatment using k_1 from BO₂ modified by the ratio $k(\text{AlO})/k(\text{BO})$ and using the same ratio of bending to stretch force constants as in BO₂.

The adopted molecular configuration and electronic ground state are in accord with the predictions of A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	8.000	INFINITE	-	2.707	43.538	43.538	INFINITE
100	8.023	48.101	57.973	1.987	44.124	46.433	86.433
200	10.160	54.373	59.723	1.070	43.639	44.556	48.668
298	11.561	58.707	59.707	0.000	44.000	44.875	32.894
300	11.583	58.779	59.708	0.021	44.003	44.861	32.696
400	12.550	62.115	61.115	0.999	44.176	45.141	22.692
500	13.131	63.127	60.066	2.050	44.176	45.141	19.649
600	13.619	67.572	61.135	3.862	44.248	45.452	16.629
700	13.912	69.695	62.210	5.240	44.333	45.879	14.324
800	14.119	71.567	63.265	6.642	44.446	46.093	12.592
900	14.269	73.239	64.282	8.042	44.561	46.283	11.165
1000	14.381	74.746	65.254	9.494	47.330	46.283	10.115
1100	14.466	76.123	66.181	10.937	47.485	46.172	9.174
1200	14.532	77.385	67.062	12.367	47.462	46.046	8.366
1300	14.585	78.550	67.902	13.683	47.601	45.906	7.618
1400	14.627	79.633	68.694	14.882	47.601	45.746	6.932
1500	14.661	80.643	69.464	16.068	47.6129	45.591	6.403
1600	14.690	81.590	70.193	18.236	48.597	45.416	6.204
1700	14.718	82.482	70.890	19.706	48.468	45.231	5.815
1800	14.734	83.323	71.557	21.176	48.483	45.034	5.468
1900	14.751	84.116	72.196	22.452	48.486	44.834	5.157
2000	14.766	84.877	72.813	24.128	49.006	44.614	4.875
2100	14.778	85.598	73.405	25.605	49.193	44.392	4.620
2200	14.790	86.286	73.975	27.084	49.365	44.159	4.387
2300	14.800	86.943	74.528	28.563	49.580	43.915	4.173
2400	14.809	87.573	75.065	30.042	49.825	43.666	3.976
2500	14.817	88.178	75.588	31.525	49.686	43.409	3.795
2600	14.825	88.759	76.064	33.007	50.195	43.139	3.626
2700	14.833	89.319	76.545	34.490	50.409	42.865	3.470
2800	14.840	89.859	77.011	35.974	120.037	41.751	3.259
2900	14.847	90.383	77.466	37.456	119.963	41.526	3.066
3000	14.853	90.883	77.902	38.943	119.963	41.261	2.838
3100	14.863	91.370	78.329	40.429	119.931	40.967	2.582
3200	14.871	91.842	78.743	41.916	119.903	40.637	2.306
3300	14.879	92.300	79.147	43.403	119.879	40.275	1.980
3400	14.886	92.744	79.541	44.889	119.859	39.886	1.637
3500	14.898	93.176	79.924	46.381	119.841	39.466	1.307
3600	14.908	93.596	80.298	47.871	119.827	39.015	1.179
3700	14.919	94.004	80.663	49.363	119.815	38.542	1.082
3800	14.930	94.402	81.019	50.855	119.807	38.048	1.000
3900	14.943	94.790	81.368	52.349	119.800	37.534	0.929
4000	14.956	95.169	81.700	53.844	119.796	37.004	0.865
4100	14.970	95.538	82.041	55.340	119.795	36.461	0.807
4200	14.984	95.899	82.366	56.837	119.795	35.900	0.752
4300	15.000	96.252	82.685	58.337	119.797	35.324	0.700
4400	15.016	96.597	82.986	59.837	119.802	34.737	0.650
4500	15.033	96.935	83.280	61.340	119.806	34.141	0.600
4600	15.050	97.265	83.603	62.844	119.815	33.537	0.550
4700	15.068	97.589	83.898	64.350	119.826	32.924	0.500
4800	15.087	97.907	84.166	65.858	119.837	32.303	0.450
4900	15.107	98.216	84.469	67.367	119.850	31.674	0.400
5000	15.127	98.523	84.747	68.879	119.865	31.039	0.350
5100	15.147	98.823	85.020	70.393	119.882	30.399	0.300
5200	15.168	99.117	85.289	71.908	119.902	29.754	0.250
5300	15.189	99.406	85.552	73.426	119.923	29.104	0.200
5400	15.211	99.691	85.812	74.946	119.946	28.450	0.150
5500	15.233	99.970	86.066	76.468	119.972	27.791	0.100
5600	15.255	100.245	86.317	77.993	120.001	27.127	0.050
5700	15.278	100.515	86.564	79.520	120.031	26.460	0.000
5800	15.300	100.781	86.807	81.048	120.067	25.791	-0.050
5900	15.323	101.042	87.044	82.580	120.104	25.117	-0.100
6000	15.346	101.300	87.281	84.113	120.146	24.440	-0.150

June 30, 1968; Dec. 31, 1968

GFW = 58.9809

(IDEAL GAS)

ALUMINUM DIOXIDE UNINEGATIVE ION (AlO₂⁻)Aluminum Dioxide Uninegative Ion (AlO₂⁻)

(Ideal Gas) GFW = 58.9809

T, °K	C _p ^o	S ^o - (G ^o - H ^o)/T	H ^o - H ^o ₂₉₈	ΔH ^o kcal/mol	ΔG ^o	Log K _p
0						
100						
200						
298	11.081	55.509	+000	-145.000	-143.434	105.140
300	11.102	55.578	+021	-145.012	-143.424	104.485
400	12.066	58.910	1.481	-145.659	-142.766	78.020
500	12.761	61.682	2.425	-146.274	-142.009	62.072
600	13.255	64.055	3.727	-146.883	-141.099	51.395
700	13.609	66.126	5.071	-147.498	-140.085	43.736
800	13.866	67.961	6.445	-148.136	-138.984	37.969
900	14.056	69.606	7.842	-148.812	-137.800	33.462
1000	14.201	71.094	9.255	-152.056	-136.354	29.600
1100	14.312	72.453	10.681	-152.725	-134.753	26.773
1200	14.400	73.702	12.117	-153.393	-133.091	24.231
1300	14.470	74.858	13.560	-154.061	-131.370	22.065
1400	14.526	75.932	15.010	-154.731	-129.600	20.231
1500	14.572	76.936	16.465	-155.403	-127.782	18.616
1600	14.611	77.878	17.928	-156.077	-125.918	17.200
1700	14.644	78.765	19.387	-156.752	-124.013	15.943
1800	14.670	79.602	20.853	-157.429	-122.065	14.821
1900	14.693	80.396	22.321	-158.112	-120.084	13.813
2000	14.713	81.150	23.791	-158.798	-118.066	12.902
2100	14.731	81.869	25.264	-159.486	-116.012	12.073
2200	14.746	82.554	26.737	-160.181	-113.926	11.316
2300	14.759	83.210	28.213	-160.875	-111.805	10.624
2400	14.770	83.839	29.689	-161.577	-109.656	9.986
2500	14.781	84.442	31.167	-162.283	-107.482	9.396
2600	14.790	85.022	32.645	-162.993	-105.274	8.849
2700	14.798	85.580	34.125	-163.707	-103.043	8.341
2800	14.805	86.118	35.603	-164.425	-100.782	7.862
2900	14.812	86.638	37.086	-165.146	-98.502	7.412
3000	14.818	87.140	38.567	-165.867	-96.212	6.982
3100	14.823	87.626	40.049	-166.589	-93.912	6.572
3200	14.828	88.097	41.532	-167.311	-91.602	6.182
3300	14.833	88.553	43.015	-168.033	-89.282	5.812
3400	14.837	88.996	44.498	-168.755	-86.952	5.462
3500	14.840	89.426	45.982	-169.477	-84.622	5.132
3600	14.846	89.844	47.465	-170.199	-82.292	4.822
3700	14.847	90.251	48.951	-170.921	-79.962	4.532
3800	14.850	90.647	50.436	-171.643	-77.632	4.262
3900	14.853	91.033	51.921	-172.365	-75.302	4.012
4000	14.855	91.409	53.406	-173.087	-72.972	3.772
4100	14.857	91.776	54.892	-173.809	-70.642	3.542
4200	14.860	92.134	56.378	-174.531	-68.312	3.332
4300	14.862	92.483	57.864	-175.253	-65.982	3.142
4400	14.864	92.825	59.350	-175.975	-63.652	2.972
4500	14.865	93.159	60.837	-176.697	-61.322	2.822
4600	14.867	93.486	62.323	-177.419	-58.992	2.682
4700	14.868	93.806	63.810	-178.141	-56.662	2.552
4800	14.870	94.119	65.297	-178.863	-54.332	2.432
4900	14.871	94.425	66.784	-179.585	-52.002	2.322
5000	14.873	94.726	68.271	-180.307	-49.672	2.222
5100	14.875	95.020	69.758	-181.029	-47.342	2.132
5200	14.876	95.309	71.245	-181.751	-45.012	2.052
5300	14.876	95.592	72.733	-182.473	-42.682	1.982
5400	14.877	95.870	74.221	-183.195	-40.352	1.922
5500	14.878	96.143	75.709	-183.917	-38.022	1.872
5600	14.879	96.412	77.197	-184.639	-35.692	1.832
5700	14.880	96.675	78.685	-185.361	-33.362	1.802
5800	14.881	96.934	80.173	-186.083	-31.032	1.772
5900	14.881	97.188	81.661	-186.805	-28.702	1.752
6000	14.882	97.436	83.149	-187.527	-26.372	1.732

June 30, 1968; Dec. 31, 1968

Aluminum Dioxide Uninegative Ion (AlO₂⁻)

(Ideal Gas) GFW = 58.9809

Point Group [D_{3h}]S_{298.15}^o = [55.5 ± 2] gibbs/mol

Ground State Quantum Weight = [1]

GFW = 58.9809

ΔH_f^o = [-144.5 ± 15] kcal/molΔH_f^o_{298.15} = [-145 ± 15] kcal/mol

(IDEAL GAS)

ALUMINUM DIOXIDE UNINEGATIVE ION (AlO₂⁻)Point Group [D_{3h}]S_{298.15}^o = [55.5 ± 2] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$$\frac{\Delta G}{\Delta T} = \frac{\Delta H}{T^2} - \frac{\Delta S}{T}$$

[800] (1)
[320] (2)
[1200] (1)

Bond Distance: Al-O = [1.66] Å

Bond Angle: O-Al-O = [180°]

Rotational Constant: B₀ = [0.1912] cm⁻¹

σ = 2

Heat of Formation

The heat of formation of AlO₂⁻ is estimated from the following considerations. The heats of the following reactions are calculated from the tables:

BO₂ → B⁻ + 2O ΔH = 411 kcalCO₂ → C + 2O ΔH = 384 kcalBO₂⁻ → B + O + O⁻ ΔH = 382 kcal

BOF + B + O + F ΔH = 355 kcal

It is apparent that the heat of dissociation of BO₂⁻ is closely predicted by use of the corresponding isoelectronic decomposition. Thus using

SiO₂ + Si + 2Owe predict AlO₂⁻ → Al⁻ + 2O ΔH = 299

and using AlOF → Al + O + F ΔH = 297

we predict AlO₂⁻ → Al + O + O⁻ ΔH = 320

From these two reactions we estimate ΔHf(AlO₂⁻, g) = -158 and -135 kcal/mol and we adopt the value -145 ± 15 kcal/mol. From the value adopted for AlO₂(g) we obtain an electron affinity of 4.38 eV (101 kcal) which is comparable to that for BO₂(g).

Heat Capacity and Entropy

The configuration of the molecule is assumed to be linear using the correlations of Walsh, (1) for 16 electron XY₂ molecules; the ground state is assumed to be ¹Σ_g from the same correlation diagrams. The bond length is taken to be that in Al₂O₃ and the vibrational frequencies are estimated between those for AlO₂ and SiO₂.

The enthalpy at 0°K is -2.630 kcal/mol.

Reference

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	6.000	∞	∞	2.172	47.975	47.975	INFINITE
100	6.981	47.055	1.476	48.401	44.157	44.157	- 96.500
200	7.449	55.010	55.804	48.283	39.920	39.920	- 43.620
298	7.982	55.090	55.090	48.000	35.868	35.868	- 26.591
300	7.991	55.139	55.090	47.994	35.793	35.793	- 26.074
400	8.334	57.489	55.408	47.115	31.768	31.768	- 17.373
500	8.542	59.373	56.019	46.395	28.052	28.052	- 12.261
600	8.674	60.943	56.713	45.743	24.446	24.446	- 8.904
700	8.727	62.181	57.099	45.142	21.021	21.021	- 6.116
800	8.763	63.069	57.359	44.590	17.820	17.820	- 4.450
900	8.784	63.655	57.534	44.085	14.812	14.812	- 3.499
1000	8.812	64.042	57.642	43.625	12.052	12.052	- 2.787
1100	8.842	64.293	57.698	43.204	9.527	9.527	- 2.226
1200	8.869	64.457	57.719	42.811	7.198	7.198	- 1.775
1300	8.890	64.535	57.725	42.441	5.045	5.045	- 1.404
1400	8.907	64.564	57.725	42.091	3.151	3.151	- 1.095
1500	8.927	64.580	57.725	41.755	1.505	1.505	- .761
1600	8.943	64.563	57.625	41.436	0.105	0.105	- .516
1700	8.957	64.511	57.481	41.134	- 2.774	- 2.774	- .340
1800	8.973	70.731	53.359	40.848	- 5.811	- 5.811	- .111
1900	9.006	71.221	63.759	40.576	- 8.458	- 8.458	.206
2000	9.099	71.687	64.144	40.321	- 10.821	- 10.821	.340
2100	9.112	72.131	64.514	40.086	- 12.921	- 12.921	.470
2200	9.135	72.496	64.833	40.000	- 14.761	- 14.761	.570
2300	9.147	73.350	65.544	40.000	- 16.349	- 16.349	.669
2400	9.158	73.724	65.864	40.000	- 17.733	- 17.733	.760
2500	9.169	74.083	66.173	40.000	- 18.951	- 18.951	.842
2600	9.180	74.763	66.733	40.000	- 20.021	- 20.021	.907
2700	9.190	75.086	67.044	40.000	- 20.951	- 20.951	.959
2800	9.201	75.086	67.044	40.000	- 21.733	- 21.733	.999
2900	9.211	75.398	67.317	40.000	- 22.442	- 22.442	1.033
3000	9.222	75.700	67.583	40.000	- 23.086	- 23.086	1.061
3100	9.232	76.278	68.093	40.000	- 23.669	- 23.669	1.084
3200	9.242	76.554	68.337	40.000	- 24.195	- 24.195	1.102
3300	9.252	76.822	68.576	40.000	- 24.669	- 24.669	1.116
3400	9.262	77.083	68.809	40.000	- 25.086	- 25.086	1.126
3500	9.272	77.583	69.258	40.000	- 25.458	- 25.458	1.133
3600	9.282	77.826	69.474	40.000	- 25.781	- 25.781	1.138
3700	9.292	78.062	69.686	40.000	- 26.058	- 26.058	1.141
3800	9.302	78.292	69.893	40.000	- 26.287	- 26.287	1.143
3900	9.312	78.517	70.098	40.000	- 26.466	- 26.466	1.144
4000	9.322	78.737	70.298	40.000	- 26.598	- 26.598	1.145
4100	9.332	78.951	70.488	40.000	- 26.686	- 26.686	1.146
4200	9.341	79.162	70.679	40.000	- 26.733	- 26.733	1.146
4300	9.351	79.368	70.866	40.000	- 26.747	- 26.747	1.146
4400	9.361	79.569	71.052	40.000	- 26.725	- 26.725	1.145
4500	9.371	79.769	71.238	40.000	- 26.666	- 26.666	1.144
4600	9.380	79.960	71.420	40.000	- 26.574	- 26.574	1.142
4700	9.389	80.150	71.597	40.000	- 26.451	- 26.451	1.139
4800	9.398	80.337	71.774	40.000	- 26.300	- 26.300	1.135
4900	9.407	80.523	71.951	40.000	- 26.125	- 26.125	1.130
5000	9.416	80.709	72.126	40.000	- 25.930	- 25.930	1.124
5100	9.425	80.894	72.300	40.000	- 25.717	- 25.717	1.117
5200	9.434	81.079	72.474	40.000	- 25.489	- 25.489	1.109
5300	9.443	81.264	72.648	40.000	- 25.247	- 25.247	1.100
5400	9.452	81.449	72.822	40.000	- 24.992	- 24.992	1.090
5500	9.461	81.634	73.000	40.000	- 24.725	- 24.725	1.080
5600	9.470	81.819	73.178	40.000	- 24.447	- 24.447	1.069
5700	9.479	82.004	73.356	40.000	- 24.158	- 24.158	1.058
5800	9.488	82.189	73.534	40.000	- 23.858	- 23.858	1.046
5900	9.497	82.374	73.712	40.000	- 23.547	- 23.547	1.034
6000	9.506	82.559	73.890	40.000	- 23.225	- 23.225	1.022
6100	9.515	82.744	74.068	40.000	- 22.892	- 22.892	1.009
6200	9.524	82.929	74.246	40.000	- 22.548	- 22.548	0.995
6300	9.533	83.114	74.424	40.000	- 22.194	- 22.194	0.980
6400	9.542	83.299	74.602	40.000	- 21.830	- 21.830	0.965
6500	9.551	83.484	74.780	40.000	- 21.457	- 21.457	0.949
6600	9.560	83.669	74.958	40.000	- 21.074	- 21.074	0.933
6700	9.569	83.854	75.136	40.000	- 20.681	- 20.681	0.916
6800	9.578	84.039	75.314	40.000	- 20.278	- 20.278	0.899
6900	9.587	84.224	75.492	40.000	- 19.865	- 19.865	0.881
7000	9.596	84.409	75.670	40.000	- 19.442	- 19.442	0.863
7100	9.605	84.594	75.848	40.000	- 19.009	- 19.009	0.844
7200	9.614	84.779	76.026	40.000	- 18.566	- 18.566	0.825
7300	9.623	84.964	76.204	40.000	- 18.113	- 18.113	0.805
7400	9.632	85.149	76.382	40.000	- 17.650	- 17.650	0.785
7500	9.641	85.334	76.560	40.000	- 17.177	- 17.177	0.764
7600	9.650	85.519	76.738	40.000	- 16.694	- 16.694	0.743
7700	9.659	85.704	76.916	40.000	- 16.201	- 16.201	0.721
7800	9.668	85.889	77.094	40.000	- 15.698	- 15.698	0.699
7900	9.677	86.074	77.272	40.000	- 15.185	- 15.185	0.676
8000	9.686	86.259	77.450	40.000	- 14.662	- 14.662	0.653
8100	9.695	86.444	77.628	40.000	- 14.129	- 14.129	0.629
8200	9.704	86.629	77.806	40.000	- 13.586	- 13.586	0.604
8300	9.713	86.814	77.984	40.000	- 13.033	- 13.033	0.578
8400	9.722	87.000	78.162	40.000	- 12.470	- 12.470	0.551
8500	9.731	87.185	78.340	40.000	- 11.897	- 11.897	0.523
8600	9.740	87.370	78.518	40.000	- 11.314	- 11.314	0.495
8700	9.749	87.555	78.696	40.000	- 10.721	- 10.721	0.466
8800	9.758	87.740	78.874	40.000	- 10.118	- 10.118	0.436
8900	9.767	87.925	79.052	40.000	- 9.505	- 9.505	0.405
9000	9.776	88.110	79.230	40.000	- 8.878	- 8.878	0.373
9100	9.785	88.295	79.408	40.000	- 8.237	- 8.237	0.340
9200	9.794	88.480	79.586	40.000	- 7.582	- 7.582	0.306
9300	9.803	88.665	79.764	40.000	- 6.913	- 6.913	0.271
9400	9.812	88.850	79.942	40.000	- 6.230	- 6.230	0.235
9500	9.821	89.035	80.120	40.000	- 5.533	- 5.533	0.198
9600	9.830	89.220	80.298	40.000	- 4.822	- 4.822	0.160
9700	9.839	89.405	80.476	40.000	- 4.100	- 4.100	0.121
9800	9.848	89.590	80.654	40.000	- 3.367	- 3.367	0.081
9900	9.857	89.775	80.832	40.000	- 2.622	- 2.622	0.040
10000	9.866	89.960	81.010	40.000	- 1.865	- 1.865	0.000

Dec. 31, 1960; Mar. 31, 1964

ALUMINUM SULFIDE (AIS) (IDEAL GAS) MOL. WT. = 59.046

Ground State Configuration \sum^+
 $S^0_{298.15} = 55.09 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^0_f = 48 \pm 20 \text{ kcal. mole}^{-1}$
 $\Delta F^0_{298.15} = 48 \pm 20 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weights

$$\frac{E_i}{k}, \text{ cm.}^{-1}$$

$$\sigma^* = 1$$

$$\omega_e x_e = 3.33 \text{ cm.}^{-1}$$

$$r_e = 2.05 \text{ \AA}$$

$$\alpha_e = 0.0018 \text{ cm.}^{-1}$$

$$B_e = 0.2799 \text{ cm.}^{-1}$$

Heat of Formation.

The dissociation energy of 4.1 e.v. was calculated by adding 17% to the dissociation energy obtained from a linear extrapolation of the vibrational levels, 3.5 e.v. This was done by analogy with the molecule $\text{AlO}(\text{g})$ whose observed D_0 is 17% larger than the linear extrapolation. The adopted value of 4.1 e.v. corresponds to a heat of formation of 48 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational and rotational constants were reported by C. N. McKimney and K. K. Innes, J. Mol. Spect. 3, 235 (1959) from an analysis of 6 bands of the $A^2\Sigma^+ - X^2\Sigma^+$ system.



MOL. WT. = 126.973

(CRYSTAL)

BERYLLIUM ALUMINATE (BeAl₂O₄)

Beryllium Aluminate (BeAl₂O₄)
(Crystal) Mol. Wt. = 126.973

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	3.911	1.320	31.600	3.028	-541.322	-541.322	INFINITE
200	15.876	7.643	17.873	2.046	-534.555	-534.555	1167.775
298	25.177	15.843	15.843	0.000	-525.270	-525.270	573.966
300	25.316	15.909	15.843	0.037	-525.270	-525.270	378.063
400	31.340	24.174	16.917	2.903	-515.606	-515.606	375.600
500	34.569	31.545	19.120	6.212	-505.762	-505.762	276.322
600	36.721	38.050	21.744	9.764	-495.907	-495.907	216.750
700	38.234	43.835	24.494	13.238	-486.083	-486.083	177.047
800	39.482	49.042	27.042	16.643	-476.299	-476.299	149.700
900	40.799	53.777	29.632	20.063	-466.558	-466.558	124.843
1000	41.853	58.131	32.537	25.594	-456.840	-456.840	110.931
1100	42.840	62.167	35.049	29.829	-447.146	-447.146	97.641
1200	43.782	65.935	37.468	34.461	-437.474	-437.474	86.743
1300	44.693	69.483	39.813	39.098	-427.823	-427.823	77.669
1400	45.578	72.821	42.036	43.699	-418.191	-418.191	69.434
1500	46.447	75.995	44.156	47.699	-408.581	-408.581	62.096
1600	47.304	79.020	46.278	52.387	-398.993	-398.993	55.772
1700	48.150	81.913	48.290	57.460	-389.426	-389.426	50.443
1800	48.989	84.673	50.193	62.917	-379.881	-379.881	46.096
1900	49.820	87.380	52.019	68.753	-370.354	-370.354	42.722
2000	50.657	89.936	53.946	74.981	-360.847	-360.847	40.096
2100	51.470	92.427	55.712	81.601	-351.356	-351.356	37.856
2200	52.266	94.840	57.443	88.624	-341.881	-341.881	35.030
2300	53.048	97.183	59.143	96.049	-332.421	-332.421	32.466
2400	53.822	99.455	60.753	103.879	-322.974	-322.974	30.143
2500	54.567	101.667	62.346	112.119	-313.541	-313.541	27.995
2600	55.293	103.821	63.899	120.769	-304.120	-304.120	26.036
2700	56.000	105.921	65.416	129.831	-294.711	-294.711	24.232
2800	56.689	107.971	66.897	139.302	-285.314	-285.314	22.560
2900	57.352	109.971	68.351	149.181	-275.930	-275.930	21.000
3000	58.000	111.926	69.771	159.467	-266.558	-266.558	19.543

ΔH_f⁰ = -541 ± 5 kcal. mole⁻¹
 ΔH_f⁰ 298.15 = -545 ± 5 kcal. mole⁻¹
 ΔH_m⁰ = [42] kcal. mole⁻¹
 S_{298.15} = 15.84 cal. deg.⁻¹ mole⁻¹
 T_m⁰ = 2143°K.

Heat of Formation.

W. A. Young, J. Phys. Chem. 64, 1003 (1960) studied the equilibria



from his results one obtains ΔH_f⁰ 1673 = -379 kcal. mole⁻¹, which corresponds to ΔH_f⁰ 298 = -545 kcal. mole⁻¹.

Heat Capacity and Entropy.

G. T. Furawaka and W. G. Saba, and T. B. Douglas and W. H. Payne, National Bureau of Standards Report 6186, Jan. 1964 have measured the low temperature heat capacities and the high temperature enthalpy in the range 15 - 1173°K.

Melting Data.

The temperature of melting was taken from National Bureau of Standards Circular 500, Washington (1952).
 The heat of melting was estimated as the sum of the ΔH_f⁰ of the constituent oxides at 2100°K.



Point Group D_{2h} $\Delta H_f^\circ = -221.0 \pm 7 \text{ kcal/mol}$ $S_{298.15}^\circ = 130.8 \text{ gibbs/mol}$ $\Delta H_f^{298.15} = -231.5 \pm 7 \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\frac{\omega}{\text{cm}^{-1}}$	$\frac{\omega}{\text{cm}^{-1}}$	$\frac{\omega}{\text{cm}^{-1}}$	$\frac{\omega}{\text{cm}^{-1}}$
407 (1)	56 (1)	[110] (1)	377 (1)
192 (1)	[33] (1)	504 (1)	63 (1)
122 (1)	162 (1)	93 (1)	[116] (1)
			68 (1)

Bond Distances: Al-Br = $2.21 \pm 0.4 \text{ \AA}$ Al-Br₂bridge = $2.33 \pm 0.4 \text{ \AA}$ Bond Angles: Br-Al-Br = $114^\circ 30'$ Br₂bridge-Al-Br₂bridge = $88^\circ 44'$ $\sigma = 4$ Product of the Moments of Inertia: $I_A I_B I_C = 8.80123 \times 10^{-110} \text{ g cm}^6$

Heat of Formation

The vapor pressures of AlBr₃(c) and AlBr₃(g) have been measured by Dunne and Gregory (1) and Fischer et al. (2), respectively. Using these data, the heats of vaporization were calculated by both second and third law methods. The adopted value of ΔH_f^{298} for Al₂Br₆(g) is $-231.5 \pm 7 \text{ kcal/mol}$. The results of these calculations are as follows with reaction (A) corresponding to $2\text{AlBr}_3(\text{c}) = \text{Al}_2\text{Br}_6(\text{c})$ and reaction (B) corresponding to $2\text{AlBr}_3(\text{g}) = \text{Al}_2\text{Br}_6(\text{g})$:

Source	Reac.	Method	No. Pts.	Range T ^o K	ΔH_f^{298} , kcal/mol	ΔH_f^{298} , kcal/mol	Diff. eu
1	A	Effusion	3	273-310	19.7 ± 0.7	20.75	2.2x2.4
2	B	Weight Loss	18**	413-523	15.6 ± 0.1	15.61	0.1x0.1
2	B	Transport	4	386-471	16.1 ± 0.2	15.60	-1.0x0.3
							-231.5

*Calculation based on third law ΔH_f^{298}
 **One point rejected due to failure of a statistical test.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from the electron diffraction work of Palmer and Elliott (3). The bond distances and angles have also been reported by Akishin et al. (4), and these values are in good agreement with those given by Palmer and Elliott (3). The principal moments of inertia are $I_A = 5.36492 \times 10^{-37}$, $I_B = 2.51547 \times 10^{-37}$, and $I_C = 6.52171 \times 10^{-37} \text{ g cm}^2$. It has been established that the condensed phases of AlBr₃ are dimeric (5), (6), thus spectroscopic studies of the crystal and liquid pertain to the structure of Al₂Br₆(g). Gerding and Smit (2) have studied the Raman spectra of Al₂Br₆(l). The eighteen fundamental vibrational frequencies of Al₂Br₆(g) have been predicted by Miller (8) based on seven of the frequencies reported by Gerding and Smit (2). Webb (9) has measured the infrared spectra of Al₂Br₆(c) in the 40-800 cm⁻¹ region, the results being in general accord with the predictions of Miller (8). The vibrational frequencies used are adjusted so that the values of ΔH_f^{298} obtained by the third law method are in agreement with the corresponding second law values. These adjustments are based on the assumption that vibrations with a wave number below 300 cm⁻¹ have a lower wave number in the gas phase than they have in the condensed phases.

References

1. T. G. Dunne and N. W. Gregory, *J. Am. Chem. Soc.* **80**, 1826 (1958).
2. W. Fischer, O. Rahlfs, and B. Benze, *Z. Anorg. Chem.* **205**, 1 (1932).
3. K. J. Palmer and N. Elliott, *J. Am. Chem. Soc.* **60**, 1852 (1938).
4. P. A. Akishin, N. G. Rambidi, and E. Z. Zaslavin, *Kristallografiya* **1**, 167 (1959).
5. R. A. Fenes and C. H. MacGillivray, *Rec. Trav. Chim.* **54**, 275 (1945).
6. K. N. Snenko and T. N. Naumova, *Russ. J. Inorg. Chem. (English Transl.)* **9**, 718 (1964).
7. H. Gerding and E. Smit, *Z. Physik. Chem.* **51B**, 217 (1942).
8. R. H. Miller, Jr., Ph.D. Dissertation, Ohio University, 1965.
9. D. U. Webb, The Dow Chemical Co., Midland, Michigan, 2nd Quarterly Report, April 1 - June 30, 1967, Contract FO4611-67-C-0009.

Dec. 31, 1961; June 30, 1964; June 30, 1967

ALUMINUM TRICHLORIDE, DIMER (Al₂Cl₆)
(IDEAL GAS)
Point Group D_{2h}
S_{298.15} = 113.647 ± 1.0 gibbs/mol
Ground State Quantum Weight = [1]
Vibrational Frequencies (all singly degenerate), cm⁻¹
A_g A_u B_g B_u C_g C_u
501 36 438 625 610 420 484
116 116 166 [130] 77
217 19
99 [170]

Aluminum Trichloride, Dimer (Al₂Cl₆)
(Ideal Gas)
GFW = 266.681

T, °K	C _p ^o	S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298/T	ΔH ^o	Log Kp
0	-0.000	INFINITE	INFINITE	6.043	-308.953	INFINITE
100	24.278	79.485	181.645	6.040	-309.610	663.700
200	33.306	84.920	114.979	3.512	-297.705	395.317
298	37.739	113.647	113.647	0.000	-309.640	213.912
300	37.769	113.691	113.688	0.070	-309.637	212.413
400	40.019	125.093	115.162	3.972	-305.274	156.137
500	41.225	134.165	118.084	8.740	-306.176	122.336
600	41.935	141.760	121.914	12.001	-306.940	99.891
700	42.465	148.094	125.094	15.019	-307.426	83.751
800	42.865	153.330	127.689	20.673	-307.726	71.704
900	43.157	157.970	130.245	24.953	-308.478	62.341
1000	43.487	163.498	134.248	29.250	-313.429	54.771
1100	43.851	167.607	137.097	33.541	-313.427	48.583
1200	44.161	171.407	139.794	37.861	-313.425	43.364
1300	44.431	174.931	142.361	42.210	-313.218	38.965
1400	44.671	178.031	144.797	46.544	-313.114	35.204
1500	44.815	181.037	147.114	50.884	-313.010	31.947
1600	44.852	183.800	149.323	55.227	-312.909	29.097
1700	44.882	186.425	151.431	59.574	-312.807	26.589
1800	44.907	188.961	153.468	63.923	-312.707	24.362
1900	44.928	191.314	155.380	68.275	-312.609	22.350
2000	44.947	193.547	157.213	72.629	-312.518	20.553
2100	44.963	195.672	158.913	76.884	-312.426	18.928
2200	44.976	197.699	160.494	81.141	-312.341	17.450
2300	44.988	199.636	162.376	85.700	-312.255	16.100
2400	44.999	201.482	164.397	90.059	-312.177	14.864
2500	45.008	203.272	166.504	94.819	-312.107	13.728
2600	45.016	204.982	168.690	98.781	-312.038	12.678
2700	45.022	206.626	170.827	102.851	-311.978	11.707
2800	45.027	208.215	172.910	107.050	-311.924	10.815
2900	45.031	209.746	174.941	111.369	-311.869	9.943
3000	45.034	211.225	177.014	116.232	-311.815	9.183
3100	45.036	212.657	179.054	120.597	-311.761	8.527
3200	45.038	214.046	181.054	125.327	-311.707	7.968
3300	45.039	215.386	182.916	129.952	-311.652	7.488
3400	45.040	216.689	184.641	134.451	-311.597	7.068
3500	45.041	217.954	186.241	138.859	-311.542	6.688
3600	45.042	219.185	187.722	143.182	-311.487	6.348
3700	45.043	220.381	189.077	147.422	-311.432	6.048
3800	45.044	221.545	190.312	151.584	-311.377	5.778
3900	45.045	222.680	191.438	155.526	-311.322	5.528
4000	45.046	223.786	192.461	159.293	-311.267	5.298
4100	45.047	224.864	193.394	162.900	-311.212	5.088
4200	45.048	225.917	194.241	166.360	-311.157	4.898
4300	45.049	226.944	195.004	169.684	-311.102	4.728
4400	45.050	227.949	195.684	172.884	-311.047	4.578
4500	45.051	228.930	196.284	175.964	-310.992	4.438
4600	45.052	229.880	196.804	178.924	-310.937	4.308
4700	45.053	230.801	197.241	181.764	-310.882	4.188
4800	45.054	231.700	197.564	184.484	-310.827	4.078
4900	45.055	232.581	197.864	187.084	-310.772	3.978
5000	45.056	233.441	198.144	189.564	-310.717	3.888
5100	45.057	234.281	198.394	191.924	-310.662	3.808
5200	45.058	235.101	198.614	194.164	-310.607	3.738
5300	45.059	235.901	198.804	196.284	-310.552	3.678
5400	45.060	236.679	198.964	198.284	-310.497	3.628
5500	45.061	237.439	199.094	200.164	-310.442	3.588
5600	45.062	238.189	199.194	201.924	-310.387	3.548
5700	45.063	238.929	199.264	203.564	-310.332	3.508
5800	45.064	239.659	199.304	205.084	-310.277	3.468
5900	45.065	240.379	199.324	206.494	-310.222	3.428
6000	45.066	241.089	199.324	207.794	-310.167	3.388

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

Bond Lengths: Al-Cl = 2.05 Å, Al-Cl-bridge = 2.23 Å
Bond Angles: Cl-Al-Cl = 120°, Cl-bridge-Al-Cl-bridge = 83°
Product of the Moments of Inertia: I_AI_BI_C = 5.986 × 10⁻¹¹¹ g cm⁶
σ = 4

The heat of formation is calculated from the value adopted for AlCl₃(g) and the heat of sublimation as derived from vapor pressure data. Vapor pressures were corrected for vapor non-ideality by means of the equation ΔG°/T = -R ln p - BP/T. The Berthelot equation of state and critical constants T_c = 625.7°K and P_c = 26.1 atm reported by Denisova and Baskova (1) were used to calculate B. Boston et al. (2) and Nisels' son and Sokolova (3) confirm T_c within ±2°K. The corrected vapor pressures were used to derive ΔH_f^o298.15 by both second law and third law methods.

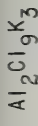
Investigator(s)	Temp. Range	Number of Data Points	ΔH _f ^o 298.15 (kcal/mol Al ₂ Cl ₆)	Drift eu
Smits and Meijering (4)	444.7-464.6	7 ^a	27.53	0.240.2
Smits and Meijering (4)	462.4-481.8	10	27.25	0.840.5
Treadwell and Terbesi (5)	388.7-461.7	11	28.33	-1.740.3
Treadwell and Terbesi (5)	466.5-476.2	3	27.43	0.450.2
Fischer et al. (6)	392.8-428.3	9	27.68	0.041.1
Fischer et al. (6)	403.8-450.4	12 ^b	27.74	0.240.3
Nisels' son et al. (7)	471.2-506.5	18 ^c	27.31	0.740.1
Friedel and Crafts (8)	441.0-455.9	5	29.81	27.86
Friedel and Crafts (8)	477.4-486.2	3	30.00	27.82
Maier (3)	392.8-454.5	8 ^d	25.87	3.641.7
Denise and Gregory (10)	294.2-322.2	12 ^e	29.96	-6.9
Denisova and Baskova (1)	467.8-511.6	8	26.34	2.540.3

Nine points reported, points at 420.8° and 433.5°K rejected by statistical test.
Fourteen points reported, points at 385.2° and 441.3°K rejected by statistical test.
Thirteen points reported, point at 472.2°K rejected by statistical test.
eleven points reported, point at 342.0°K rejected by statistical test.

These points not reported, their vapor pressure equation was used to calculate 2 points at extremes of temperature range covered.
The first seven data sets show good agreement between second and third law values and an average of ΔH_f^o298.15 = 27.66 ± 0.55 kcal/mol Al₂Cl₆ is adopted. The remaining data sets show serious discrepancies between second and third law values, indicating temperature dependent errors in measurement, and are given no weight.

Heat Capacity and Entropy
Electron diffraction data by Palmer and Elliott (11) and by Akishin et al. (12) are in agreement within experimental error and average values for bond angles and distances as given above are selected. The principal moments of inertia are: I_A = 2.2172 × 10⁻³⁷, I_B = 9.931 × 10⁻³⁸, and I_C = 2.7023 × 10⁻³⁷ g cm². Klemperer (13) observed three frequencies in the infrared spectrum of Al₂Cl₆ vapor, Beattie and Horder (14) and Maroni et al. (15) reported gas phase Raman spectra, and Gerding and Smit (16) and Pershina and Raskin (17) measured liquid phase Raman frequencies. With previous vibrational assignments and normal coordinate calculations by Onishi and Shimomuchi (18), Miller (19), and Maroni et al. (15) as a starting point, a new assignment was made (see above) which incorporates additional frequencies observed by Beattie and Horder (14) and Pershina and Raskin (17). Raman and infrared spectra of Al₂Br₆ and Al₂I₆ determined by Beattie, et al. (20) were very helpful. The new assignment differs with earlier calculations primarily in the assumption that the frequencies at 36 cm⁻¹ and 19 cm⁻¹ observed by Pershina and Raskin in the liquid can be assigned to modes not ordinarily Raman active. This assumption is supported by the compatibility of thermodynamic functions based on the new assignment with vapor pressure data as listed above. Use of the frequencies 89 cm⁻¹ and 56 cm⁻¹ of Miller (19) gives 3rd law heats of sublimation nearly 2 kcal/mol Al₂Cl₆ higher than the average of 2nd law values.

References
1. N. D. Denisova and A. P. Baskova, Zh. Fiz. Khim. 43, 2353 (1969).
2. C. R. Boston, S. J. Yosin, and L. F. Grantham, J. Chem. Phys. 51, 1669 (1969).
3. L. A. Nisels' son and T. D. Sokolova, Zh. Neorg. Khim. 10, 1516 (1965).
4. A. Smits and J. L. Meijering, Z. Phys. Chem. B, 98 (1938).
5. W. Treadwell and L. Terbesi, Helv. Chim. Acta 25, 1053 (1932).
6. W. Fischer, Ber. Bunsenges. Physik. Chem. 66, 201 (1962).
7. L. A. Nisels' son, A. Pustil'nik, O. R. Gavrison, and V. A. Rodin, Zh. L. Friedel and J. M. Crafts, Compt. Rend. 109, 1764 (1889).
8. C. G. Maier, U. S. Bur. Mines Tech. Paper 360, (1929).
9. T. G. Dunne and N. W. Gregory, J. Amer. Chem. Soc. 80, 1530 (1958).
10. R. J. Palmer and N. Elliott, J. Amer. Chem. Soc. 80, 1652 (1958).
11. W. Klemperer, J. Chem. Phys. 28, 353 (1958).
12. W. Klemperer, J. Chem. Phys. 28, 353 (1958).
13. I. R. Beattie and J. R. Horder, J. Chem. Soc. 1938A, 2655.
14. V. A. Maroni, D. M. Gruen, R. L. McBride, and E. J. Cairns, Spectrochim. Acta 26A, 418 (1970).
15. H. Gerding and E. Smit, Z. Phys. Chem. B50, 171 (1941).
16. V. Pershina and Sh. Sh. Raskin, Opt. Spect. 13, 272 (1962).
17. V. Pershina and Sh. Sh. Raskin, Opt. Spect. 13, 272 (1962).
18. R. H. Onishi and Ph. D. Shimomuchi, Spectrochim. Acta 20, 321 (1964).
19. I. R. Beattie, T. Gilson, and G. A. Ozin, J. Chem. Soc. 1958A, 1694.



MOL. WT. = 490.373

(CRYSTAL)

TRIPOTASSIUM NONACHLOROALUMINATE ($\text{K}_3\text{Al}_2\text{Cl}_9$)

Tripotassium Nonachloroaluminate ($\text{K}_3\text{Al}_2\text{Cl}_9$)
(Crystal) Mol. Wt. = 490.373

T, °K.	C_p	$S^\circ - (F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	Log K _p
0					
100					
200					
298	80.400	112.000	0.000	- 627.634	460.046
300	80.750	112.499	0.149	- 627.287	456.957
400	84.400	136.236	8.409	- 608.366	332.380
500	87.780	155.440	17.021	- 589.553	237.681
600	90.760	171.712	25.951	- 571.022	207.984
700	93.405	185.905	35.162	- 552.766	172.573
800	95.760	198.534	44.622	- 534.775	146.087
900	97.500	209.910	54.292	- 517.021	125.344
1000	98.600	220.288	64.134	- 499.439	109.081
1100	102.060	229.893	74.214	- 478.238	95.013
1200	104.880	238.892	84.558	- 455.239	82.906
1300	108.060	247.410	95.202	- 432.540	72.713
1400	111.600	255.345	106.182	- 410.130	64.021
1500	115.500	263.376	117.534	- 388.024	56.552

$\Delta H^\circ_f 0$ = Unknown
 $\Delta H^\circ_f 298.15 = -683.6 \pm 3 \text{ kcal. mole}^{-1}$
 ΔH°_m = Unknown

$S^\circ_{298.15} = [112] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

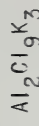
T_m = Unknown

Heat of Formation.

The value of $\Delta H^\circ_f 298.15$ for $\text{K}_3\text{Al}_2\text{Cl}_9(c)$ was calculated from the heat of solution, $\Delta H^\circ_s = -112.07 \text{ kcal. mole}^{-1}$, of $\text{K}_3\text{Al}_2\text{Cl}_9(c)$ in water (one mole of solute in 36 l. of water) determined by E. Baud, Ann. chim. phys. 1, 8 (1904).

Heat Capacity and Entropy.

Heat capacities and $S^\circ_{298.15}$ were estimated based on an assumption that the property of the mixed chloride ($2\text{AlCl}_3 \cdot 3\text{KCl}$) is the sum of the corresponding values for its component chlorides, i.e. $\text{AlCl}_3(c)$ and $\text{KCl}(c)$.



June 30, 1962; Sept. 30, 1964

GFW = 167.9534

(IDEAL GAS)

ALUMINUM TRIFLUORIDE, DIMER (Al₂F₆)Point Group [D_{2h}]S_{298.15} = 92.5 ± 3 gibbs/mol

Ground State Quantum Weight = [1]

ΔH_f⁰ = -627.3 ± 4 kcal/molΔH_f⁰_{298.15} = -629.45 ± 4 kcal/molAluminum Trifluoride, Dimer (Al₂F₆)
(Ideal Gas) GFW = 167.9534

T, °K	Cp°	S°	-(G°-H°)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	17.000	INFINITE		6.326	-627.254	INFINITE
100	17.000	18.000	18.000	6.326	-627.254	18.000
200	17.000	18.000	18.000	6.326	-627.254	18.000
300	17.000	18.000	18.000	6.326	-627.254	18.000
400	17.000	18.000	18.000	6.326	-627.254	18.000
500	17.000	18.000	18.000	6.326	-627.254	18.000
600	17.000	18.000	18.000	6.326	-627.254	18.000
700	17.000	18.000	18.000	6.326	-627.254	18.000
800	17.000	18.000	18.000	6.326	-627.254	18.000
900	17.000	18.000	18.000	6.326	-627.254	18.000
1000	17.000	18.000	18.000	6.326	-627.254	18.000
1100	17.000	18.000	18.000	6.326	-627.254	18.000
1200	17.000	18.000	18.000	6.326	-627.254	18.000
1300	17.000	18.000	18.000	6.326	-627.254	18.000
1400	17.000	18.000	18.000	6.326	-627.254	18.000
1500	17.000	18.000	18.000	6.326	-627.254	18.000
1600	17.000	18.000	18.000	6.326	-627.254	18.000
1700	17.000	18.000	18.000	6.326	-627.254	18.000
1800	17.000	18.000	18.000	6.326	-627.254	18.000
1900	17.000	18.000	18.000	6.326	-627.254	18.000
2000	17.000	18.000	18.000	6.326	-627.254	18.000
2100	17.000	18.000	18.000	6.326	-627.254	18.000
2200	17.000	18.000	18.000	6.326	-627.254	18.000
2300	17.000	18.000	18.000	6.326	-627.254	18.000
2400	17.000	18.000	18.000	6.326	-627.254	18.000
2500	17.000	18.000	18.000	6.326	-627.254	18.000
2600	17.000	18.000	18.000	6.326	-627.254	18.000
2700	17.000	18.000	18.000	6.326	-627.254	18.000
2800	17.000	18.000	18.000	6.326	-627.254	18.000
2900	17.000	18.000	18.000	6.326	-627.254	18.000
3000	17.000	18.000	18.000	6.326	-627.254	18.000
3100	17.000	18.000	18.000	6.326	-627.254	18.000
3200	17.000	18.000	18.000	6.326	-627.254	18.000
3300	17.000	18.000	18.000	6.326	-627.254	18.000
3400	17.000	18.000	18.000	6.326	-627.254	18.000
3500	17.000	18.000	18.000	6.326	-627.254	18.000
3600	17.000	18.000	18.000	6.326	-627.254	18.000
3700	17.000	18.000	18.000	6.326	-627.254	18.000
3800	17.000	18.000	18.000	6.326	-627.254	18.000
3900	17.000	18.000	18.000	6.326	-627.254	18.000
4000	17.000	18.000	18.000	6.326	-627.254	18.000
4100	17.000	18.000	18.000	6.326	-627.254	18.000
4200	17.000	18.000	18.000	6.326	-627.254	18.000
4300	17.000	18.000	18.000	6.326	-627.254	18.000
4400	17.000	18.000	18.000	6.326	-627.254	18.000
4500	17.000	18.000	18.000	6.326	-627.254	18.000
4600	17.000	18.000	18.000	6.326	-627.254	18.000
4700	17.000	18.000	18.000	6.326	-627.254	18.000
4800	17.000	18.000	18.000	6.326	-627.254	18.000
4900	17.000	18.000	18.000	6.326	-627.254	18.000
5000	17.000	18.000	18.000	6.326	-627.254	18.000
5100	17.000	18.000	18.000	6.326	-627.254	18.000
5200	17.000	18.000	18.000	6.326	-627.254	18.000
5300	17.000	18.000	18.000	6.326	-627.254	18.000
5400	17.000	18.000	18.000	6.326	-627.254	18.000
5500	17.000	18.000	18.000	6.326	-627.254	18.000
5600	17.000	18.000	18.000	6.326	-627.254	18.000
5700	17.000	18.000	18.000	6.326	-627.254	18.000
5800	17.000	18.000	18.000	6.326	-627.254	18.000
5900	17.000	18.000	18.000	6.326	-627.254	18.000
6000	17.000	18.000	18.000	6.326	-627.254	18.000

June 30, 1970

Vibrational Frequencies and Degeneracies			
ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
[830] (1)	[200] (1)	[210] (1)	[60] (1)
[600] (1)	[90] (1)	[970] (1)	[80] (1)
[370] (1)	[630] (1)	[260] (1)	[300] (1)

Bond Distance: Al-F [1.63] Å Al-F' [1.80] Å (F is external, F' is in the bridge)

Bond Angle: F-Al-F [120°] F'-Al-F' [90°]

Angle between F'-Al-F' plane and F-Al-F plane = [90°]

Product of the Moments of Inertia: I_{AlF} = [2.669 × 10⁻¹¹²] g cm²

Heat of Formation

The existence of small amounts of dimer in the saturated vapor was inferred from the intensities of AlF₃⁺, AlF₂⁺, and AlF₃⁺ observed by mass spectrometry (1, 2, 3). Büchler et al. (1) concluded that the precursor of the first two ions was mainly AlF₃⁺, while the dimer was the precursor of AlF₂⁺. Intensities of AlF₂⁺ relative to those of AlF₃⁺ were observed as 0.0057 (1), 0.007 (2), and 0.025 (3) at ionizing energies of 60, 90 and 100 V for vapor at 1025, 1100 and 1025°K, respectively.

The temperature dependence of ion intensities was used to derive 2nd-law values of ΔH_f⁰ for monomer and dimer (1, 2) and a value of ΔH(dimerization) based on an estimate for the entropy of dimerization (3). The absolute pressure of the monomer was obtained (2) from integration of the intensity of AlF₂⁺ during total sublimation at 1100°K, then the pressure of dimer was estimated from the relative ion intensity assuming a relative ionization cross section equal to two and neglecting other effects. Krause and Douglas (4) reported ΔH_f⁰(monomer) plus ΔH⁰ and ΔS⁰ for dimerization; these were derived by combination of ΔH_f⁰(dimer) (1) with precise sublimation pressures from entrainment data near 1200°K, where the dimer is more abundant. After reduction to 1000 K with JANAF functions, these results may be summarized as follows:

Source		Method		ΔH _f ⁰ , kcal/mol*		ΔS _f ⁰ , gibbs/mol*	
				c + m	2c + d	c + m	2c + d
Krause (4)		Entrainment		68.1 ± 0.4	[86]	-50 ± 3	[44.04]
Büchler (1)		Ion Intensities		67.3 ± 3	85.8 ± 3	-48.8 ± 3	---
Ecklin (2)		Ion Intensities		70.5	92.1	-49.0	55.1
Porter (3)		Ion Intensities		---	---	-48.0 ± 4	---
JANAF		Adopted		68.4	87.8	[44.37]	[52.83]
		Reactions are abbreviated by c = crystal, d = dimer gas and m = monomer gas. Brackets enclose those values assumed in deriving the other values.				[32 ± 3]	
						[35.9]	

JANAF values are given in the last line. These are based on JANAF entropies, on ΔH⁰(dimerization) = -49 kcal/mol for which there is close agreement, and on the entrainment pressures of Krause and Douglas (4). Reduction of the dimer value to 298.15°K gives ΔH_f⁰ = 92.55 ± 4 and ΔH_f⁰ = -629.45 ± 4 kcal/mol. The table for AlF₃(g) gives a detailed comparison of observed and predicted total pressures along with predictions of the mole fraction of dimer in the saturated vapor. The latter are reasonably consistent with the relative ion intensities.

Heat Capacity and Entropy

The molecular structure is assumed to be similar to that of Al₂Cl₆. Bond distances and bond angles are estimated by comparison with AlF₃(g), AlCl₃(g), and Al₂Cl₆(g). Principal moments of inertia are I_A = 35.36 × 10⁻³⁹, I_B = 79.74 × 10⁻³⁹ and I_C = 94.66 × 10⁻³⁹ g cm².

Six observed vibrational frequencies are from infrared spectra of the dimer isolated in rare-gas matrices (2). Unobserved fundamentals (2 in infrared, 9 in Raman and 1 inactive) are estimated such that the entropy is consistent with the result of Krause and Douglas (4) as given above. The estimated fundamentals are based on comparisons with Al₂Cl₆, Al₂Br₆, and Al₂I₆ which have been restudied extensively (8-11) since the calculations of Miller (12). Assignments used in the comparisons are minor modifications of those given by Beattie et al. (3).

References

1. A. Büchler, E. P. Marram and J. L. Stauffer, *J. Phys. Chem.*, **71**, 4139 (1967).
2. E. V. Erolkin, N. A. Zhigul'skaya, L. N. Sidorov and P. A. Akishin, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **3** (5), 873 (1967).
3. R. F. Porter and E. Zeller, *J. Chem. Phys.*, **33**, 858 (1960).
4. R. F. Porter and E. Zeller, *J. Chem. Phys.*, **33**, 858 (1960).
5. P. F. Krause and T. B. Douglas, *J. Phys. Chem.*, **72**, 475 (1968).
6. E. Z. Zaslavskii, N. G. Rumbidi and E. Z. Zaslavskii, *Kristallografiya*, **13**, 186 (1959); English translation, p. 187.
7. E. Z. Zaslavskii, *Kristallografiya*, **13**, 186 (1959); English translation, p. 187.
8. I. R. Beattie and J. R. Horder, *J. Chem. Soc. A*, 1965; I. R. Beattie, T. Gilson and G. A. Ozin, *ibid.*, **A1968**, 813.
9. E. V. Perehina and Sh. Sh. Raskin, *Optics and Spectroscopy* (English translation), **13**, 272 (1968).
10. V. V. Webb, B. H. Justice and H. Prophet, *J. Chem. Thermodynamics*, **1**, 227 (1969).
11. V. V. Webb, B. H. Justice and H. Prophet, *J. Chem. Thermodynamics*, **1**, 227 (1969).
12. R. H. Miller, Ph.D. Thesis, Ohio University, Aug. 21, 1965.

Aluminum Triiodide, Dimeric (AlI₃)₂
(Ideal Gas) Mol. Wt. = 815.42

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	Log K _p
0	∞	INFINITE	9.679	119.029	INFINITE
100	31.382	99.308	7.843	119.192	271.946
200	38.295	123.756	3.905	120.072	181.370
298	40.892	139.608	0.000	121.000	96.044
300	40.922	139.661	-0.076	121.018	97.497
400	42.054	151.809	4.232	133.572	75.154
500	42.654	161.261	8.468	145.159	59.248
600	42.947	169.063	12.708	156.582	47.227
700	43.147	175.699	17.058	167.667	36.554
800	43.278	181.470	21.375	178.461	27.232
900	43.370	186.573	25.706	188.934	19.242
1000	43.435	191.146	30.068	199.253	12.172
1100	43.484	195.288	34.394	209.428	6.812
1200	43.521	199.074	38.785	219.466	3.459
1300	43.551	202.558	43.006	229.378	1.715
1400	43.574	205.787	47.435	239.167	0.800
1500	43.592	208.794	51.813	248.837	0.078
1600	43.608	211.607	56.173	258.394	0.387
1700	43.620	214.252	60.513	267.850	0.799
1800	43.631	216.745	64.897	277.121	1.264
1900	43.640	219.104	69.261	286.228	1.735
2000	43.648	221.343	73.625	295.172	2.274
2100	43.655	223.473	77.990	303.963	2.822
2200	43.660	225.504	82.356	312.605	3.345
2300	43.665	227.445	86.739	321.106	3.841
2400	43.670	229.303	91.089	329.472	4.309
2500	43.674	231.086	95.456	337.713	4.752
2600	43.677	232.799	99.824	345.832	5.168
2700	43.680	234.447	104.192	353.835	5.563
2800	43.683	236.036	108.560	361.722	5.937
2900	43.686	237.569	112.928	369.495	6.292
3000	43.688	239.050	117.297	377.153	6.628
3100	43.690	240.482	121.666	384.700	6.945
3200	43.692	241.870	126.035	392.132	7.245
3300	43.693	243.214	130.404	399.452	7.528
3400	43.695	244.518	134.774	406.663	7.792
3500	43.696	245.785	139.143	413.765	8.033
3600	43.698	247.016	143.513	420.768	8.256
3700	43.699	248.213	147.883	427.672	8.463
3800	43.700	249.379	152.253	434.487	8.655
3900	43.701	250.514	156.623	441.212	8.832
4000	43.702	251.620	160.993	447.847	8.997
4100	43.703	252.699	165.363	454.392	9.150
4200	43.703	253.753	169.733	460.847	9.292
4300	43.704	254.781	174.104	467.212	9.425
4400	43.705	255.786	178.474	473.487	9.549
4500	43.705	256.768	182.845	479.672	9.666
4600	43.706	257.728	187.215	485.767	9.775
4700	43.707	258.668	191.586	491.772	9.878
4800	43.707	259.589	195.956	497.687	9.975
4900	43.708	260.490	200.327	503.512	10.067
5000	43.708	261.373	204.698	509.247	10.154
5100	43.709	262.238	209.069	514.892	10.236
5200	43.709	263.087	213.440	520.447	10.313
5300	43.709	263.920	217.811	525.912	10.386
5400	43.710	264.737	222.182	531.287	10.455
5500	43.710	265.539	226.553	536.572	10.519
5600	43.711	266.326	230.924	541.767	10.579
5700	43.711	267.100	235.295	546.872	10.635
5800	43.711	267.860	239.666	551.887	10.687
5900	43.711	268.607	244.037	556.812	10.736
6000	43.712	269.342	248.408	561.647	10.781

Dec. 31, 1961; June 30, 1964

ALUMINUM TRIIODIDE, DIMERIC ((AlI₃)₂) (IDEAL GAS) MOL. WT. = 815.42

Point Group D_{2h} ΔH_f^o 0 = -119.0 ± 3.0 kcal. mole⁻¹
S_{298.15} = [139.608] cal. deg.⁻¹ mole⁻¹
ΔH_f^o 298.15 = -121.0 ± 3.0 kcal. mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
ω, cm.⁻¹ ω, cm.⁻¹ ω, cm.⁻¹

544 (1)	[53] (1)	[290] (1)
146 (1)	[430] (1)	[53] (1)
94 (1)	[130] (1)	[50] (1)
53 (1)	[20] (1)	[330] (1)
[30] (1)	410 (1)	[140] (1)
[500] (1)	[65] (1)	[55] (1)

Bond Distance: Al-I = 2.53 Å Al-I-bridge = 2.58 Å

Bond Angle: I-Al-I = 112 ± 1° I-bridge-Al-I-bridge = 68 ± 1° σ = 4

Product of the Moments of Inertia: I_AI_BI_C = 5.21725 X 10⁻¹⁰⁹ g.³ cm.⁶

Heat of Formation.

W. Fischer, O. Rahlfs and B. Benze, Z. anorg. allgem. Chem. 205, 1 (1932) measured the vapor pressure of AlI₃(l). The vapor consists of both Al₂I₆(g) and AlI₃(g) species. The partial pressures of Al₂I₆(g) and AlI₃(g) at different temperatures for the equilibrium Al₂I₆(g) → 2AlI₃(g) were determined by M. Fischer, O. Rahlfs and B. Benze, loc. cit. From these partial pressures the mole ratios of Al₂I₆(g) and AlI₃(g) at other temperatures were estimated. The partial pressures of Al₂I₆(g) over AlI₃(l) were calculated from the total pressure using the estimated mole ratio values. The heat of vaporization, ΔH_v 298.15 = 20.5 ± 1.0 kcal. mole⁻¹, was evaluated employing the vapor pressures obtained by second law method. The corresponding third law value is 22.4 kcal. mole⁻¹. It was not used due to the uncertainties involved in the estimation of the vibrational frequencies. The heat of formation for Al₂I₆(g) was calculated from ΔH_f^o(l) and ΔH_v^o obtained.

Heat Capacity and Entropy.

Molecular structure, bond distances and angles were reported by K. J. Palmer and N. Elliott, J. Am. Chem. Soc. 60, 1952 (1938). Five vibrational frequencies (344, 146, 94, 53 and 410 cm.⁻¹) were adopted from the Raman spectrum of Al₂I₆(l) measured by H. Gerdung and E. Smit, Z. physik. Chem. 50B, 171 (1941). The remaining ones were estimated by comparison with those for Al₂O₃(g) and Al₂Se₃(g) and adjusted so that the value of ΔH_f^o 298.15 obtained by the third law method is in reasonable agreement with the corresponding second law value. The three principal moments of inertia are: I_A = 9.32506 X 10⁻³⁷, I_B = 4.60265 X 10⁻³⁷, and I_C = 1.21558 X 10⁻³⁶ g. cm.².

Magnesium Aluminate (MgAl_2O_4)
(Crystal) Mol. Wt. = 142.28

T, °K.	C_p°	$\left[\text{cal. mole}^{-1} \text{deg.}^{-1} \right]$	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _F
0	.000	.000	INFINITE	3.663	547.349	547.349	INFINITE
100	5.418	2.075	37.331	3.531	548.969	548.969	1180.844
200	19.659	19.777	2.514	2.514	550.578	550.578	580.360
298	27.771	19.266	19.266	.000	551.200	551.200	362.167
300	27.905	19.440	19.269	.052	551.208	551.208	379.656
400	33.247	26.269	20.438	3.140	551.349	551.349	279.254
500	36.088	36.040	22.602	6.619	551.228	551.228	219.013
600	37.923	42.789	25.593	10.324	551.014	551.014	178.845
700	39.284	48.753	28.475	14.188	550.773	550.773	150.200
800	40.392	54.063	31.347	18.173	550.541	550.541	128.711
900	41.353	58.877	34.142	22.262	550.335	550.335	112.003
1000	42.222	63.280	36.839	26.441	550.273	550.273	98.522
1100	43.038	67.323	39.430	30.704	550.280	550.280	87.454
1200	43.801	71.121	41.935	35.047	550.279	550.279	78.258
1300	44.519	74.656	44.259	39.464	550.270	550.270	70.445
1400	45.261	77.953	46.587	43.854	550.262	550.262	63.697
1500	45.967	81.130	48.786	48.215	550.260	550.260	57.604
1600	46.658	84.119	50.902	53.147	550.259	550.259	52.289
1700	47.321	86.948	52.940	57.847	550.260	550.260	47.585
1800	48.018	89.653	54.907	62.415	550.267	550.267	43.434
1900	48.650	92.307	56.807	67.450	550.278	550.278	39.719
2000	49.356	94.822	58.645	72.352	550.285	550.285	36.363
2100	49.932	97.254	60.424	77.317	550.285	550.285	33.371
2200	50.475	99.579	62.153	82.338	550.285	550.285	30.618
2300	50.994	101.834	63.859	87.411	550.285	550.285	28.150
2400	51.459	104.014	65.459	92.533	550.285	550.285	25.873
2500	51.900	106.124	67.043	97.702	550.285	550.285	23.785
2600	52.308	108.167	68.586	102.912	550.285	550.285	21.861
2700	52.681	110.149	70.089	108.165	550.285	550.285	20.004
2800	53.021	112.071	71.554	113.447	550.285	550.285	18.191
2900	53.328	113.937	72.983	118.765	550.285	550.285	16.474
3000	53.600	115.749	74.379	124.112	550.285	550.285	14.899

Al_2MgO_4

MOL. WT. = 142.28

(CRYSTAL)

MAGNESIUM ALUMINATE (MgAl_2O_4)

$\Delta H_f^\circ 0 = -547.3 \pm 1.9 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -551.2 \pm 1.9 \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = \text{Unknown}$

$S_{298.15}^\circ = 19.27 \pm 0.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 2403^\circ\text{K.}$

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ was calculated from $\Delta H_f^\circ 298.15 = 124.6 \pm 1.5 \text{ kcal. mole}^{-1}$ for the reaction:
 $4\text{MgO}(c) + 2\text{Al}(l) = \text{MgAl}_2\text{O}_4(c) + 3\text{Mg}(g)$. The value of $\Delta H_f^\circ 298.15$ was obtained by the third-law method, using vapor pressure data reported by K. Grjotheim, O. Herstad, and J. M. Toguri, Can. J. Chem. **39**, 443 (1961). From the Knudsen experiments with $\text{MgAl}_2\text{O}_4(c)$, R. L. Altman, J. Phys. Chem., **57**, 366 (1963) calculated the value of $\Delta H_f^\circ 298.15$ as $-552 \text{ kcal. mole}^{-1}$ which agrees with the value used.

Heat Capacity and Entropy.

The low temperature heat capacity, $53-296^\circ\text{K.}$, was measured by E. G. King, J. Phys. Chem. **59**, 218 (1955). The high temperature heat capacity, $400-1800^\circ\text{K.}$, was reported by K. R. Bónnickson, J. Phys. Chem. **59**, 220 (1955). These two sets of data were joined smoothly and extrapolated to 3000°K. $S_{298.15}^\circ$ was reported by E. G. King, loc. cit., based on S_{21}° (extrap.) = $0.32 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Melting.

T_m was taken from "Data on Chemicals for Ceramic Use," U. S. National Research Council Bulletin 118, 1949.

$$\Delta H_f^\circ = -31.0 \pm 7 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -31.4 \pm 7 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 62.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta S^\circ_{298.15} = -31.4 \pm 7 \text{ kcal. mole}^{-1}$$

$$\Delta S^\circ_{298.15} = -31.4 \pm 7 \text{ kcal. mole}^{-1}$$

$$\Delta S^\circ_{298.15} = -31.4 \pm 7 \text{ kcal. mole}^{-1}$$

Vibrational Frequencies and Degeneracies

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\omega, \text{ cm.}^{-1}$$

$$\text{Bond Distances: Al-O} = 1.66 \text{ \AA}$$

$$\text{Bond Angle: Al-O-Al} = 145^\circ$$

$$\text{Product of the Moments of Inertia: } I_{A,B,C} = 283.2477 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$$

$$C^\circ = 2$$

Heat of Formation.

The value of ΔH_f° 298 = -31.4 \pm 7 kcal. mole⁻¹ for Al₂O(g) was calculated from ΔH_f° 298 = 247 \pm 7 kcal. mole⁻¹ for the reaction Al₂O(g) = 2Al(g) + O(g) and ΔH_f° 298 = 131 \pm 7 kcal. mole⁻¹ for the reaction Al₂O(g) = AlO(g) + Al(g). The values of ΔH_f° 298 were obtained by the third law method, using the partial pressure data reported by J. Drowart, G. Delmarie, R. Burns and M. Ingraham, *J. Chem. Phys.* **32**, 1368 (1960). (The second law values which are in poor agreement with the third law values, are ΔH_f° 298 = 271 \pm 10 kcal. mole⁻¹ and ΔH_f° = 154 \pm 10 kcal. mole⁻¹, respectively.) L. Brewer and A. Searcy, *J. Am. Chem. Soc.*, **75**, 5508 (1953), reported that under reducing condition, Al₂O₃ vaporizes mostly to Al₂O(g), but under neutral condition AlO(g) and O(g) are the major products. Brewer and Searcy also measured the vapor pressures of the Al-Al₂O₃ system by Knudsen effusion method, and obtained the heat of formation of Al₂O(g) from gaseous atoms as ΔH_f° 298 = -248 kcal. mole⁻¹. This value leads the heat of formation for Al₂O(g), ΔH_f° 298 = -32.4 \pm 7, which agrees with the value selected.

Other references appearing in the recent literature were:

1. Leo Brewer, AEC Report UCR-8356 (1958).
2. G. Delmarie, J. Drowart, M. Ingraham, *J. Chem. Phys.*, **30**, 318 (1959).
3. R. Porter, P. Shissel and M. Ingraham, *J. Chem. Phys.*, **23**, 339 (1955).
4. R. J. Ackerman and R. J. Thorn, *J. Am. Chem. Soc.*, **76**, 4169 (1954).
5. C. N. Cochran, *J. Am. Chem. Soc.*, **77**, 2180 (1955).
6. M. Cook, A. Faller, R. Keyes, W. Partridge and W. Ursenbach, *J. Phys. Chem.*, **61**, 189 (1957).

Heat Capacity and Entropy.

The matrix isolation of high temperature vapors for the investigation of the infrared spectrum of Al₂O has been used to determine the bond distance, angle and vibrational frequencies by M. Linevsky, D. White and D. Mann, *J. Chem. Phys.*, **41**, 542 (1964). These reported data have been adopted in this table. The symmetric structure Al-O-Al instead of Al-Al-O for Al₂O(g) was chosen for two reasons: (1) The dissociation energy of Al₂O(g), $D_{298}^\circ = 247 \pm 7$ kcal/mole, is approximately twice the dissociation energy of AlO(g), $D_{298}^\circ = 115 \pm 5$ kcal. mole⁻¹, which implies that the symmetric structure is more reasonable. (2) The dissociation energy of Al₂O(g) has been estimated to be only 39 kcal. mole⁻¹ by J. Drowart and R. Honig, *J. Phys. Chem.*, **61**, 980 (1957). This implies that the Al-O bond energy in "Al-Al-O" structure would be as large as 208 kcal. mole⁻¹ if D'Al-Al = 39 kcal. mole⁻¹. Therefore Al₂O(g) must have a symmetric structure. Linevsky et al., loc. cit., have also concluded the bent symmetric structure (instead of a linear one) and the calculated ω_2 from the observed infrared spectra and the re-analysis of the ultraviolet spectra. The three principal moments of inertia are $I_A = 0.5105 \times 10^{-39}$, $I_B = 22.4539 \times 10^{-39}$ and $I_C = 22.9644 \times 10^{-39}$ g. cm.²

Drowart, et al. (loc. cit.), also postulated a bent symmetric molecule for Al₂O(g), and estimated the bond distance Al-O = [1.67-1.76] Å and angle Al-O-Al = [110]° and the vibrational frequencies as [1079] cm.⁻¹, [351] cm.⁻¹ and [921] cm.⁻¹.

The National Bureau of Standards Report No. 6484 "Preliminary Report on the Thermodynamic Properties of Li, Be, Mg, Al and Their Compounds with Hydrogen, Oxygen, Nitrogen, Fluorine and Chlorine" July, 1959, has proposed a trigonal structure for Al₂O(g) with bond distance Al-O = [1.87] Å, and Al-Al = [2.0] Å. Its vibration frequencies were estimated as [450] cm.⁻¹, [1000] cm.⁻¹ and [1000] cm.⁻¹.

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1965

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S [°] -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f [°]	ΔF _f [°]	Log K _p
0	∞	∞	∞	∞	∞	∞
100	6.767	1.375	2.777	30.951	30.951	INFINITE
200	8.905	57.618	1.959	33.433	33.433	73.065
298	10.916	61.766	1.023	36.990	36.990	38.446
300	10.934	62.033	1.020	37.534	37.534	38.578
400	11.749	65.297	1.157	40.904	40.904	28.103
500	12.321	67.284	1.362	43.128	43.128	18.950
600	12.711	70.267	1.615	45.266	45.266	16.487
700	12.982	72.268	1.900	47.329	47.329	14.776
800	13.174	73.994	2.208	49.319	49.319	13.473
900	13.314	75.555	2.533	51.240	51.240	12.442
1000	13.416	76.963	2.870	53.075	53.075	11.522
1100	13.498	78.246	3.216	54.828	54.828	10.726
1200	13.561	79.423	3.569	56.500	56.500	10.054
1300	13.610	80.511	3.928	58.099	58.099	9.479
1400	13.650	81.521	4.291	59.627	59.627	8.981
1500	13.682	82.464	4.657	61.084	61.084	8.564
1600	13.709	83.347	5.024	62.469	62.469	8.157
1700	13.731	84.179	5.391	63.782	63.782	7.762
1800	13.750	84.965	5.756	65.024	65.024	7.383
1900	13.766	85.709	6.119	66.194	66.194	7.021
2000	13.780	86.415	6.478	67.292	67.292	6.676
2100	13.792	87.088	6.834	68.318	68.318	6.344
2200	13.802	87.730	7.186	69.271	69.271	6.022
2300	13.812	88.343	7.533	70.151	70.151	5.710
2400	13.820	88.931	7.875	70.957	70.957	5.407
2500	13.827	89.496	8.211	71.690	71.690	5.113
2600	13.833	90.038	8.541	72.351	72.351	4.827
2700	13.838	90.556	8.865	72.940	72.940	4.549
2800	13.843	91.063	9.184	73.457	73.457	4.278
2900	13.848	91.549	9.497	73.892	73.892	4.014
3000	13.852	92.019	9.804	74.246	74.246	3.756
3100	13.856	92.473	10.104	74.519	74.519	3.502
3200	13.859	92.913	10.397	74.711	74.711	3.251
3300	13.862	93.340	10.685	74.823	74.823	3.003
3400	13.865	93.754	10.967	74.856	74.856	2.758
3500	13.868	94.155	11.243	74.810	74.810	2.517
3600	13.870	94.546	11.514	74.684	74.684	2.279
3700	13.872	94.926	11.780	74.479	74.479	2.044
3800	13.874	95.296	12.041	74.194	74.194	1.812
3900	13.876	95.657	12.288	73.829	73.829	1.583
4000	13.878	96.008	12.521	73.384	73.384	1.357
4100	13.879	96.351	12.740	72.859	72.859	1.132
4200	13.881	96.685	12.945	72.254	72.254	0.907
4300	13.882	97.012	13.136	71.569	71.569	0.682
4400	13.883	97.331	13.313	70.804	70.804	0.457
4500	13.885	97.643	13.476	69.959	69.959	0.232
4600	13.886	97.948	13.625	69.034	69.034	0.007
4700	13.887	98.247	13.760	68.029	68.029	-0.218
4800	13.888	98.539	13.881	66.944	66.944	-0.443
4900	13.889	98.825	13.989	65.779	65.779	-0.668
5000	13.890	99.106	14.086	64.534	64.534	-0.893
5100	13.890	99.381	14.171	63.209	63.209	-1.118
5200	13.891	99.651	14.244	61.804	61.804	-1.343
5300	13.892	99.915	14.306	60.319	60.319	-1.568
5400	13.893	100.175	14.357	58.754	58.754	-1.793
5500	13.893	100.430	14.400	57.109	57.109	-2.018
5600	13.894	100.680	14.436	55.384	55.384	-2.243
5700	13.894	100.926	14.465	53.579	53.579	-2.468
5800	13.895	101.168	14.489	51.694	51.694	-2.693
5900	13.895	101.405	14.508	49.729	49.729	-2.918
6000	13.896	101.639	14.522	47.684	47.684	-3.143

Dialuminum Monoxide Unipositive Ion (Al₂O⁺)

(Ideal Gas) GFW = 69.9618

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
250							
288	10.618	62.697	62.697	.000	146.000	137.161	-100.542
300	10.935	62.765	62.698	.020	146.001	137.106	-99.861
350	11.252	62.833	62.716	.117	146.002	137.051	-99.180
500	12.374	63.718	63.592	1.123	146.156	131.133	-97.538
600	12.714	71.001	64.975	3.616	146.211	128.122	-96.669
700	12.954	72.983	65.980	6.001	146.233	125.105	-95.060
800	13.175	74.728	66.967	7.210	146.209	122.088	-93.353
900	13.381	76.284	67.842	8.264	146.185	119.071	-91.646
1000	13.519	77.668	68.627	9.272	146.151	116.054	-89.941
1100	13.609	78.981	69.362	10.218	146.107	113.028	-88.236
1200	13.651	80.158	70.016	11.071	146.055	110.001	-86.531
1300	13.650	81.246	71.300	12.529	146.037	106.974	-84.826
1400	13.628	82.284	72.459	13.843	146.035	103.947	-83.121
1500	13.622	83.199	72.759	15.059	146.395	100.920	-81.416
1600	13.709	84.083	73.440	17.029	146.305	101.954	-79.711
1700	13.731	84.915	74.091	18.401	146.215	99.560	-78.006
1800	13.750	85.700	74.714	19.775	146.125	97.166	-76.301
1900	13.764	86.444	75.314	21.149	146.035	94.771	-74.596
2000	13.760	87.150	75.882	22.528	139.939	92.408	-72.891
2100	13.792	87.823	76.439	23.907	139.844	90.032	-71.186
2200	13.802	88.465	76.971	25.286	139.746	87.662	-69.481
2300	13.811	89.078	77.484	26.667	139.649	85.300	-67.776
2400	13.816	89.666	77.976	28.048	139.552	82.938	-66.071
2500	13.826	90.231	78.458	29.431	139.446	80.579	-64.366
2600	13.832	90.773	78.922	30.814	139.342	78.229	-62.661
2700	13.838	91.295	79.370	32.197	139.235	75.879	-60.956
2800	13.843	91.799	79.803	33.581	139.128	73.529	-59.251
2900	13.847	92.284	80.227	34.955	139.021	71.179	-57.546
3000	13.852	92.754	80.657	36.351	138.914	68.829	-55.841
3100	13.855	93.208	81.035	37.736	138.807	66.479	-54.136
3200	13.859	93.648	81.423	39.122	138.700	64.129	-52.431
3300	13.862	94.075	81.800	40.506	138.593	61.779	-50.726
3400	13.865	94.492	82.176	41.891	138.486	59.429	-49.021
3500	13.867	94.880	82.554	43.281	138.379	57.079	-47.316
3600	13.869	95.281	82.873	44.667	138.272	54.729	-45.611
3700	13.872	95.661	83.214	46.055	138.165	52.379	-43.906
3800	13.875	96.031	83.586	47.442	138.058	50.029	-42.201
3900	13.877	96.391	83.941	48.830	137.951	47.679	-40.496
4000	13.877	96.743	84.189	50.217	137.844	45.329	-38.791
4100	13.879	97.086	84.459	51.605	137.737	42.979	-37.086
4200	13.880	97.420	84.803	52.993	137.630	40.629	-35.381
4300	13.882	97.747	85.100	54.380	137.523	38.279	-33.676
4400	13.884	98.068	85.376	55.757	137.416	35.929	-31.971
4500	13.884	98.378	85.676	57.157	137.309	33.579	-30.266
4600	13.885	98.683	85.956	58.546	137.202	31.229	-28.561
4700	13.886	98.962	86.230	59.934	137.095	28.879	-26.856
4800	13.887	99.274	86.498	61.323	136.988	26.529	-25.151
4900	13.887	99.581	86.748	62.712	136.881	24.179	-23.446
5000	13.889	99.881	87.021	64.101	136.774	21.829	-21.741
5100	13.890	100.116	87.275	65.489	136.667	19.479	-20.036
5200	13.891	100.386	87.524	66.878	136.560	17.129	-18.331
5300	13.891	100.650	87.769	68.266	136.453	14.779	-16.626
5400	13.891	100.909	87.999	69.654	136.346	12.429	-14.921
5500	13.893	101.155	88.247	71.046	136.239	10.079	-13.216
5600	13.893	101.415	88.460	72.435	136.132	7.729	-11.511
5700	13.894	101.661	88.709	73.825	136.025	5.379	-9.806
5800	13.894	101.900	88.954	75.214	135.918	3.029	-8.101
5900	13.895	102.134	89.175	76.603	135.811	0.679	-6.396
6000	13.895	102.374	89.375	77.993	135.704	-1.679	-4.691

June 30, 1968



GFW = 69.9618

(IDEAL GAS)

ΔH°₀ = 146.5 ± 10 kcal/mol

ΔH°_{298.15} = 146 ± 10 kcal/mol

Point Group [C_{2v}]

S°_{298.15} = [62.7 ± 2] gibbs/mol.

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
[700] (1)	
[250] (1)	
[1000] (1)	

Bond Distance: Al-O = [1.66] Å

Bond Angle: Al-O-Al = [155°] σ = 2

Product of the Moments of Inertia: I_AI_BI_C = [1.481 x 10⁻¹¹⁵] g³ cm⁶

Heat of Formation

The ionization potential of Al₂O has been reported as 7.7 ± 0.2eV (177.6 kcal) by R. F. Porter, P. Schiesel, and M. G. Inghram, J. Chem. Phys. 23, 339 (1955), and has been confirmed as 7.7 ± 0.5eV by G. DeMaria, J. Drowart, M. G. Inghram, J. Chem. Phys. 30, 318 (1959). Using this value with ΔH°₀(Al₂O, g) = -31.4 kcal/mol, we obtain ΔH°₂₉₈(Al₂O⁺, g) = 146 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecule is assumed to be bent by analogy with Al₂O, although both these molecules are predicted to be linear according to A. D. Walsh, J. Chem. Soc. 2266 (1953). The electronic ground state is doublet, since there is an odd number of electrons. The bond length is estimated to be the same as that in Al₂O and the vibrational frequencies are also assumed to be close to those for Al₂O. Since normally the molecule Al₂O ought to be linear, the bending must occur due to the occupancy of an outermost orbital with strong angular variation. Presumably this orbital is occupied by a pair of electrons, one of which will be removed in Al₂O⁺, thus causing an opening of the bond angle. On this basis the angle is estimated to be greater than that in Al₂O. The individual moments of inertia are: I_A = 2.645 x 10⁻⁴⁰ g cm², I_B = 2.353 x 10⁻³⁸ g cm² and I_C = 2.380 x 10⁻³⁸ g cm². The enthalpy at 0°K is -2.769 kcal/mol.



Point Group [V_h]
 $S_{298.15}^0 = [63.7] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = -95.7 \pm 7 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = -97.0 \pm 7 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$
[200] [1]	[950] [1]
[600] [1]	[1000] [1]
[950] [1]	[1000] [1]

Bond Distances: Al-O = [1.60] Å
 Bond Angles: Al-O-Al = [90]°, O-Al-O = [90]°
 Products of the Moments of Inertia: $I_{A^2} I_{B^2} I_{C^2} = [1.4246 \times 10^{-11}] \text{ g.}^3 \text{ cm.}^6$

σ = [4]

Heat of Formation.

The value of ΔH_f^0 298 = -97 ± 7 kcal. mole⁻¹ for Al₂O₂(g) was calculated from ΔH_f^0 298 = 372 ± 7 kcal. mole⁻¹ for the reaction $\text{Al}_2\text{O}_3(\text{g}) = 2\text{Al}(\text{g}) + 3\text{O}(\text{g})$. The value of ΔH_f^0 298 was obtained by the third law method, using the partial pressure data reported by J. Drowart, G. Demaria, R. Burns and M. Inghram, J. Chem. Phys. 32, 1366 (1960). (The second law value for ΔH_f^0 , which is in poor agreement with the third law value, is 461 ± 25 kcal. mole⁻¹.)

Heat Capacity and Entropy.

The molecular structure (plane cyclic model) and vibrational frequencies of Al₂O₂(g) were obtained from Drowart, et al., J. Chem. Phys., 32, 1366 (1960). The bond distance Al-O in Al₂O₂ was assumed to be the same as that in AlO (g.). The three principal moments of inertia are $I_A = 6.8005 \times 10^{-59}$, $I_B = 11.4874 \times 10^{-59}$ and $I_C = 10.2679 \times 10^{-59} \text{ g. cm.}^2$.

The configuration was proposed by Drowart, et al., instead of the alternate linear structure OAl-AlO for the reason discussed below. The O-B-O bond 1,2 compares to the B₂ dissociation energy 3,4 in the same way as the NC-ON bond compares to the C-C single bond. However, for Al₂O₂(g), the relationship between OAl-AlO and Al₂O would be quite different.

- References (1) M. Inghram, R. Porter and W. Chupka, J. Chem. Phys., 25, 488 (1956).
 (2) D. White, F. Walsh and D. Mann, J. Chem. Phys., 28, 508 (1958).
 (3) T. L. Cottrell, "The Strength of Chemical Bonds", Butterworths Scientific Publications, London (1958).
 (4) G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., (1950).

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	INFINITE	2.929	-95.666	-95.666	INFINITE
100	9.017	52.453	73.450	2.100	-95.762	-96.525	210.045
200	19.510	59.136	64.772	1.127	-96.353	-97.105	106.106
298	12.446	63.695	63.695	0.000	-97.000	-97.334	71.351
300	12.534	63.772	63.695	.023	-97.012	-97.346	70.913
400	16.394	67.643	64.210	1.373	-97.567	-97.370	53.108
500	15.780	71.013	65.241	2.966	-98.039	-97.266	42.513
600	16.758	73.982	66.456	4.516	-98.476	-97.070	35.356
700	17.447	76.620	67.423	6.228	-98.802	-96.802	30.221
800	17.941	78.983	68.085	7.968	-99.376	-96.468	26.353
900	18.304	81.118	70.217	9.812	-99.870	-96.074	23.329
1000	18.576	83.062	71.405	11.656	-100.397	-95.255	20.817
1100	18.785	84.842	72.547	13.525	-100.767	-94.323	18.719
1200	18.948	86.484	73.641	15.412	-100.128	-93.157	16.068
1300	19.078	88.006	74.688	17.313	-100.484	-92.063	13.476
1400	19.182	89.424	75.691	19.226	-100.835	-90.940	11.106
1500	19.268	90.750	76.651	21.149	-101.183	-89.792	9.150
1600	19.338	91.996	77.572	23.080	-101.529	-88.621	7.2104
1700	19.398	93.171	78.445	25.016	-101.875	-87.430	5.4299
1800	19.448	94.281	79.264	26.959	-102.221	-86.218	4.0468
1900	19.490	95.333	80.120	28.906	-102.569	-84.983	3.0775
2000	19.527	96.334	80.906	30.857	-102.918	-83.734	2.4136
2100	19.558	97.287	81.643	32.811	-103.269	-82.467	1.982
2200	19.585	98.198	82.344	34.768	-103.624	-81.182	1.6064
2300	19.609	99.069	83.100	36.728	-103.980	-79.882	1.2790
2400	19.631	99.904	83.783	38.690	-110.340	-78.564	7.154
2500	19.649	100.706	84.444	40.654	-110.704	-77.234	6.751
2600	19.668	101.477	85.095	42.620	-111.070	-75.899	6.379
2700	19.681	102.210	85.706	44.587	-111.441	-74.529	6.032
2800	19.694	102.935	86.308	46.556	-252.823	-69.848	5.452
2900	19.706	103.627	86.864	48.526	-252.895	-63.313	4.771
3000	19.717	104.295	87.463	50.497	-252.871	-56.773	4.136
3100	19.727	104.942	88.016	52.469	-252.850	-50.237	3.542
3200	19.736	105.568	88.555	54.442	-252.835	-43.702	2.985
3300	19.744	106.175	89.080	56.416	-252.821	-37.166	2.461
3400	19.751	106.765	89.581	58.391	-252.811	-30.635	1.969
3500	19.758	107.338	90.090	60.366	-252.806	-24.105	1.505
3600	19.764	107.894	90.577	62.343	-252.803	-17.581	1.066
3700	19.770	108.436	91.052	64.319	-252.805	-11.052	.682
3800	19.775	108.963	91.517	66.296	-252.809	-4.494	.258
3900	19.780	109.477	91.971	68.274	-252.817	2.040	-.114
4000	19.785	109.978	92.415	70.252	-252.829	8.571	-.468
4100	19.789	110.466	92.849	72.231	-252.845	15.107	-.805
4200	19.793	110.943	93.274	74.210	-252.865	21.643	-1.126
4300	19.796	111.409	93.691	76.180	-252.887	28.182	-1.432
4400	19.800	111.864	94.098	78.170	-252.916	34.712	-1.724
4500	19.803	112.309	94.498	80.150	-252.947	41.258	-2.004
4600	19.806	112.744	94.890	82.130	-252.984	47.801	-2.271
4700	19.809	113.170	95.275	84.111	-253.025	54.331	-2.526
4800	19.811	113.588	95.652	86.092	-253.071	60.868	-2.771
4900	19.814	113.996	96.022	88.073	-253.123	67.416	-3.007
5000	19.816	114.396	96.385	90.055	-253.180	73.955	-3.232
5100	19.818	114.789	96.742	92.036	-253.244	80.500	-3.450
5200	19.820	115.174	97.093	94.018	-253.314	87.037	-3.658
5300	19.822	115.551	97.438	96.000	-253.389	93.592	-3.859
5400	19.824	115.922	97.773	97.983	-253.473	100.135	-4.052
5500	19.826	116.286	98.110	99.965	-253.564	106.681	-4.239
5600	19.828	116.643	101.948	101.948	-253.665	113.236	-4.419
5700	19.829	116.994	98.760	103.931	-253.774	119.781	-4.592
5800	19.831	117.339	99.078	105.914	-253.892	126.344	-4.761
5900	19.832	117.678	107.897	107.897	-254.021	132.901	-4.929
6000	19.833	118.011	99.668	109.880	-254.163	139.461	-5.080

Dialuminum Dioxide Unipositive Ion (Al₂O₂⁺)

GFW = 85.9612

(Ideal Gas)

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o /T)	H ^o - H ^o ₂₉₈ /T	ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	13.059	64.387	64.387	.000	128.963	- 94.532
300	13.139	64.468	64.387	-.024	128.949	- 93.939
400	15.011	68.519	64.927	1.437	130.999	- 70.084
500	16.319	72.018	66.003	3.007	131.073	- 55.765
600	17.205	75.077	67.266	4.656	131.176	- 46.213
700	17.514	76.168	68.569	6.233	131.246	- 38.260
800	17.714	76.578	69.816	7.749	131.286	- 31.260
900	17.856	76.939	71.149	9.204	131.346	- 25.273
1000	18.000	77.232	72.539	10.604	131.366	- 20.273
1100	18.145	77.467	73.979	11.952	131.366	- 16.164
1200	18.290	77.647	75.467	13.246	131.346	- 12.846
1300	18.435	77.772	76.907	14.494	131.306	- 10.276
1400	18.579	77.847	78.297	15.698	131.246	- 8.306
1500	18.722	77.872	79.647	16.858	131.166	- 6.836
1600	18.864	77.847	80.957	17.974	131.066	- 5.786
1700	19.005	77.772	82.227	19.048	130.946	- 5.016
1800	19.145	77.647	83.457	20.080	130.806	- 4.446
1900	19.283	77.467	84.647	21.070	130.646	- 4.016
2000	19.419	77.232	85.797	22.018	130.466	- 3.706
2100	19.552	76.939	86.907	22.924	130.266	- 3.496
2200	19.682	76.578	87.972	23.788	130.046	- 3.346
2300	19.808	76.168	89.000	24.610	129.806	- 3.246
2400	19.930	75.714	90.000	25.390	129.546	- 3.196
2500	20.048	75.218	91.000	26.128	129.266	- 3.196
2600	20.162	74.682	92.000	26.824	128.966	- 3.246
2700	20.272	74.107	93.000	27.478	128.646	- 3.346
2800	20.378	73.492	94.000	28.090	128.306	- 3.496
2900	20.480	72.837	95.000	28.660	127.946	- 3.696
3000	20.578	72.142	96.000	29.188	127.566	- 3.946
3100	20.672	71.407	97.000	29.674	127.166	- 4.246
3200	20.762	70.632	98.000	30.118	126.746	- 4.596
3300	20.848	69.816	99.000	30.518	126.306	- 4.996
3400	20.930	68.957	100.000	30.874	125.846	- 5.446
3500	21.008	68.057	101.000	31.188	125.366	- 5.946
3600	21.082	67.117	102.000	31.458	124.866	- 6.496
3700	21.152	66.137	103.000	31.684	124.346	- 7.096
3800	21.218	65.117	104.000	31.866	123.806	- 7.746
3900	21.280	64.057	105.000	32.004	123.246	- 8.446
4000	21.338	62.957	106.000	32.198	122.666	- 9.196
4100	21.392	61.817	107.000	32.348	122.066	- 9.996
4200	21.442	60.637	108.000	32.454	121.446	- 10.846
4300	21.488	59.417	109.000	32.516	120.806	- 11.746
4400	21.530	58.157	110.000	32.536	120.146	- 12.696
4500	21.568	56.857	111.000	32.512	119.466	- 13.696
4600	21.602	55.517	112.000	32.444	118.766	- 14.746
4700	21.632	54.137	113.000	32.332	118.046	- 15.846
4800	21.658	52.717	114.000	32.176	117.306	- 16.996
4900	21.680	51.257	115.000	31.976	116.546	- 18.196
5000	21.698	49.757	116.000	31.732	115.766	- 19.446
5100	21.712	48.217	117.000	31.444	114.966	- 20.746
5200	21.722	46.637	118.000	31.112	114.146	- 22.096
5300	21.728	45.017	119.000	30.736	113.306	- 23.496
5400	21.730	43.357	120.000	30.316	112.446	- 24.946
5500	21.728	41.657	121.000	29.852	111.566	- 26.446
5600	21.722	39.917	122.000	29.344	110.666	- 27.996
5700	21.712	38.137	123.000	28.792	109.746	- 29.596
5800	21.698	36.317	124.000	28.196	108.806	- 31.246
5900	21.680	34.457	125.000	27.556	107.846	- 32.946
6000	21.658	32.557	126.000	26.872	106.866	- 34.696

June 30, 1968

DIALUMINUM DIOXIDE UNIPosITIVE ION (Al₂O₂⁺) (IDEAL GAS)

GFW = 85.9612

ΔH_f^o = 132.3 ± 20 kcal/mol

ΔH_f^o_{298.15} = 131 ± 20 kcal/mol

Point Group [D_{2h}]

S_{298.15}^o = [64.4 ± 3] gibbs/mol

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies	
ω_1 , cm ⁻¹	ω_1 , cm ⁻¹
[180] (1)	[850] (1)
[550] (1)	[900] (1)
[850] (1)	[900] (1)

Bond Distance: Al-O = [1.66] Å
Bond Angle: O-Al-O = [90°]
Product of the Moments of Inertia: I_AI_BI_C = [1.777 × 10⁻¹¹⁴] g³ cm⁶

Heat of Formation

G. DeMaria, J. Drowart, and M. G. Inghram, J. Chem. Phys. 30, 318 (1959), have reported an ionization potential for Al₂O₂⁺ of 9.9 ± 0.5 eV (228 kcal). Using this value in conjunction with ΔH_f^o (Al₂O₂⁺, g) = -97 kcal/mol, we obtain ΔH_f^o (Al₂O₂⁺, g) = 131 ± 20 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is assumed to be the same as that used for Al₂O₂. The bond length is assumed to be longer than that in Al₂O₂ and is made equal to that reported for Al₂O. The bond angle is arbitrarily estimated to be the same as that in Al₂O₂. The vibrational frequencies are estimated to be slightly lower than those for Al₂O₂, since the Al₂O₂⁺ molecule should be less rigidly bound. The ground state is assumed to be doublet, since there is an odd number of electrons. The individual moments of inertia are I_A = 7.32 × 10⁻³⁹ g cm², I_B = 1.234 × 10⁻³⁸ g cm², and I_C = 1.966 × 10⁻³⁸ g cm². The enthalpy at 0°K is -3.010 kcal/mole.

Al₂O₂⁺

Aluminum Oxide (alpha Al₂O₃)
(Crystal) Mol. Wt. = 101.960

ALUMINUM OXIDE (ALPHA Al₂O₃)

(CRYSTAL)

MOL. WT. = 101.960

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	ΔH° _f	ΔF° _f	Log K _p
0	+000	+000	INFINITE	- 397.494	- 397.494	INFINITE
100	3.069	1.024	24.184	- 392.241	- 392.241	857.201
200	12.223	5.846	13.711	- 389.838	- 389.838	421.047
298	18.889	12.174	12.174	- 387.078	- 387.078	277.125
300	18.979	12.201	12.174	- 387.040	- 377.940	275.316
400	22.986	18.339	12.072	- 400.455	- 370.418	202.378
500	25.345	23.752	14.598	- 400.475	- 362.891	158.612
600	26.889	28.517	16.529	- 400.404	- 355.389	129.444
700	27.999	32.149	18.569	- 400.098	- 347.920	108.620
800	28.720	34.934	20.618	- 399.697	- 340.500	92.075
900	29.154	36.961	22.633	- 399.497	- 333.066	80.475
1000	29.414	38.078	24.634	- 404.522	- 325.301	71.091
1100	30.176	43.938	26.761	- 404.181	- 317.396	63.058
1200	30.994	49.314	29.012	- 403.847	- 309.250	56.360
1300	31.760	54.253	31.297	- 403.019	- 299.868	49.873
1400	31.420	55.509	32.439	- 402.481	- 286.086	41.681
1500	31.920	57.559	34.321	- 402.119	- 278.334	38.017
1600	32.490	61.253	37.117	- 401.633	- 262.920	31.026
1700	32.760	63.116	38.439	- 400.613	- 255.254	28.359
2000	33.000	64.803	39.716	- 400.075	- 247.619	27.057
2100	33.220	66.419	40.949	- 399.521	- 240.011	24.977
2200	33.470	67.869	42.142	- 398.956	- 232.442	23.086
2300	33.660	69.188	43.303	- 397.776	- 224.915	21.390
2400	34.100	72.286	45.405	- 397.172	- 209.834	18.343
2600	34.310	73.027	46.561	- 396.550	- 202.354	17.009
2700	34.520	74.926	47.589	- 395.915	- 194.899	15.775
2800	34.730	77.008	48.596	- 395.307	- 187.470	14.631
2900	34.940	78.608	49.660	- 394.727	- 179.958	13.531
3000	35.140	79.596	50.608	- 394.172	- 172.472	12.478
3100	35.340	79.751	51.433	- 393.642	- 164.984	10.334
3200	35.520	80.076	52.135	- 393.132	- 157.500	9.161
3300	35.720	80.577	52.716	- 392.642	- 150.028	8.000
3400	35.906	81.042	53.177	- 392.172	- 142.577	7.028
3500	36.095	81.085	54.021	- 391.727	- 135.152	6.056

Dec. 31, 1980; Sept. 30, 1961; Mar. 31, 1964

$$\Delta H_f^0 = -397.5 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -400.4 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_m = 298.30 \pm 0.56 \text{ kcal. mole}^{-1}$$

$$S_m^{298.15} = 12.174 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 2315^\circ \text{K.}$$

Heat of Formation.

The value of ΔH_f derived from the direct combustion of pure aluminum in oxygen was taken from A. D. Mah, J. Phys. Chem. **61**, 1572 (1957). Other values for ΔH_f obtained in the same way are: $-399.04 \pm .24 \text{ kcal. mole}^{-1}$ reported by P. E. Snyder and H. Seitz, J. Am. Chem. Soc. **87**, 683 (1945); $-400.4 \pm .3 \text{ kcal. mole}^{-1}$ reported by C. E. Holley, Jr., and E. J. Huber, Jr., J. Am. Chem. Soc. **72**, 5577 (1951); and $-402 \pm 2 \text{ kcal. mole}^{-1}$ reported by A. Schneider and O. Gattow, Z. anorg. u. allgem. Chem. **277**, 41 (1954).

Heat Capacity and Entropy.

The heat capacity measurements reported by G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, (15° to 1200°K.), J. Research Natl. Bur. Standards **57**, 67 (1956), were employed in this table. Low temperature measurements were also made by P. Simon and R. C. Swain (30-280°K.), Z. Physik. Chem. **28B**, 169 (1935); E. C. Kerr, H. L. Johnston, and M. C. Hallett (20° to 295°K.), J. Am. Chem. Soc. **72**, 4740 (1950); J. W. Edwards and G. L. Kingdon (53-291°K.), Trans. Faraday Soc. **59**, 1313-22 (1962); E. N. Rodigina and K. Z. Gmel'skii, (100-900°K.), Zhur. Fiz. Khim. **32**, 1859-62 (1956); B. E. Walker, J. A. Grand, and R. R. Miller (300-900°K.), J. Phys. Chem. **60**, 231-3 (1956); R. Dawson, E. B. Brackett, and T. E. Brackett (700-1400°K.), J. Phys. Chem. **67**, 1669 (1963), and L. Terebesi (0-1300°K.), Helv. Chim. Acta. **47**, 804 (1954). All of the above low temperature data are in good agreement with Furukawa's work.

The heat capacities above 1200°K. (1200-2500°K.) were taken from the enthalpy measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and S. M. Ponomchikov, Ukr. Fiz. Zh. **7**, 205-10 (1962). The heat capacity values above 2500°K. were extrapolated. High temperature measurements were also made by the following investigators: V. Ya. Chekhovskoi (500-2000°K.), Inzh. Fiz. Zh., Akad. Nauk. Belorussk SSR **5**, 62-5 (1962); A. Perrier and M. Olette (1100-2300°K.), Compt. Rend. **254**, 4293-95 (1962); C. H. Shomate and B. P. Naylor (500-1800°K.), J. Am. Chem. Soc. **87**, 72 (1945) and H. L. Johnston and M. Hoch (1000-2000°K.), J. Phys. Chem. **65**, 1184-5 (1961); and V. A. Kirillin, A. E. Sheidlin, and V. Ya. Chekhovskii (500-2000°K.), Doklady Akad. Nauk. SSSR **135**, 125-8 (1960). Numerical values were not available from Kirillin, et al., but graphical values were in close agreement with an extrapolation of Furukawa's data. The entropy at 298.15 was reported by T. Furukawa, et al., loc. cit., using $S_{15}^0 = 0.0105 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The melting data were obtained from the measurements of P. B. Kantor, L. S. Lazareva, V. V. Kandyba, and E. M. Ponomchikov, loc. cit. S. J. Schneider "Compilation of the Melting Points of the Metal Oxides," NRS Monograph **68**, p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°K.

Aluminum Oxide, Gamma (γ - Al_2O_3)
(Crystal) Mol. Wt. = 101.9612

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0							
100							
200							
298	19.833	12.550	12.550	0.000	-396.000	-373.790	273.982
300	19.928	12.673	12.550	0.037	-396.005	-373.652	272.193
400	24.135	13.368	12.550	2.254	-396.052	-366.184	200.064
500	26.612	14.091	13.043	4.799	-395.866	-356.736	156.796
600	28.233	14.694	12.550	7.545	-395.570	-351.337	127.068
700	29.367	15.135	11.238	10.428	-395.224	-343.991	107.394
800	30.196	15.453	9.812	13.407	-394.876	-336.697	91.977
900	30.804	15.685	8.387	16.458	-394.570	-329.443	79.996
1000	31.305	15.837	6.962	19.565	-394.370	-321.853	70.336
1100	31.623	15.912	5.537	22.711	-394.000	-314.122	62.407
1200	31.987	15.943	4.112	25.991	-393.610	-306.423	55.805
1300	32.447	15.932	2.687	29.413	-393.190	-298.756	50.223
1400	32.855	15.887	1.262	32.878	-392.738	-291.123	45.444
1500	33.193	15.812	-0.163	36.381	-392.260	-283.527	41.306
1600	33.516	15.707	-1.588	39.916	-391.758	-275.960	37.693
1700	33.824	15.573	-3.013	42.384	-391.232	-268.425	34.507
1800	34.115	15.415	-4.438	44.781	-390.684	-260.921	31.679
1900	34.390	15.232	-5.863	47.109	-390.119	-253.451	29.152
2000	34.650	15.037	-7.288	49.378	-389.535	-246.013	26.882
2100	34.889	14.824	-8.703	51.595	-388.934	-238.601	24.830
2200	35.123	14.591	-10.118	53.759	-388.319	-231.219	22.968
2300	35.348	14.348	-11.533	55.876	-387.686	-223.862	21.271
2400	35.574	14.095	-12.948	57.946	-387.036	-216.533	19.717
2500	35.801	13.833	-14.363	60.000	-386.362	-209.242	18.291
2600	36.026	13.561	-15.778	62.049	-385.666	-201.965	16.976
2700	36.252	13.280	-17.193	64.094	-384.947	-194.721	15.761
2800	36.472	13.000	-18.608	66.135	-384.204	-187.504	14.595
2900	36.687	12.719	-20.023	68.171	-383.438	-180.313	13.485
3000	36.897	12.438	-21.438	70.200	-382.656	-173.147	12.423

Al_2O_3

MOL. WT. = 101.9612

ALUMINUM OXIDE, GAMMA (γ - Al_2O_3) (CRYSTAL)

$\Delta H^\circ_f 0$ = Unknown

$\Delta H^\circ_f 298.15 = [-396.0 \pm 0.5] \text{ kcal. mole}^{-1}$

$\Delta H^\circ_m = [20.9] \text{ kcal. mole}^{-1}$

$S^\circ_{298.15} = [12.55] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 2323^\circ\text{K.}$

Heat of Formation.

The enthalpy change (ΔH°_f) for the transition $\text{Al}_2\text{O}_3(\gamma, c) \rightarrow \text{Al}_2\text{O}_3(\alpha, c)$ has been determined by (1) V. Kottomarov and M. Rey, *Silicates Ind.* 28, 9 (1963); and (2) T. Yokokawa and O. J. Kleppa, *J. Phys. Chem.* 68, 3246 (1964). The results obtained are presented in the table. The enthalpies of solution for $\text{Al}_2\text{O}_3(\gamma, c)$ and $\text{Al}(c)$ in 2N KOH(aq.) have been measured by (3) K. K. Kelley, C. H. Shonate, F. E. Young, E. F. Naylor, A. E. Salo and E. H. Hurfman, U. S. Bur. Mines Tech. Rept. 668 (1946). Based on their reported values, -16.13 ± 1.0 and $-196.02 \pm 0.25 \text{ kcal. mole}^{-1}$, respectively, the heat of formation ($\Delta H^\circ_f 298.15$) for $\text{Al}_2\text{O}_3(\gamma, c)$ was evaluated to be $-384.84 \pm 1.1 \text{ kcal. mole}^{-1}$. Hence, the enthalpy of transition ($\gamma \rightarrow \alpha$) was calculated as $-15.6 \pm 1.1 \text{ kcal. mole}^{-1}$, using $\Delta H^\circ_f 298.15 (\text{Al}_2\text{O}_3, \alpha, c) = -400.4 \text{ kcal. mole}^{-1}$.

Source	Method	Temperature, °K.	ΔH°_f , kcal. mole ⁻¹	ΔH°_f , 298.15, kcal. mole ⁻¹
(2)	solution calorimetry	978	-5.3	-4.4
(1)	differential thermal analysis	1473	-11.0	-9.4
(3)	solution calorimetry	298.15	-15.6	-15.6

The heat of formation for $\text{Al}_2\text{O}_3(\gamma, c)$ was calculated from that for $\text{Al}_2\text{O}_3(\alpha, c)$ and the ΔH°_f value reported by Yokokawa and Kleppa, loc. cit., which was arbitrarily selected.

Heat Capacity and Entropy.

The heat capacities were assumed to be larger than those for $\text{Al}_2\text{O}_3(\alpha, c)$ by 5% at each temperature. The value of $S^\circ_{298.15}$ was estimated such that at T_m , $\Delta H^\circ_f (\text{Al}_2\text{O}_3, \gamma, c) > \Delta H^\circ_f (\text{Al}_2\text{O}_3, \alpha, c)$.

Melting Data.

T_m was reported by M. Plummer, *J. Appl. Chem.* 9, 35 (1958). The difference between ΔH°_f for $\text{Al}_2\text{O}_3(\gamma, c)$ and $\text{Al}_2\text{O}_3(\alpha, c)$ at T_m is ΔH°_m .

Al_2O_3

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	(F°-H ₂₉₈)/T S°	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o kcal. mole ⁻¹	Log K _p
0						
100						
200						
298	18.889	23.728	23.728	4.000	- 354.478	259.827
300						
350	18.970	23.845	23.728	4.038	- 354.362	258.140
400	19.051	23.962	23.728	4.077	- 354.246	256.453
500	19.345	24.292	24.150	4.571	- 341.623	149.316
600	20.689	40.062	28.080	7.189	- 335.276	122.118
700	27.969	44.291	30.090	9.494	- 328.961	102.701
800	28.756	45.601	32.114	12.753	- 322.615	78.432
900	28.514	46.022	34.082	16.660	- 316.245	54.704
1000	28.514	46.022	35.982	21.660	- 309.805	67.704
1100	30.176	57.481	37.808	21.660	- 303.054	60.208
1200	30.464	60.110	39.550	24.672	- 296.355	53.967
1300	30.935	62.980	41.236	27.724	- 289.700	47.972
1400	31.420	66.090	42.863	30.843	- 283.090	42.264
1500	31.620	67.060	44.387	34.009	- 276.533	40.264
1600	34.623	69.110	45.869	37.186	- 269.966	36.847
1700	34.623	71.200	47.298	40.669	- 263.208	33.836
1800	34.623	73.188	48.682	44.511	- 256.405	31.165
1900	34.623	75.000	50.000	48.511	- 249.555	28.807
2000	34.623	76.836	51.314	51.036	- 242.780	26.638
2100	34.623	78.525	52.574	54.498	- 236.178	24.703
2200	34.623	80.136	53.790	57.960	- 229.771	22.948
2300	34.623	81.676	54.960	61.422	- 223.503	21.348
2400	34.623	83.142	56.082	64.887	- 217.403	19.890
2500	34.623	84.562	57.223	68.347	- 211.485	18.540
2600	34.623	85.920	58.301	71.809	- 205.833	17.301
2700	34.623	87.226	59.348	75.272	- 200.407	16.156
2800	34.623	88.486	60.366	78.734	- 195.196	15.097
2900	34.623	89.700	61.344	82.197	- 190.196	14.077
3000	34.623	90.874	62.281	85.659	- 185.407	13.200
3100	34.623	92.010	63.261	89.121	- 180.827	12.412
3200	34.623	93.109	64.177	92.583	- 176.453	11.701
3300	34.623	94.174	65.044	96.045	- 172.283	11.062
3400	34.623	95.201	65.869	99.508	- 168.317	10.492
3500	34.623	96.211	66.791	102.970	- 164.556	9.962

$S_{298.15}^o = [23.728] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta F_{298.15}^o = [373.356] \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = 28.30 \pm 0.55 \text{ kcal. mole}^{-1}$
 $T_m = 2315^\circ\text{K.}$

Heat of Formation.

The heat of formation for the liquid was obtained from $\Delta H_f^o 298.15$ for a crystal by adding on ΔH_m plus the difference between $H_{2315}^o-H_{298.15}^o$ for crystal and liquid.

Heat Capacity and Entropy.

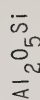
The heat capacities of the liquid $\alpha\text{-Al}_2\text{O}_3$ was taken from the crystal heat capacities up to 1600°K. where a glass transition was assumed. From 1600°K. to 3500°K. the heat capacities were assumed to be the constant value of 34.623 measured by P. B. Kantor, L. S. Lazareva, V. V. Kandyba and E. M. Fonichov ($2300\text{-}2500^\circ\text{K.}$) Ukr. Fiz. Zh. 7, 205-10 (1962).

The entropy at 298.15°K. was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting data was taken from the measurements of P. B. Kantor, et al., loc. cit. S. J. Schneider, "Compilation of the Melting Points of the Metal Oxides," NBS Monograph 68 p. 6, Oct. 10, 1963, gives a review of the melting points that range from 2267 to 2345°K.

Sillimanite (Al₂SiO₅)
(Crystal)



GFW = 162.046

T, °K	Cp°	S°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	INFINITE	4.164	614.830	614.830	INFINITE
100	7.714	3.609	42.667	3.908	614.584	606.175	1324.794
200	20.500	13.048	25.407	2.472	618.053	595.168	650.369
298	29.210	22.987	22.987	∞	618.810	593.760	427.907
300	29.342	23.169	22.988	0.54	618.819	583.543	425.111
400	35.248	32.674	24.217	3.303	619.053	571.736	312.382
500	39.005	40.769	26.714	7.027	618.962	559.912	244.737
600	41.354	48.090	29.680	11.051	618.712	548.125	199.654
700	43.000	54.640	32.682	19.631	618.383	536.384	161.340
800	44.215	60.620	36.882	24.107	617.981	524.684	124.583
900	45.294	65.491	38.906	28.685	617.556	513.039	109.505
1000	46.256	70.514	41.829	33.394	622.535	501.051	97.141
1100	47.122	74.964	44.641	38.354	622.117	489.926	86.148
1200	47.827	78.975	47.316	42.931	621.617	478.791	76.483
1300	48.427	82.575	49.836	47.873	621.048	467.618	70.429
1400	49.012	86.423	52.428	52.872	620.518	456.429	64.229
1500	50.377	90.072	54.823	57.948	619.909	445.229	58.366
1600	51.126	93.347	57.129	63.920	619.299	434.010	53.600
1700	51.592	96.154	59.408	69.920	618.690	422.782	48.879
1800	51.913	98.584	61.571	73.615	618.081	411.549	44.166
1900	52.131	102.316	63.571	78.983	617.472	400.300	39.401
2000	54.024	105.069	65.578	84.421	626.809	389.051	34.636
2100	54.735	107.722	67.522	89.509	626.199	377.802	30.201
2200	55.144	110.785	69.428	95.509	625.590	366.553	25.738
2300	55.484	113.694	71.239	101.158	624.981	355.304	21.275
2400	56.845	115.169	73.020	106.878	624.372	344.055	16.812
2500	57.544	117.504	74.753	112.667	623.763	332.806	12.349
2600	58.241	119.774	76.441	118.667	623.154	321.557	7.886
2700	58.428	121.181	78.494	124.858	622.545	310.308	3.423
2800	58.612	122.446	80.441	131.258	621.936	299.059	-1.040
2900	60.319	126.346	81.263	138.451	755.014	287.810	-5.507
3000	61.007	128.302	82.796	146.518	752.974	276.561	-9.974

SILLIMANITE (Al₂SiO₅)

(CRYSTAL)

GFW = 162.046

ΔHf° = -614.83 ± 0.5 kcal/mol

ΔHf°_{298.15} = -618.81 ± 0.5 kcal/mol

S°_{298.15} = 22.987 ± 0.1 gibbs/mol

Heat of Formation

The heat of the reaction Al₂O₃(s) + SiO₂(quartz) → Al₂SiO₅ (sillimanite) has been determined at 968°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -1.51 ± 0.15 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔHr° = -0.71 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 245, 193 (1975); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957) suggested that ΔHr° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔHr° should lie between 0 and -6 kcal/mol. C. R. Waldhaug, Am. Mineralogist 50, 186 (1965), calculated ΔHr° = -0.356 kcal/mol from high temperature - high pressure equilibria. These later values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.4° to 296.5°K by S. S. Todd, J. Am. Chem. Soc. 72, 4742 (1950). The entropy is based on S°_{298.15} = 0.73 gibbs/mol. The high temperature enthalpy has been measured to 1500°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot (C. H. Shomate, J. Phys. Chem. 58, 368 (1954)). The crystal structure of sillimanite, L. Bragg and G. F. Claringbull, "Crystal Structure of Minerals," Vol. IV, G. Bell and Sons Ltd., London, 1965, indicates that there is no mixing of the tetra-coordinated aluminum and silicon atoms. Thus there should be no residual entropy at 0°K.



T, °K	Cp°	gkcal/mol S° - (C° - H° ₂₉₈)/T	gkcal/mol H° - H° ₂₉₈	gkcal/mol ΔH°	ΔG°	Log Kp
0	7.000	INFINITE	-	-	-	INFINITE
100	20.237	3.282	4.085	-615.461	-615.461	1.115
200	20.237	21.695	-	-615.752	-595.735	650.949
298	29.339	22.240	-	-619.520	-584.259	428.273
300	29.474	22.462	.054	-619.529	-584.041	425.473
400	35.747	31.654	3.334	-619.732	-572.367	312.607
500	39.524	40.266	7.111	-619.589	-560.287	244.791
600	41.710	47.675	11.478	-619.295	-548.454	199.774
700	43.276	54.227	15.430	-618.943	-536.673	167.557
800	44.484	60.086	19.820	-618.582	-524.947	143.409
900	45.495	65.363	24.320	-618.253	-513.261	120.167
1000	46.377	70.225	28.914	-618.018	-501.423	100.547
1100	47.175	74.683	33.592	-622.589	-489.089	97.173
1200	47.916	78.820	38.347	-622.117	-476.974	86.869
1300	48.617	82.683	43.174	-621.604	-464.898	78.156
1400	49.289	86.311	48.069	-621.051	-452.864	70.685
1500	49.940	89.734	53.031	-620.460	-440.872	64.235
1600	50.578	92.977	58.057	-619.830	-428.919	58.588
1700	51.195	96.062	63.145	-631.152	-416.902	53.596
1800	51.806	99.005	68.295	-630.391	-404.317	49.091
1900	52.410	101.823	73.506	-628.565	-391.782	45.065
2000	53.007	104.526	78.777	-625.732	-379.290	41.447
2100	53.599	107.127	84.108	-627.832	-366.840	38.178
2200	54.186	109.634	89.497	-626.891	-354.437	35.210
2300	54.768	112.055	94.945	-625.899	-342.069	32.504
2400	55.345	114.398	100.450	-624.967	-329.746	30.027
2500	55.917	116.669	106.013	-623.792	-317.482	27.754
2600	56.484	118.873	111.634	-622.669	-305.246	25.658
2700	57.044	121.016	117.310	-621.506	-293.064	23.722
2800	57.603	123.100	123.043	-759.119	-279.256	21.797
2900	58.155	125.131	128.830	-757.345	-262.150	19.656
3000	58.705	127.112	134.673	-755.529	-245.104	17.656

ΔH°₀ = -615.46 ± 0.5 kcal/mol

ΔH°_{298.15} = -619.52 ± 0.5 kcal/mol

S°_{298.15} = 22.28 ± 0.1 gibbs/mol

Heat of Formation

The heat of the reaction $Al_2O_3(\alpha) + SiO_2(\text{quartz}) + Al_2SiO_5(\text{andalusite})$ has been determined at 968°K by J. L. Holm and O. J. Kleppa, *J. Phys. Chem.* **70**, 1690 (1966) and *Am. Mineralogist* **51**, 1608 (1966), to be -1.99 ± 0.17 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta H^\circ_{298} = -1.42$ kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, *Z. Anorg. Allgem. Chem.* **115**, 193 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, *J. Am. Ceram. Soc.* **40**, 206 (1957), suggested that ΔH° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, *U. S. Bur. Mines RI 6370*, 1964, conclude that ΔH° should lie between 0 and -6 kcal/mol. C. R. Waldbaum, *Am. Mineralogist* **50**, 186 (1965), calculated $\Delta H^\circ = -1.108$ kcal/mol from high temperature - high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.9° to 796.2°K by S. S. Todd, *J. Am. Chem. Soc.* **72**, 4742 (1950). The entropy is based on $S^\circ_{298} = 0.62$ gibbs/mol. The high temperature enthalpy has been measured to 1600°K by L. B. Pankratz and K. K. Kelley, *U. S. Bur. Mines RI 6370*, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, *J. Phys. Chem.* **58**, 368 (1954)]. Since all the aluminum and silicon atoms occupy differently coordinated sites, there is no possibility of any residual entropy of mixing in this polymorph.

Kyanite (Al₂SiO₅)

(Crystal)

GFW = 162.046

T, °K	Cp°	S°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	5.000	0.000	INFINITE	- 3.835	- 615.760	- 615.760	INFINITE
100	5.649	2.195	19.143	- 3.678	- 617.604	- 607.037	195.706
200	19.354	16.143	22.411	- 2.414	- 619.245	- 595.818	651.080
298	26.099	20.632	20.632	.000	- 620.060	- 584.159	626.178
300	26.239	20.213	20.533	3.054	- 620.070	- 593.907	425.376
400	37.148	29.174	21.774	10.424	- 620.372	- 590.603	312.439
500	39.555	31.498	23.765	7.007	- 620.173	- 559.487	247.439
600	42.120	45.350	26.754	11.158	- 619.655	- 547.619	199.470
700	43.795	51.275	26.893	15.457	- 619.456	- 535.609	167.225
800	45.000	57.404	33.030	19.899	- 619.043	- 523.663	143.058
900	45.845	63.751	38.046	24.484	- 618.603	- 511.751	124.772
1000	46.896	69.153	39.661	29.092	- 623.398	- 499.553	109.173
1100	47.744	72.663	41.913	33.825	- 622.696	- 487.174	96.793
1200	48.558	76.453	44.652	38.641	- 622.363	- 474.860	86.484
1300	49.259	80.768	47.282	43.532	- 621.768	- 462.591	77.769
1400	49.841	84.843	49.841	48.484	- 621.167	- 450.361	70.305
1500	50.334	88.508	52.332	53.534	- 620.517	- 438.151	63.844
1600	51.178	91.190	54.565	58.600	- 619.627	- 426.057	58.197
1700	51.799	94.311	56.812	63.749	- 618.662	- 413.862	53.206
1800	52.414	97.289	58.979	68.959	- 617.627	- 401.104	48.701
1900	53.024	100.140	61.011	74.231	- 616.480	- 388.394	44.676
2000	53.626	102.475	63.093	79.564	- 626.405	- 375.741	41.059
2100	54.220	105.506	65.050	84.956	- 627.524	- 363.127	37.791
2200	54.609	108.642	66.947	90.408	- 626.520	- 350.563	34.825
2300	55.394	110.491	68.787	95.918	- 625.466	- 338.088	32.121
2400	56.156	112.458	70.572	101.467	- 624.270	- 325.580	29.456
2500	56.562	112.158	72.312	107.114	- 623.251	- 313.153	27.375
2600	57.141	117.368	74.003	112.799	- 622.044	- 300.759	25.281
2700	57.718	119.555	75.650	118.542	- 620.614	- 288.428	23.347
2800	58.293	121.664	77.256	124.363	- 619.068	- 276.359	21.424
2900	58.864	123.725	78.831	130.261	- 617.406	- 264.566	19.587
3000	59.434	125.725	80.353	136.116	- 734.626	- 250.061	17.887

(CRYSTAL)

KYANITE (Al₂SiO₅)

GFW = 162.046

Al₂O₅Si

ΔHf° = -615.75 ± 0.5 kcal/mol

ΔHf°_{298.15} = -620.06 ± 0.5 kcal/mol

S°_{298.15} = 20.032 ± 0.1 gibbs/mol

Heat of Formation

The heat of the reaction Al₂O₃(g) + SiO₂(quartz) → Al₂SiO₅(kyanite) has been determined at 968° by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be -2.37 ± 0.15 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔHf°₂₉₈ = -1.96 kcal/mol, which is used to calculate the adopted value.

The above value is in serious disagreement with the solution data of F. Neumann, Z. Anorg. Allgem. Chem. 145, 183 (1925); this work, however, has recently been questioned by several workers. H. Flood and W. J. Knapp, J. Am. Ceram. Soc. 40, 206 (1957), suggested that ΔHf° was between 0 and -10 kcal/mol. L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964, conclude that ΔHf° should lie between 0 and -6 kcal/mol. R. W. Haskell and R. C. DeVries, J. Am. Ceram. Soc. 47, 202 (1964), from phase equilibria obtained ΔHf° = -2 ± 7 kcal/mol. C. R. Waldbaum, Am. Mineralogist 50, 186 (1965), calculated ΔHf° = -0.622 kcal/mol from high temperature - high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.8° to 296.3° by S. S. Todd, J. Am. Chem. Soc. 72, 4742 (1950). The entropy is based on S°_{298.15} = 0.33 gibbs/mol. The high temperature enthalpy has been measured to 1500°K by L. B. Pankratz and K. K. Kelley, U. S. Bur. Mines RI 6370, 1964. The low and high temperature data were joined smoothly together by means of a Shomate function plot [C. H. Shomate, J. Phys. Chem. 58, 368 (1954)]. The high temperature heat capacity has been measured between 100° and 1200°C by V. Ya. Leonidov, Yu. P. Barskii and N. I. Khitarov, Geochemistry (English Transl.) 1984, 409 (1984). The values reported are in excellent agreement with the adopted functions. Since the aluminum atoms and the silicon atoms occupy different types of sites there is no possibility of any residual entropy of mixing in this polymorph.

Al₂O₅Si

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	-0.00	0.00	INFINITE	= 11.011	-1619.252	-1619.252	INFINITE
100	20.379	14.508	117.651	= 10.334	-1623.850	-1597.221	3490.722
200	54.005	39.355	72.126	= 6.954	-1627.808	-1566.994	1714.516
298	77.830	65.700	65.700	= 0.000	-1627.830	-1536.630	1128.600
300	78.142	66.193	65.701	= 0.144	-1629.854	-1536.101	1121.234
400	93.390	90.882	68.966	8.767	-1630.461	-1508.724	824.328
500	103.250	112.840	75.590	16.625	-1630.228	-1478.303	646.165
600	109.900	132.283	83.451	20.990	-1629.552	-1447.980	527.824
700	114.000	145.134	90.912	40.236	-1628.252	-1417.783	442.652
800	116.000	155.136	97.912	52.177	-1627.700	-1387.731	379.110
900	120.650	179.196	107.953	64.119	-1626.845	-1357.783	329.715
1000	122.700	192.016	115.728	76.288	-1626.141	-1326.823	289.977
1100	124.212	203.782	123.299	88.635	-1625.598	-1295.834	257.379
1200	125.672	214.617	130.624	101.232	-1625.192	-1265.141	230.231
1300	126.940	224.740	137.294	113.757	-1624.991	-1235.941	207.276
1400	128.134	234.212	143.846	126.512	-1624.935	-1207.835	187.615
1500	129.270	243.092	150.169	139.384	-1625.029	-1179.827	170.569
1600	130.097	251.461	156.291	152.352	-1625.285	-1153.003	155.703
1700	130.737	259.480	162.207	165.407	-1625.697	-1127.852	142.552
1800	131.237	267.200	167.863	178.536	-1626.269	-1103.952	130.725
1900	132.551	274.624	173.103	191.751	-1626.991	-1081.666	120.154
2000	133.360	280.844	178.320	205.046	-1627.865	-1061.548	110.649
2100	134.106	287.368	183.359	218.419	-1628.880	-1043.220	102.725
2200	134.672	293.657	188.244	231.795	-1629.995	-1026.403	95.800
2300	135.072	299.657	192.924	245.195	-1631.268	-1011.018	89.717
2400	135.424	305.429	197.511	258.603	-1632.661	-996.909	84.418
2500	135.730	311.018	201.940	272.049	-1634.131	-983.713	79.632
2600	136.212	316.421	206.200	286.572	-1635.724	-971.451	75.109
2700	136.800	321.648	210.398	301.332	-1637.488	-960.001	70.801
2800	137.430	326.730	214.482	316.395	-1639.368	-949.289	66.675
2900	140.978	331.660	218.438	328.345	-1641.406	-939.331	62.704
3000	141.950	336.456	222.292	342.491	-1643.656	-930.000	58.904

Sept. 30, 1966; Sept. 30, 1967

MULLITE (Al₆Si₂O₁₃)

(CRYSTAL)

GFW = 426.053

ΔH_f^o = -1619.25 ± 1.5 kcal/mol

ΔH_f^o 298.15 = -1629.83 ± 1.5 kcal/mol

S_{298.15} = 65.7 ± 3 gibbs/mol

T_m = 2023°K

Heat of Formation

The heat of the reaction 3Al₂O₃(s) + 2SiO₂(quartz) + Al₆Si₂O₁₃ has been determined at 988°K by J. L. Holm and O. J. Kleppa, J. Phys. Chem. 70, 1690 (1966) and Am. Mineralogist 51, 1608 (1966), to be +5.44 ± 0.35 kcal/mol. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to ΔH_f 298 = +4.11 kcal/mol, which is used to calculate the adopted value.

Heat Capacity and Entropy

The low temperature heat capacity and high temperature enthalpy of mullite have been measured by L. B. Pankratz, W. W. Waller and K. K. Kelley, U. S. Bur. Mines RI 6287, 1963. The low temperature investigations extended from 53.5°K to 296.4°K; the Debye-Einstein equation 3D(182/T) + 15E(350/T) + 10E(502/T) + 15E(997/T) represented the data from 53.5° to 114.6°K within 1.4 percent and gave a smooth extrapolation to zero. From this equation the entropy at 51°K was found to be 2.17 gibbs/mol as opposed to the value 1.96 gibbs/mol found by Pankratz et al. However, since it is known that mullite has some of its Al atoms on Si sites, there will be configurational entropy remaining at 0°K. This is borne out by the free energy determinations of R. H. Rein and J. Chipman, Trans. Met. Soc. AIME 233, 415 (1965), and D. A. R. Kay and J. Taylor, Trans. Faraday Soc. 56, 1372 (1960), who obtain ΔG_f 1823 = -5.7 ± 0.1 kcal/mol for the formation from oxide. If the entropies and enthalpies reported by Pankratz et al. are used with the heat of formation, they yield ΔG_f 1823 = +2.9 kcal/mol. Holm and Kleppa, loc. cit., calculate that random mixing of tetra-coordinated aluminum and silicon atoms could produce 7 eu residual entropy. We have added 4.7 eu in order to match the measured ΔG_f 1823.

A review of the enthalpy determination indicated that the values might easily be 2 percent low if as little as 4 percent of kyanite remained unchanged in the sample used for measurement. Since X-ray could not detect this amount, it is not an unreasonable assumption. Accordingly we have checked the effect of increasing the heat capacity above 298°K by 2 percent; this then gives ΔG_f 1823 = -2.10 kcal/mol. In order to bring this within reasonable agreement with the observations a residual configurational entropy of 2 gibbs/mol would be needed. Thus the uncertainty in the residual entropy is of the order of 2 eu due to possible uncertainty in the high temperature heat capacity.

Melting Data

The congruent melting point of mullite was reported by S. Aramaki and R. Roy, Nature 189, 631 (1959).

Boron (B)

(Reference State) At. Wt. = 10.82

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	•000	INFINITE	•	•292	•000	•000	INFINITE
100	•000	•000	•000	•286	•000	•000	•000
200	1.447	•988	1.418	•206	•000	•000	•000
298	2.650	1.403	1.403	•000	•000	•000	•000
300	2.666	1.419	1.403	•005	•000	•000	•000
400	3.760	2.459	1.471	•427	•000	•000	•000
500	4.440	3.257	1.777	•740	•000	•000	•000
600	4.990	4.122	2.097	1.215	•000	•000	•000
700	5.320	4.917	2.444	1.731	•000	•000	•000
800	5.560	5.664	2.799	2.276	•000	•000	•000
900	5.760	6.310	3.153	2.842	•000	•000	•000
1000	5.950	6.827	3.500	3.427	•000	•000	•000
1100	6.120	7.502	3.838	4.031	•000	•000	•000
1200	6.260	8.041	4.166	4.650	•000	•000	•000
1300	6.410	8.548	4.483	5.284	•000	•000	•000
1400	6.540	9.028	4.791	5.931	•000	•000	•000
1500	6.670	9.493	5.089	6.592	•000	•000	•000
1600	6.790	9.918	5.377	7.265	•000	•000	•000
1700	6.900	10.333	5.657	7.950	•000	•000	•000
1800	7.000	10.730	5.927	8.645	•000	•000	•000
1900	7.092	11.110	6.190	9.348	•000	•000	•000
2000	7.170	11.474	6.445	10.057	•000	•000	•000
2100	7.177	11.823	6.693	10.772	•000	•000	•000
2200	7.228	12.158	6.934	11.492	•000	•000	•000
2300	7.274	12.480	7.168	12.217	•000	•000	•000
2400	7.315	12.791	7.396	12.947	•000	•000	•000
2500	7.350	13.098	7.612	13.678	•000	•000	•000
2600	7.300	13.575	7.961	14.408	•000	•000	•000
2700	7.300	14.051	8.248	15.138	•000	•000	•000
2800	7.300	14.524	8.524	15.868	•000	•000	•000
2900	7.300	14.998	8.798	16.598	•000	•000	•000
3000	7.300	15.470	9.067	17.328	•000	•000	•000
3100	7.300	15.940	9.296	18.058	•000	•000	•000
3200	7.300	16.409	9.536	18.788	•000	•000	•000
3300	7.300	16.878	9.768	19.518	•000	•000	•000
3400	7.300	17.346	9.993	20.248	•000	•000	•000
3500	7.300	17.814	10.212	20.978	•000	•000	•000
3600	7.300	18.282	10.424	21.708	•000	•000	•000
3700	7.300	18.750	10.630	22.438	•000	•000	•000
3800	7.300	19.218	10.830	23.168	•000	•000	•000
3900	7.300	19.686	11.026	23.898	•000	•000	•000
4000	4.292	20.154	11.212	24.628	•000	•000	•000
4100	4.985	49.674	12.675	151.596	•000	•000	•000
4200	4.988	49.795	13.558	152.194	•000	•000	•000
4300	4.997	49.912	14.402	152.693	•000	•000	•000
4400	4.997	49.977	15.212	153.193	•000	•000	•000
4500	5.002	50.159	15.995	153.693	•000	•000	•000
4600	5.008	50.246	16.729	154.193	•000	•000	•000
4700	5.015	50.337	17.443	154.694	•000	•000	•000
4800	5.022	50.463	18.130	155.196	•000	•000	•000
4900	5.028	50.568	18.798	155.698	•000	•000	•000
5000	5.039	50.668	19.427	156.202	•000	•000	•000
5100	5.048	50.768	20.041	156.707	•000	•000	•000
5200	5.058	50.866	20.633	157.212	•000	•000	•000
5300	5.069	50.962	21.204	157.718	•000	•000	•000
5400	5.078	51.058	21.766	158.226	•000	•000	•000
5500	5.093	51.151	22.290	158.734	•000	•000	•000
5600	5.107	51.242	22.806	159.244	•000	•000	•000
5700	5.121	51.333	23.306	159.756	•000	•000	•000
5800	5.132	51.416	23.799	160.268	•000	•000	•000
5900	5.142	51.500	24.279	160.780	•000	•000	•000
6000	5.166	51.597	24.714	161.299	•000	•000	•000

Dec. 31, 1960; Dec. 31, 1964

AT. WT. = 10.82

(REFERENCE STATE)

BORON (B)

0 to 2450°K. Crystal
2450 to 3931°K. Liquid
3931 to 6000°K. Ideal Monatomic Gas

See crystal, liquid and ideal monatomic gas for details.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+0.00	INFINITE	+292	+0.00	INFINITE	
100	1.256	2.941	+286	+0.00	+0.00	
200	2.450	1.403	+0.00	+0.00	+0.00	
298	2.650	1.403	+0.00	+0.00	+0.00	
300	2.667	1.419	+0.05	+0.00	+0.00	
400	3.720	2.339	+327	+0.00	+0.00	
500	4.490	3.257	+760	+0.00	+0.00	
600	4.990	4.122	+1,215	+0.00	+0.00	
700	5.320	4.917	+2,444	+0.00	+0.00	
800	5.560	5.644	+2,276	+0.00	+0.00	
900	5.760	6.310	+2,862	+0.00	+0.00	
1000	5.950	6.927	+3,427	+0.00	+0.00	
1100	6.120	7.502	+3,838	+0.00	+0.00	
1200	6.260	8.041	+4,166	+0.00	+0.00	
1300	6.410	8.548	+4,483	+0.00	+0.00	
1400	6.540	9.028	+4,791	+0.00	+0.00	
1500	6.670	9.483	+5,089	+0.00	+0.00	
1600	6.790	9.918	+5,377	+0.00	+0.00	
1700	6.900	10.333	+5,657	+0.00	+0.00	
1800	7.000	10.730	+5,927	+0.00	+0.00	
1900	7.082	11.110	+6,190	+0.00	+0.00	
2000	7.120	11.474	+6,445	+0.00	+0.00	
2100	7.176	11.823	+6,693	+0.00	+0.00	
2200	7.228	12.156	+6,934	+0.00	+0.00	
2300	7.274	12.480	+7,168	+0.00	+0.00	
2400	7.316	12.791	+7,396	+0.00	+0.00	
2500	7.350	13.090	+7,618	+0.00	+0.10	
2600	7.374	13.379	+7,834	+0.28	+0.28	
2700	7.396	13.657	+8,044	+0.51	+0.45	
2800	7.416	13.927	+8,250	+0.767	+0.60	
2900	7.434	14.187	+8,450	+1.009	+0.75	
3000	7.450	14.440	+8,646	+1.264	+0.88	
3100	7.464	14.684	+8,836	+1.422	+1.00	
3200	7.476	14.921	+9,023	+1.641	+1.12	
3300	7.486	15.151	+9,205	+1.859	+1.23	
3400	7.494	15.375	+9,383	+2.075	+1.33	
3500	7.500	15.592	+9,558	+2.289	+1.43	

Dec. 31, 1960; Dec. 31, 1964

$S_{298.15}^0 = 1.403 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 2450 \pm 20^\circ \text{K.}$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Low temperature heat capacities, 18.90 - 303.71°K., were measured by H. L. Johnston, H. N. Hersh and E. C. Kerr, J. Am. Chem. Soc. 73, 1112 (1951). The high temperature heat capacities, 282.8 - 1667.8°K., were measured by R. A. McDonald and D. R. Stull, J. Chem. Eng. Data, 7, 84 (1962). These two sets of data were joined smoothly at 298.15°K. by graphical method. The heat capacity values above 1667.8°K. were estimated by graphical extrapolation. The high temperature Cp, 530 - 800°K., were also determined by S. S. Wise, J. L. Margrave and R. L. Altman, J. Phys. Chem. 64, 915 (1960). The other principal investigators are: (1) J. A. Robertson, Ph. D. Thesis, Cornell University, 1944; (2) A. Magnus and H. Danz, Ann. Phys. (4) 81, 407 (1926); (3) H. Moissan and H. Gautier, Compt. rend. 116, 924 (1893); (4) H. F. Weber, Ann. Phys. (2) 154, 367, 555 (1875); (5) H. Kopp, Trans. Roy. Soc. [London] 155, 71 (1865); and (6) V. Regnault, Ann. chim. et phys. (3) 63, 5 (1861) and Phil. Mag. (4) 23, 103 (1862). The value of $S_{298.15}^0$ was obtained from H. L. Johnston, H. N. Hersh and E. C. Kerr, loc. cit., based on $S_{17}^0 = 0.00139 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The melting point (T_m) of B(c) has been measured by many investigators. The values of T_m reported are in the range 2273 - 2675°K. Based on the relationship between the values of T_m determined and the purities of the boron sample used, the value $T_m = 2450 \pm 20^\circ \text{K.}$ was estimated. The data employed for estimation are those reported by C. F. Oline, J. Electrochem. Soc. 106 (4), 332 (1959), and A. W. Saary and C. E. Myers, J. Phys. Chem. 61, 957 (1957). The estimated value for T_m is in agreement with the value taken by H. I. Schick, et al., "Thermodynamics of Certain Refractory Compounds", ASD-TR-61-260, Part I, Vol. 1, May 1962, in which the reported melting points of boron were reviewed. The heat of melting was calculated assuming entropy of melting is 2.2 cal. deg.⁻¹ mole⁻¹ at 2450°K.

Heat of Sublimation.

The adopted value of ΔH_g^0 298.15 is the weighted average of eight ΔH_g^0 298.15 values derived from vapor pressure data. See B(g) table for details.

Boron (B)

(Liquid) At. Wt. = 10.82

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200							
298	2.650	3.533	3.533	0.000	5.260	4.625	- 3.390
300	2.666	3.549	3.533	0.005	5.260	4.621	- 3.366
400	3.720	5.469	3.651	3.277	5.260	4.408	- 2.408
500	4.480	5.367	3.907	1.740	5.260	4.195	- 1.833
600	4.990	6.252	4.227	1.215	5.260	3.982	- 1.450
700	5.320	7.047	4.574	1.731	5.260	3.769	- 1.177
800	5.560	7.774	4.929	2.276	5.260	3.556	- 0.971
900	5.760	8.440	5.283	2.842	5.260	3.343	- 0.812
1000	5.950	9.057	5.650	3.427	5.260	3.130	- 0.684
1100	6.120	9.632	5.968	4.031	5.260	2.917	- 0.580
1200	6.260	10.171	6.296	4.650	5.260	2.704	- 0.492
1300	6.410	10.678	6.613	5.284	5.260	2.491	- 0.419
1400	6.540	11.158	6.921	5.921	5.260	2.278	- 0.356
1500	6.670	11.613	7.219	6.562	5.260	2.065	- 0.301
1600	6.790	12.046	7.507	7.262	5.257	1.852	- 0.253
1700	7.300	12.474	7.787	7.968	5.278	1.639	- 0.211
1800	7.300	12.891	8.059	8.698	5.313	1.423	- 0.173
1900	7.300	13.286	8.324	9.428	5.340	1.206	- 0.139
2000	7.300	13.660	8.581	10.158	5.361	0.989	- 0.108
2100	7.300	14.016	8.832	10.888	5.376	0.771	- 0.080
2200	7.300	14.356	9.075	11.618	5.386	0.551	- 0.055
2300	7.300	14.681	9.312	12.348	5.391	0.329	- 0.031
2400	7.300	14.991	9.542	13.078	5.391	0.111	- 0.010
2500	7.300	15.288	9.766	13.808	5.391	0.000	0.000
2600	7.300	15.576	9.984	14.538	5.391	0.000	0.000
2700	7.300	15.851	10.196	15.268	5.391	0.000	0.000
2800	7.300	16.116	10.403	15.998	5.391	0.000	0.000
2900	7.300	16.373	10.604	16.728	5.391	0.000	0.000
3000	7.300	16.620	10.801	17.458	5.391	0.000	0.000
3100	7.300	16.860	10.992	18.188	5.391	0.000	0.000
3200	7.300	17.091	11.179	18.918	5.391	0.000	0.000
3300	7.300	17.316	11.362	19.648	5.391	0.000	0.000
3400	7.300	17.534	11.540	20.378	5.391	0.000	0.000
3500	7.300	17.745	11.715	21.108	5.391	0.000	0.000
3600	7.300	17.951	11.885	21.838	5.391	0.000	0.000
3700	7.300	18.151	12.052	22.568	5.391	0.000	0.000
3800	7.300	18.346	12.215	23.298	5.391	0.000	0.000
3900	7.300	18.535	12.375	24.028	5.391	0.000	0.000
4000	7.300	18.720	12.531	24.758	5.391	0.000	0.000
4100	7.300	18.900	12.684	25.488	5.391	0.000	0.000
4200	7.300	19.076	12.834	26.218	5.391	0.000	0.000
4300	7.300	19.248	12.981	26.948	5.391	0.000	0.000
4400	7.300	19.416	13.125	27.678	5.391	0.000	0.000
4500	7.300	19.580	13.267	28.408	5.391	0.000	0.000
4600	7.300	19.740	13.406	29.138	5.391	0.000	0.000
4700	7.300	19.897	13.543	29.868	5.391	0.000	0.000
4800	7.300	20.051	13.677	30.598	5.391	0.000	0.000
4900	7.300	20.201	13.811	31.328	5.391	0.000	0.000
5000	7.300	20.349	13.938	32.058	5.391	0.000	0.000

AT. WT. = 10.82

(LIQUID)

BORON (B)

$\Delta H_f^{298.15} = [5.260] \text{ kcal. mole}^{-1}$
 $\Delta H_m^{298.15} = [5.39] \text{ kcal. mole}^{-1}$
 $\Delta H_v^{298.15} = [121.3 \pm 4] \text{ kcal. mole}^{-1}$

$S_{298.15}^{298.15} = [3.533] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = [2450 \pm 20]^\circ \text{K.}$
 $T_b = [5951]^\circ \text{K.}$

Heat of Formation.

$\Delta H_f^{298.15}$ for B(l) was obtained from $\Delta H_f^{298.15}$ for B(c) by adding $\Delta H_m^{298.15}$ and the difference between $H_m^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of liquid was estimated by comparison with the heat capacity of solid at the melting temperature. The value of $S_{298.15}^{298.15}$ was obtained in a manner analogous to that of the heat of formation. A glass transition temperature at 1600°K. is assumed.

Melting Data.

See B(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation (ΔF_p^{298}) for both B(l) and B(g) are equal. The difference in heat of formation (ΔH_f^{298} of B(l) and B(g) at the boiling point is the heat of vaporization (ΔH_v^{298}).

Boron Unipositive Ion (B⁺)

(Ideal Gas)

GFW = 10.81045

T, K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
100	4.968	33.086	33.086	0.000	324.084	313.151	-229.54
200	4.968	33.117	33.086	-0.009	324.097	-228.040	
300	4.968	33.146	33.086	-0.019	324.109	-226.997	
400	4.968	33.171	33.086	-0.029	324.119	-225.954	
500	4.968	33.193	33.086	-0.039	324.128	-224.911	
600	4.968	33.212	33.086	-0.049	324.136	-223.868	
700	4.968	33.228	33.086	-0.059	324.143	-222.825	
800	4.968	33.242	33.086	-0.069	324.149	-221.782	
900	4.968	33.254	33.086	-0.079	324.154	-220.739	
1000	4.968	33.264	33.086	-0.089	324.159	-219.696	
1100	4.968	33.272	33.086	-0.099	324.163	-218.653	
1200	4.968	33.279	33.086	-0.109	324.166	-217.610	
1300	4.968	33.284	33.086	-0.119	324.169	-216.567	
1400	4.968	33.288	33.086	-0.129	324.171	-215.524	
1500	4.968	33.291	33.086	-0.139	324.173	-214.481	
1600	4.968	33.293	33.086	-0.149	324.174	-213.438	
1700	4.968	33.294	33.086	-0.159	324.175	-212.395	
1800	4.968	33.295	33.086	-0.169	324.175	-211.352	
1900	4.968	33.295	33.086	-0.179	324.175	-210.309	
2000	4.968	33.295	33.086	-0.189	324.175	-209.266	
2100	4.968	33.295	33.086	-0.199	324.175	-208.223	
2200	4.968	33.295	33.086	-0.209	324.175	-207.180	
2300	4.968	33.295	33.086	-0.219	324.175	-206.137	
2400	4.968	33.295	33.086	-0.229	324.175	-205.094	
2500	4.968	33.295	33.086	-0.239	324.175	-204.051	
2600	4.968	33.295	33.086	-0.249	324.175	-203.008	
2700	4.968	33.295	33.086	-0.259	324.175	-201.965	
2800	4.968	33.295	33.086	-0.269	324.175	-200.922	
2900	4.968	33.295	33.086	-0.279	324.175	-199.879	
3000	4.968	33.295	33.086	-0.289	324.175	-198.836	
3100	4.968	33.295	33.086	-0.299	324.175	-197.793	
3200	4.968	33.295	33.086	-0.309	324.175	-196.750	
3300	4.968	33.295	33.086	-0.319	324.175	-195.707	
3400	4.968	33.295	33.086	-0.329	324.175	-194.664	
3500	4.968	33.295	33.086	-0.339	324.175	-193.621	
3600	4.968	33.295	33.086	-0.349	324.175	-192.578	
3700	4.968	33.295	33.086	-0.359	324.175	-191.535	
3800	4.968	33.295	33.086	-0.369	324.175	-190.492	
3900	4.968	33.295	33.086	-0.379	324.175	-189.449	
4000	4.968	33.295	33.086	-0.389	324.175	-188.406	
4100	4.968	33.295	33.086	-0.399	324.175	-187.363	
4200	4.968	33.295	33.086	-0.409	324.175	-186.320	
4300	4.968	33.295	33.086	-0.419	324.175	-185.277	
4400	4.968	33.295	33.086	-0.429	324.175	-184.234	
4500	4.968	33.295	33.086	-0.439	324.175	-183.191	
4600	4.968	33.295	33.086	-0.449	324.175	-182.148	
4700	4.968	33.295	33.086	-0.459	324.175	-181.105	
4800	4.968	33.295	33.086	-0.469	324.175	-180.062	
4900	4.968	33.295	33.086	-0.479	324.175	-179.019	
5000	4.968	33.295	33.086	-0.489	324.175	-177.976	
5100	4.968	33.295	33.086	-0.499	324.175	-176.933	
5200	4.968	33.295	33.086	-0.509	324.175	-175.890	
5300	4.968	33.295	33.086	-0.519	324.175	-174.847	
5400	4.968	33.295	33.086	-0.529	324.175	-173.804	
5500	4.968	33.295	33.086	-0.539	324.175	-172.761	
5600	4.968	33.295	33.086	-0.549	324.175	-171.718	
5700	4.968	33.295	33.086	-0.559	324.175	-170.675	
5800	4.968	33.295	33.086	-0.569	324.175	-169.632	
5900	4.968	33.295	33.086	-0.579	324.175	-168.589	
6000	4.968	33.295	33.086	-0.589	324.175	-167.546	

Dec. 31, 1967

BORON UNIPOSITIVE ION (B⁺)

(IDEAL GAS)

GFW = 10.81045

ΔHf° = 322.9 ± 4.0 kcal/mol

Ground State Configuration 1s₀

S°_{298.15} = 33.086 gibbs/mol

ΔHf°_{298.15} = 324.1 ± 4.0 kcal/mol

Electronic Levels and Quantum Weights				
E _i , cm ⁻¹	E _i , cm ⁻¹	E _i , cm ⁻¹	E _i , cm ⁻¹	E _i , cm ⁻¹
0.0	1	144019.32	12	184793.57
37348.4	9	151858.48	20	189126.6
73386.7	3	166741.85	4	184753.14
100152.89	14	174212.71	57	187721.0
129245.18	4	181473.27	12	200484.6
135946.0	1			

Heat of Formation

We calculate the heat of formation at 0°K from the reaction B(g) + e⁻(g) + B⁺(g) using the JANAF auxiliary value for B(g) and an ionization potential of 191.34 kcal/mol from C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, Vol. I, 1949.

Heat Capacity and Entropy

We obtain the electronic levels and quantum weights from C. E. Moore, loc. cit. H° - H°₂₉₈ = -1.481 kcal/mol at 0°K.

B⁺

T, °K	C _p ^o	S ^o	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	-	-2.771	-115.136	-115.136	INFINITE
100	6.188	52.913	70.634	-1.972	-115.066	-116.184	253.820
200	9.912	59.053	64.435	-1.076	-115.068	-117.313	128.193
298	11.990	63.404	63.404	0.000	-115.200	-118.395	86.786
300	12.027	63.478	63.404	0.022	-115.203	-118.415	86.265
400	13.475	67.155	64.884	2.735	-115.596	-120.455	52.651
500	15.009	70.394	66.894	2.795	-115.596	-120.455	38.191
600	15.951	73.218	66.042	4.306	-115.811	-121.408	28.026
700	16.663	75.733	67.250	5.938	-116.045	-122.322	21.378
800	17.212	77.995	68.454	7.693	-116.288	-123.203	16.559
900	17.626	80.000	69.627	9.486	-116.542	-124.052	13.785
1000	17.980	81.825	70.767	11.338	-116.812	-124.871	11.294
1100	18.281	83.452	71.861	12.970	-117.107	-125.664	9.195
1200	18.471	84.950	72.911	14.807	-117.426	-126.428	7.416
1300	18.650	86.336	73.916	16.663	-117.773	-127.164	6.059
1400	18.818	87.627	74.886	18.547	-118.147	-127.872	5.156
1500	18.972	88.843	75.810	20.422	-118.553	-128.555	4.502
1600	19.027	90.049	76.700	22.319	-121.745	-129.127	4.014
1700	19.115	91.406	77.555	24.227	-122.097	-129.578	3.678
1800	19.200	92.900	78.377	26.142	-122.464	-130.008	3.407
1900	19.281	94.429	79.165	28.068	-122.848	-130.415	3.196
2000	19.312	95.872	79.933	29.993	-123.231	-130.807	3.036
2100	19.361	97.281	80.669	31.926	-123.631	-131.174	2.916
2200	19.404	98.674	81.381	33.865	-124.042	-131.524	2.826
2300	19.442	99.957	82.069	35.797	-124.464	-131.854	2.759
2400	19.475	101.176	82.733	37.723	-124.898	-132.164	2.701
2500	19.505	102.340	83.380	39.642	-125.345	-132.452	2.650
2600	19.532	103.471	84.006	41.554	-125.797	-132.719	2.606
2700	19.556	104.569	84.613	43.460	-126.262	-132.964	2.569
2800	19.577	105.637	85.203	45.355	-126.738	-133.188	2.536
2900	19.596	106.678	85.775	47.240	-127.225	-133.392	2.506
3000	19.614	107.697	86.333	49.114	-127.723	-133.575	2.479
3100	19.630	108.691	86.876	50.977	-128.231	-133.738	2.454
3200	19.644	109.655	87.404	52.827	-128.750	-133.881	2.430
3300	19.658	110.599	87.919	54.664	-129.279	-134.004	2.407
3400	19.671	111.527	88.421	56.488	-129.818	-134.108	2.385
3500	19.681	112.440	88.911	58.299	-130.366	-134.193	2.364
3600	19.691	113.341	89.390	60.097	-130.923	-134.259	2.344
3700	19.700	114.230	89.857	61.878	-131.488	-134.306	2.324
3800	19.709	115.107	90.314	63.642	-132.061	-134.334	2.304
3900	19.717	115.973	90.760	65.390	-132.641	-134.344	2.284
4000	19.725	116.828	91.198	67.114	-133.228	-134.336	2.264
4100	19.732	117.673	91.625	68.824	-133.822	-134.310	2.244
4200	19.738	118.507	92.044	70.519	-134.423	-134.266	2.224
4300	19.744	119.330	92.454	72.200	-135.030	-134.204	2.204
4400	19.750	120.143	92.854	73.867	-135.643	-134.124	2.184
4500	19.755	120.946	93.250	75.520	-136.262	-134.026	2.164
4600	19.760	121.740	93.637	77.159	-136.886	-133.910	2.144
4700	19.765	122.524	94.016	78.784	-137.515	-133.776	2.124
4800	19.769	123.298	94.388	80.395	-138.149	-133.624	2.104
4900	19.773	124.062	94.754	81.991	-138.788	-133.454	2.084
5000	19.777	124.816	95.113	83.574	-139.432	-133.266	2.064
5100	19.781	125.560	95.465	85.143	-140.081	-133.060	2.044
5200	19.784	126.294	95.812	86.698	-140.734	-132.836	2.024
5300	19.787	127.018	96.152	88.239	-141.391	-132.594	2.004
5400	19.790	127.732	96.486	89.766	-142.051	-132.334	1.984
5500	19.793	128.436	96.816	91.279	-142.714	-132.056	1.964
5600	19.796	129.130	97.140	92.777	-143.380	-131.760	1.944
5700	19.799	129.814	97.459	94.260	-144.049	-131.446	1.924
5800	19.801	130.488	97.773	95.728	-144.720	-131.114	1.904
5900	19.804	131.152	98.082	97.181	-145.393	-130.764	1.884
6000	19.806	131.806	98.386	98.619	-146.068	-130.396	1.864

Point Group [C₂]

S°_{298.15} = [63.4] gibbs/mol

Ground State Quantum Weight = [2]

ΔH_f^{o = [-115.1 ± 8] kcal/mol}

ΔH_f^{o = [-115.2 ± 8] kcal/mol}

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
{2000}(1)	{600}(1)
{1000}(1)	{400}(1)
{900}(1)	{800}(1)

Bond Distance: Be-O = [1.40] Å O-B = [1.36] Å B-O = [1.20] Å

Bond Angle: Be-O-B = [120]° O-B-O = [180]°

Product of the Moments of Inertia: I_AI_BI_C = [2.450656] X 10⁻¹¹⁵ g³ cm⁶

σ = [1]

Heat of Formation.

Since P. E. Blackburn and A. Büchler, J. Phys. Chem. 69, 4250 (1965), have postulated that the Be₂ group has the pseudochloride character in bond strength, the heat of formation of BeB₂O₂(g) is estimated by adding the difference of the heats of formation of BeCl(g) and AlCl(g) to the heat of formation of AlB₂O₂(g), using all JANAP values ΔH_f^{o (BeCl, g) = 3.0, ΔH_f^{o (AlCl, g) = -11.2 and ΔH_f^{o (AlB₂O₂, g) = -129.4 kcal/mol.}}}

Heat Capacity and Entropy.

All molecular constants are estimated by comparison with those in LiB₂O₂(g), AlB₂O₂(g), B₂O₃(g) and BeCl(g). The three principal moments of inertia are I_A = 1.1015 X 10⁻³⁹, I_B = 14.3751 X 10⁻³⁹ and I_C = 15.4766 X 10⁻³⁹ g cm².

Boron Monobromide (BBR)

(Ideal Gas) Mol. Wt. = 90.736

BBR

MOL. WT. = 90.736

(IDEAL GAS)

BORON MONOBROMIDE (BBR)

T, °K. $\left(\frac{C_p}{S^\circ} - (R^\circ - H_{298}^\circ)/T \right) \left(\frac{H^\circ - H_{298}^\circ}{\Delta H_f^\circ} \right) \Delta F_f^\circ$

Ground State Configuration $1s^2 +$

$\Delta H_f^\circ = 53.750$ cal. deg.⁻¹ mole⁻¹

$\Delta H_f^\circ = 57 \pm 10$ kcal. mole⁻¹

$S_{298.15}^\circ = 53.750$ cal. deg.⁻¹ mole⁻¹

$\Delta H_f^\circ = 56 \pm 10$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

$$\frac{\bar{e}_1}{0}, \text{ cm.}^{-1} \quad \frac{g_1}{1}$$

$$\lambda_{\text{ex}} = 3.57 \text{ cm.}^{-1}$$

$\sigma = 1$

$$\omega_e = 689.04 \text{ cm.}^{-1}$$

$r_e = 1.887 \text{ \AA}$

$$B_e = 0.497 \text{ cm.}^{-1}$$

$\alpha_c = 0.0036 \text{ cm.}^{-1}$

Heat of Formation.

O. Herzberg, "Spectra of Diatomic Molecules" D. Van Nostrand Co. New York 1950 reports a D_0° of 4.1 e.v. which corresponds to a heat of formation of 64 kcal. mole⁻¹ A. G. Gaydon "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, London 1953, gives essentially the same value, with a rider that the value is unreliable due to the ionic nature of the bonding. R. F. Barrow, Trans. Farad. Soc. 56, 952 (1960) made a critical evaluation of the bond dissociation energies of the group III halides and concluded $D_0 \text{ BBr} = 103.5$ which gives $\Delta H_f^\circ = 56$ kcal. mole⁻¹. An estimate of the dissociation energy by taking the ratio $D(\text{BrF})/(\Delta H_f^\circ(\text{BrF}_3)/3) = 1.177$ and applying this to BBr_3 yields $D(\text{BBR}) = 103$ kcal. mole⁻¹, this was the value adopted.

Heat Capacity and Entropy.

The vibrational and rotational constants were all taken from National Bureau Standards Report 7083, Jan. 1, 1962.

T, °K.	C_p	S°	$\left(\frac{C_p}{S^\circ} - (R^\circ - H_{298}^\circ)/T \right)$	$\left(\frac{H^\circ - H_{298}^\circ}{\Delta H_f^\circ} \right)$	ΔF_f°	Log K _p
0	0.000	0.000	INFINITE	2.150	57.071	INFINITE
100	6.968	45.817	50.369	1.455	57.426	-116.910
200	7.323	50.728	54.451	0.745	57.471	-54.125
298	7.837	53.750	57.750	0.000	56.000	-33.583
300	7.845	53.799	57.751	0.015	55.993	-33.330
400	8.216	56.111	54.063	0.819	52.355	-23.541
500	8.451	57.971	54.665	1.653	52.335	-17.820
600	8.604	59.526	55.349	2.506	52.269	-14.010
700	8.700	60.845	56.070	3.372	52.180	-11.282
800	8.783	62.029	56.750	4.242	52.076	-9.060
900	8.859	63.067	57.369	5.125	51.921	-7.680
1000	8.883	64.000	57.986	6.015	51.772	-6.422
1100	8.919	64.849	58.572	6.905	51.607	-5.394
1200	8.972	65.613	59.130	7.796	51.426	-4.551
1300	9.044	66.298	59.656	8.694	51.230	-3.873
1400	9.094	67.009	60.157	9.592	51.038	-3.208
1500	9.014	67.630	60.635	10.493	50.823	-2.678
1600	9.032	68.212	61.091	11.395	50.598	-2.216
1700	9.064	68.762	61.529	12.299	50.362	-1.811
1800	9.094	69.278	61.942	13.205	50.116	-1.459
1900	9.078	69.725	62.341	14.112	49.865	-1.132
2000	9.092	70.235	62.743	15.020	49.608	-0.846
2100	9.105	70.679	63.093	15.930	49.346	-0.589
2200	9.117	71.058	63.476	16.841	49.079	-0.356
2300	9.130	71.508	63.789	17.754	48.808	-0.147
2400	9.142	71.897	64.119	18.667	48.532	-0.068
2500	9.153	72.270	64.437	19.582	48.256	-0.215
2600	9.165	72.629	64.746	20.498	47.972	-0.358
2700	9.177	72.973	65.049	21.414	47.680	-0.490
2800	9.187	73.309	65.333	22.330	47.380	-0.612
2900	9.198	73.632	65.614	23.252	47.073	-0.725
3000	9.209	73.944	65.886	24.173	46.761	-0.830
3100	9.219	74.246	66.151	25.094	46.443	-0.927
3200	9.229	74.539	66.410	26.016	46.119	-1.018
3300	9.240	74.823	66.660	26.940	45.790	-1.103
3400	9.250	75.099	66.904	27.864	45.456	-1.181
3500	9.261	75.367	67.142	28.790	45.117	-1.255
3600	9.271	75.628	67.374	29.717	44.773	-1.324
3700	9.281	75.883	67.600	30.644	44.425	-1.388
3800	9.291	76.130	67.822	31.573	44.073	-1.449
3900	9.301	76.372	68.038	32.502	43.717	-1.506
4000	9.311	76.607	68.249	33.433	43.358	-1.559
4100	9.321	76.837	68.456	34.365	42.995	-1.607
4200	9.331	77.062	68.658	35.298	42.628	-1.651
4300	9.341	77.282	68.856	36.231	42.257	-1.692
4400	9.351	77.497	69.050	37.165	41.882	-1.730
4500	9.360	77.707	69.240	38.101	41.503	-1.766
4600	9.370	77.913	69.426	39.037	41.120	-1.800
4700	9.380	78.114	69.609	39.975	40.734	-1.832
4800	9.390	78.312	69.788	40.913	40.345	-1.862
4900	9.400	78.506	69.964	41.853	39.953	-1.890
5000	9.409	78.696	70.137	42.793	39.558	-1.916
5100	9.419	78.882	70.307	43.735	39.161	-1.941
5200	9.429	79.065	70.473	44.677	38.762	-1.964
5300	9.438	79.245	70.637	45.620	38.361	-1.986
5400	9.448	79.421	70.798	46.565	37.958	-2.006
5500	9.458	79.595	70.956	47.510	37.553	-2.024
5600	9.467	79.765	71.112	48.456	37.146	-2.040
5700	9.477	79.933	71.264	49.402	36.737	-2.055
5800	9.487	80.098	71.416	50.352	36.326	-2.069
5900	9.496	80.260	71.565	51.301	35.913	-2.081
6000	9.506	80.420	71.711	52.251	35.498	-2.092

BBR

Boron Bromide Chloride (BBrCl)

(Ideal Gas) Mol. Wt. = 126.193

BORON BROMIDE CHLORIDE (BBrCl)

(IDEAL GAS)

MOL. WT. = 126.193

Point Group C_{2v}
 $S_{298.15}^\circ = [69.056] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = [-1.0 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = [-2.5 \pm 10] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

ΔH_f° cm.⁻¹
 [660](1)
 [195](1)
 [905](1)

Bond Distance B-Cl = [1.75] Å B-Br = [1.87] Å
 Bond Angle Cl-B-Br = [120°]
 $\sigma = 1$

Product of the Moments of Inertia: $I_A I_B I_C = [2.192176] \times 10^{-114} \text{ g.}^3 \text{ cm.}^2$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction $\text{BCl}_2 + \text{Br}_2 \rightarrow 2\text{BBrCl}$.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for BBr_2 and BCl_2 . The bond distances, angles, and quantum weight were assumed the same as in the dibromides. The individual moments of inertia were $I_A = 1.2997 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 40.4239 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 41.7236 \times 10^{-39} \text{ g. cm.}^2$.

Dec. 31, 1962; Dec. 31, 1964

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF°	Log K_p
0	0.000	0.000	INFINITE	-2.842	-1.023	-1.023	INFINITE
100	9.035	50.183	78.289	-2.011	-0.893	-0.893	9.282
200	10.111	57.141	78.046	-1.606	-0.806	-0.806	9.466
298	11.197	60.056	69.056	-0.000	-2.500	-9.933	6.019
300	11.214	60.126	69.057	0.021	-2.508	-9.345	6.808
400	12.003	72.467	62.507	1.184	-6.202	-10.868	5.938
500	12.951	79.206	70.381	2.413	-6.254	-12.059	5.258
600	12.882	77.924	71.383	3.684	-6.336	-13.176	4.799
700	13.120	79.529	72.407	4.985	-6.437	-14.309	4.467
800	13.287	81.292	73.410	6.306	-6.552	-15.426	4.214
900	13.407	82.864	74.374	7.641	-6.677	-16.528	4.013
1000	13.496	84.282	75.295	8.986	-6.814	-17.615	3.850
1100	13.564	85.572	76.172	10.340	-6.964	-18.689	3.713
1200	13.617	86.754	77.005	11.699	-7.125	-19.747	3.596
1300	13.659	87.846	77.798	13.063	-7.299	-20.782	3.495
1400	13.692	88.859	78.552	14.430	-7.483	-21.822	3.406
1500	13.720	89.805	79.271	15.801	-7.681	-22.862	3.328
1600	13.742	90.691	79.957	17.174	-7.890	-23.894	3.257
1700	13.761	91.525	80.614	18.549	-8.108	-24.934	3.193
1800	13.777	92.312	81.242	19.926	-8.337	-25.981	3.134
1900	13.790	93.057	81.844	21.305	-8.574	-26.776	3.080
2000	13.802	93.765	82.423	22.684	-8.818	-27.779	3.030
2100	13.812	94.438	82.979	24.065	-9.067	-28.667	2.983
2200	13.821	95.081	83.515	25.447	-9.322	-29.595	2.940
2300	13.828	95.696	84.031	26.829	-9.582	-30.511	2.899
2400	13.835	96.284	84.529	28.212	-9.849	-31.413	2.860
2500	13.841	96.849	85.011	29.596	-10.125	-32.318	2.815
2600	13.846	97.392	85.477	30.980	-10.410	-33.218	2.762
2700	13.851	97.915	85.928	32.365	-10.704	-34.113	2.713
2800	13.855	98.419	86.365	33.750	-11.005	-35.005	2.665
2900	13.859	98.905	86.789	35.136	-11.316	-35.896	2.621
3000	13.862	99.375	87.201	36.522	-11.635	-36.786	2.580
3100	13.865	99.829	87.601	37.908	-11.960	-37.673	2.540
3200	13.868	100.270	87.990	39.295	-12.291	-38.556	2.502
3300	13.870	100.696	88.369	40.682	-12.627	-39.436	2.465
3400	13.872	101.110	88.737	42.069	-12.967	-40.313	2.430
3500	13.873	101.513	89.097	43.457	-13.311	-41.188	2.397
3600	13.877	101.904	89.447	44.844	-13.659	-42.060	2.364
3700	13.879	102.284	89.789	46.232	-14.011	-42.929	2.335
3800	13.880	102.654	90.122	47.620	-14.366	-43.796	2.305
3900	13.882	103.014	90.448	49.008	-14.725	-44.661	2.277
4000	13.883	103.366	90.767	50.396	-15.087	-45.525	2.252
4100	13.885	103.709	91.078	51.785	-15.452	-46.388	2.226
4200	13.886	104.043	91.383	53.173	-15.819	-47.250	2.200
4300	13.887	104.370	91.681	54.562	-16.188	-48.111	2.175
4400	13.888	104.689	91.973	55.950	-16.558	-48.971	2.150
4500	13.889	105.002	92.259	57.339	-16.929	-49.830	2.126
4600	13.890	105.307	92.540	58.728	-17.301	-50.689	2.102
4700	13.891	105.606	92.815	60.117	-17.674	-51.548	2.078
4800	13.892	105.898	93.084	61.506	-18.048	-52.407	2.054
4900	13.892	106.184	93.349	62.896	-18.423	-53.266	2.030
5000	13.893	106.465	93.608	64.285	-18.798	-54.125	2.006
5100	13.894	106.740	93.863	65.674	-19.174	-54.984	1.982
5200	13.894	107.010	94.113	67.064	-19.550	-55.843	1.958
5300	13.895	107.275	94.359	68.453	-19.926	-56.702	1.934
5400	13.896	107.534	94.601	69.843	-20.302	-57.561	1.910
5500	13.896	107.789	94.838	71.232	-20.678	-58.420	1.886
5600	13.897	108.040	95.072	72.622	-21.054	-59.279	1.862
5700	13.897	108.286	95.301	74.012	-21.430	-60.138	1.838
5800	13.898	108.527	95.527	75.401	-21.806	-60.997	1.814
5900	13.898	108.765	95.750	76.791	-22.182	-61.856	1.790
6000	13.899	108.999	95.968	78.181	-22.558	-62.715	1.766

Boron Bromide Dichloride (BBrCl₂)
(Ideal Gas) Mol. Wt. = 161.65



MOL. WT. = 161.65

BORON BROMIDE DICHLORIDE (BBrCl₂) (IDEAL GAS)

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	+∞	INFINITE	-	3.477	- 78.561	-	INFINITE
100	10.218	60.250	86.414	2.616	- 78.742	- 79.596	173.040
200	13.421	68.410	75.513	1.421	- 78.933	- 80.376	87.626
298	15.392	74.163	80.000	1.000	- 80.500	- 80.881	59.285
300	15.422	74.258	80.163	1.029	- 80.508	- 80.884	58.021
400	16.753	78.689	84.163	1.461	- 84.167	- 80.257	43.848
500	17.467	82.725	87.001	1.862	- 84.154	- 79.281	34.652
600	18.179	85.989	89.401	2.153	- 84.151	- 78.307	28.522
700	18.569	88.892	91.321	2.352	- 84.148	- 77.356	23.843
800	18.862	91.321	80.242	8.463	- 84.163	- 76.356	20.889
900	19.040	93.552	81.559	10.758	- 84.171	- 75.383	18.305
1000	19.188	95.566	82.897	12.569	- 84.188	- 74.405	16.260
1100	19.300	97.400	84.133	14.594	- 84.216	- 73.426	14.588
1200	19.385	99.084	85.610	16.728	- 84.252	- 72.444	13.193
1300	19.445	100.658	87.147	18.958	- 84.293	- 71.468	11.940
1400	19.511	102.082	88.447	20.419	- 84.353	- 70.497	10.822
1500	19.556	103.430	89.6515	22.372	- 84.421	- 69.476	9.9122
1600	19.593	104.693	89.487	24.330	- 84.599	- 68.475	9.353
1700	19.621	105.882	90.437	26.291	- 84.587	- 67.470	8.673
1800	19.641	106.997	91.401	28.254	- 84.582	- 66.462	7.957
1900	19.673	108.067	92.112	30.221	- 84.790	- 65.444	7.197
2000	19.692	109.077	92.682	32.189	- 84.902	- 64.424	6.404
2100	19.709	110.038	93.772	34.159	- 85.019	- 63.398	5.598
2200	19.735	111.832	95.232	36.101	- 85.144	- 62.365	4.781
2300	19.761	113.479	96.658	38.019	- 85.282	- 61.322	3.952
2400	19.786	114.983	98.051	40.078	- 85.409	- 60.282	3.116
2500	19.756	113.479	96.658	42.053	- 90.939	- 59.124	2.186
2600	19.765	114.254	97.320	44.079	- 91.077	- 57.848	1.262
2700	19.775	115.719	98.592	46.066	- 91.210	- 56.567	0.346
2800	19.780	116.413	99.185	48.016	- 91.310	- 55.286	- 0.581
2900	19.782	117.084	99.771	50.000	- 91.387	- 54.008	- 1.506
3000	19.792	117.734	100.360	51.941	- 91.659	- 52.694	- 2.439
3100	19.797	118.360	100.950	53.920	- 91.812	- 51.393	- 3.373
3200	19.800	118.971	101.540	55.900	- 91.967	- 50.097	- 4.307
3300	19.803	119.563	102.130	57.880	- 92.126	- 48.800	- 5.241
3400	19.809	119.563	101.956	59.861	- 92.286	- 47.459	- 6.175
3500	19.813	120.137	102.468	61.842	- 92.451	- 46.141	- 7.109
3600	19.816	120.695	102.966	63.824	- 92.618	- 44.812	- 8.043
3700	19.819	121.217	103.458	65.806	- 92.786	- 43.481	- 8.977
3800	19.822	121.767	103.928	67.789	- 92.960	- 42.150	- 9.911
3900	19.824	122.282	104.356	69.770	- 93.136	- 40.809	- 10.845
4000	19.827	122.783	104.845	71.752	- 93.318	- 39.468	- 11.779
4100	19.829	123.273	105.289	73.735	- 93.499	- 38.127	- 12.713
4200	19.831	123.751	105.699	75.718	- 93.680	- 36.786	- 13.647
4300	19.833	124.218	106.148	77.701	- 93.861	- 35.445	- 14.581
4400	19.835	124.674	106.563	79.683	- 94.042	- 34.104	- 15.515
4500	19.836	125.119	106.971	81.668	- 94.223	- 32.763	- 16.449
4600	19.838	125.555	107.370	83.652	- 94.404	- 31.422	- 17.383
4700	19.839	125.982	107.750	85.635	- 94.585	- 30.081	- 18.317
4800	19.841	126.400	108.146	87.620	- 94.766	- 28.740	- 19.251
4900	19.842	126.809	108.522	89.604	- 94.947	- 27.399	- 20.185
5000	19.843	127.210	108.892	91.588	- 95.128	- 26.058	- 21.119
5100	19.844	127.603	109.255	93.573	- 95.309	- 24.717	- 22.053
5200	19.845	127.998	109.602	95.558	- 95.490	- 23.376	- 22.987
5300	19.846	128.386	109.942	97.542	- 95.671	- 22.035	- 23.921
5400	19.847	128.737	110.306	99.527	- 95.852	- 20.694	- 24.855
5500	19.848	129.101	110.645	101.511	- 96.033	- 19.353	- 25.789
5600	19.849	129.459	110.977	103.496	- 96.214	- 18.012	- 26.723
5700	19.850	129.810	111.300	105.480	- 96.395	- 16.671	- 27.657
5800	19.851	130.155	111.627	107.464	- 96.576	- 15.330	- 28.591
5900	19.852	130.495	111.944	109.451	- 96.757	- 13.989	- 29.525
6000	19.852	130.828	112.256	111.436	- 96.938	- 12.648	- 30.459

Sept. 30, 1962; Dec. 31, 1964

Point Group C_{2v}

S_{298.15} = 74.163 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight [1]

ΔH_f^o = -78.5 ± 10 kcal. mole⁻¹

ΔH_f^o 298.15 = -80.5 ± 10 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω_e , cm. ⁻¹	ω_e , cm. ⁻¹
885(1)	959(1)
406(1)	[209](1)
218(1)	435(1)

Bond Distances: B-Cl = 1.73 Å B-Br = 1.87 Å

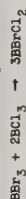
Bond Angle: Cl-B-Cl = [120°] Br-B-Cl = [120°]

Product of the Moments of Inertia: I_AI_BI_C = 9.19303 X 10⁻¹¹³ g.³ cm.⁶

σ^o = 2

Heat of Formation.

The heat of formation was estimated by assuming ΔH_f^o = 0 for the reaction



Heat Capacity and Entropy.

Vibrational frequencies were obtained from L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956). The b₁ mode was the only unobserved frequency and was calculated from a normal coordinate treatment. Bond distances were reported by T. Wentink and V. H. Tienau, J. Chem. Phys. 28, 826 (1956). Bond angles were estimated by analogy with the other trihalides of boron. The individual moments of inertia were I_A = 26.4242 X 10⁻³⁹ g. cm.², I_B = 47.2327 X 10⁻³⁹ g. cm.² and I_C = 73.6569 X 10⁻³⁹ g. cm.²



Boron Bromide Fluoride (BBrF)

(Ideal Gas) Mol. Wt. = 109.736

MOL. WT. = 109.736

(IDEAL GAS)

BORON BROMIDE FLUORIDE (BBrF)

Point Group C_{2v}

$\Delta H_f^\circ = [65.887] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ 298.15 = [57.5 \pm 10] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

$(\lambda), \text{ cm.}^{-1}$

[860](1)

[310](1)

[1140](1)

Bond Distance: B-Br = $[1.3] \text{ \AA}$ B-Br = $[1.87] \text{ \AA}$

Bond Angle: Br-B-Br = $[120^\circ]$

Product of the Moments of Inertia: $I_A I_B I_C = [4.13196] \times 10^{-115} \text{ g. cm.}^6$

$\sigma = 1$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction $\text{BBr}_2 + \text{Br}_2 \rightarrow 2\text{BBrF}$.

Heat Capacity and Entropy.

The vibrational frequencies, bond lengths, angles and quantum weight were estimated by comparison with the respective dihalides. The individual moments of inertia were $I_A = 0.8407 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 21.7537 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 22.5944 \times 10^{-39} \text{ g. cm.}^2$.

Boron Bromide Difluoride (BBrF₂)
(Ideal Gas) Mol. Wt. 128.736

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	+∞	INFINITE	-3.054	-193.723	-193.723	INFINITE
100	8.742	78.971	-2.243	-193.947	-194.879	425.888
150	11.442	69.596	-1.831	-194.300	-195.672	213.811
200	13.492	63.424	-1.480	-194.600	-196.114	143.746
300	13.524	68.508	-0.825	-196.011	-196.115	142.863
400	14.997	72.611	-0.794	-199.793	-195.378	106.745
500	16.088	76.089	-0.705	-198.897	-194.263	84.908
600	16.896	79.089	-0.663	-199.997	-193.127	70.343
700	17.496	81.741	-0.638	-200.089	-191.974	59.934
800	17.944	84.108	-0.617	-200.175	-190.810	52.414
900	18.283	86.242	-0.596	-200.254	-189.635	46.047
1000	18.545	88.182	-0.571	-200.332	-188.449	41.184
1100	18.749	89.959	-0.547	-200.414	-187.258	37.203
1200	18.911	91.598	-0.526	-200.498	-186.057	33.684
1300	19.041	93.117	-0.508	-200.580	-184.850	31.075
1400	19.148	94.532	-0.492	-200.667	-183.635	28.665
1500	19.235	95.856	-0.476	-200.754	-182.414	26.576
1600	19.308	97.100	-0.462	-200.809	-181.185	24.747
1700	19.369	98.274	-0.448	-200.834	-179.948	23.133
1800	19.421	99.381	-0.433	-200.860	-178.706	21.697
1900	19.465	100.432	-0.418	-200.885	-177.452	20.411
2000	19.504	101.432	-0.403	-200.910	-176.194	19.253
2100	19.537	102.384	-0.388	-200.932	-174.927	18.204
2200	19.566	103.294	-0.373	-200.955	-173.655	17.240
2300	19.591	104.164	-0.358	-200.978	-172.372	16.378
2400	19.613	104.998	-0.343	-200.999	-171.083	15.578
2500	19.633	105.799	-0.328	-201.016	-169.782	14.833
2600	19.651	106.570	-0.313	-201.032	-168.471	14.134
2700	19.667	107.312	-0.297	-201.047	-167.150	13.487
2800	19.681	108.027	-0.281	-201.061	-165.826	12.886
2900	19.694	108.718	-0.265	-201.074	-164.499	12.335
3000	19.705	109.386	-0.249	-201.086	-163.168	11.832
3100	19.716	110.032	-0.233	-201.097	-161.833	11.371
3200	19.725	110.658	-0.217	-201.107	-160.496	10.952
3300	19.734	111.265	-0.201	-201.116	-159.156	10.573
3400	19.742	111.855	-0.185	-201.124	-157.812	10.232
3500	19.749	112.427	-0.169	-201.131	-156.465	9.927
3600	19.756	112.984	-0.153	-201.138	-155.116	9.654
3700	19.762	113.523	-0.137	-201.144	-153.764	9.409
3800	19.768	114.052	-0.121	-201.149	-152.409	9.184
3900	19.773	114.566	-0.105	-201.154	-151.052	8.978
4000	19.778	115.066	-0.089	-201.159	-149.692	8.790
4100	19.782	115.555	-0.073	-201.164	-148.328	8.611
4200	19.786	116.031	-0.057	-201.168	-146.961	8.441
4300	19.790	116.497	-0.041	-201.172	-145.592	8.284
4400	19.794	116.952	-0.025	-201.176	-144.220	8.131
4500	19.797	117.397	-0.009	-201.179	-142.844	7.984
4600	19.801	117.832	0.007	-201.182	-141.464	7.841
4700	19.804	118.258	0.021	-201.185	-140.080	7.700
4800	19.807	118.675	0.035	-201.188	-138.692	7.561
4900	19.809	119.083	0.049	-201.191	-137.300	7.424
5000	19.812	119.484	0.063	-201.194	-135.904	7.290
5100	19.814	119.876	0.077	-201.197	-134.504	7.157
5200	19.816	120.261	0.091	-201.200	-133.100	7.024
5300	19.818	120.638	0.105	-201.203	-131.692	6.891
5400	19.820	121.009	0.119	-201.206	-130.280	6.758
5500	19.822	121.372	0.133	-201.209	-128.864	6.624
5600	19.824	121.729	0.147	-201.212	-127.444	6.491
5700	19.826	122.080	0.161	-201.215	-126.020	6.358
5800	19.827	122.425	0.175	-201.218	-124.592	6.224
5900	19.828	122.764	0.189	-201.221	-123.160	6.091
6000	19.830	123.097	0.203	-201.224	-121.724	5.958

Sept. 30, 1982 Dec. 31, 1984

BBrF₂

MOL. WT. = 128.736

(IDEAL GAS)

BORON BROMIDE DIFLUORIDE (BBrF₂)

Point Group C_{2v}
S_{298.15} = 68.424 cal. deg⁻¹ mole⁻¹
ΔH_f⁰ = [-193.7 ± 10] kcal. mole⁻¹
ΔH_f⁰ 298.15 = [-196.0 ± 10] kcal. mole⁻¹
Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹
1215 (1)	1427 (1)
633 (1)	[346](1)
[330](1)	573 (1)

Bond Distance: B-F = 1.295 Å B-Br = 1.87 Å
Bond Angle: F-B-F = [120°] Br-B-F = [120°]
Product of the Moments of Inertia: I_AI_BI_C = 8.46916 X 10⁻¹¹⁴ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation was estimated by assuming ΔH_f = 0 for the reaction 2BF₃ + BBr₃ → 3BBrF₂.

Heat Capacity and Entropy.

All but two of the vibrational frequencies have been observed and assigned by L. P. Lindeman and M. K. Wilson J. Chem. Phys. 24, 242 (1956), the two remaining frequencies were calculated by a normal coordinate treatment. The bond distances were reported by T. Wentink and V. H. Tiemann, J. Chem. Phys. 28, 826 (1958). The bond angles were estimated by analogy with the other boron trihalides. The individual moments of inertia were I_A = 7.9349 X 10⁻³⁹ g. cm.², I_B = 28.9426 X 10⁻²⁹ g. cm.² and I_C = 36.8775 X 10⁻³⁹ g. cm.².

Boron Oxide Bromide (BOBr)
(Ideal Gas) Mol. Wt. = 106.736

BORON OXIDE BROMIDE (BOBr)

MOL. WT. = 106.736

(IDEAL GAS)

Point Group [C_{∞v}] $\Delta H_f^\circ 0 = [-59 \pm 7] \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ 298.15 = [-60 \pm 7] \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = [59.46] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$

[550] (1)

[370] (2)

[3800] (1)

Bond Distance: O-B = [1.20] Å B-Br = [1.87] Å

Bond Angle: O-B-Br = [180]°

Rotation Constant: $B_0 = [0.11742] \text{ cm.}^{-1}$ $\sigma^\circ = 1$

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ for BOBr (g) was calculated based on an assumption that $D(\text{BO-Br}) = 92.5 \text{ kcal. mole}^{-1}$ which was estimated by comparison with the following related bond energy values: $D(\text{BF}_2\text{-F}) = 159$, $D(\text{BO-F}) = 169$, $D(\text{BCl}_2\text{-Cl}) = 105$, $D(\text{BO-Cl}) = 110$ and $D(\text{BBr}_2\text{-Br}) = 90.5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the ω values calculated by the valence force method described by O. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, $k_1 = 4.2 \times 10^5$, $k_2 = 16.9 \times 10^5 \text{ dynes cm.}^{-1}$ and $k_3 = 0.37 \times 10^{-11} \text{ dynes cm. rad.}^{-1}$. The B=O and B-F bond distances were assumed to be the same as those in BO(g) and BBr₃(g), respectively. The moment of inertia is $2.58357 \times 10^{-38} \text{ g. cm.}^2$.

BBrO

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔF _f ° kcal. mole ⁻¹	Log K _p
0	7.000	INFINITE	-	-	-	INFINITE
100	40.242	58.463	2.820	-58.361	-58.361	18.563
200	9.867	58.463	0.000	-58.463	-58.463	18.563
298	11.188	59.463	0.000	-59.463	-59.463	18.563
300	11.206	59.463	0.021	-60.007	-60.007	18.563
400	11.969	62.869	2.407	-63.643	-63.643	18.563
500	12.498	65.800	5.076	-66.356	-66.356	18.563
600	12.809	67.916	7.678	-68.274	-68.274	18.563
700	13.239	69.932	10.066	-69.607	-69.607	18.563
800	13.505	71.718	12.166	-70.548	-70.548	18.563
900	13.720	73.321	13.966	-71.134	-71.134	18.563
1000	13.893	74.776	15.500	-71.481	-71.481	18.563
1100	14.034	76.107	16.863	-71.632	-71.632	18.563
1200	14.149	77.333	18.072	-71.682	-71.682	18.563
1300	14.244	78.470	19.152	-71.648	-71.648	18.563
1400	14.323	79.528	20.113	-71.525	-71.525	18.563
1500	14.390	80.519	20.966	-71.343	-71.343	18.563
1600	14.445	81.449	21.759	-71.123	-71.123	18.563
1700	14.493	82.326	22.500	-70.868	-70.868	18.563
1800	14.534	83.156	23.197	-70.581	-70.581	18.563
1900	14.569	83.943	23.859	-70.266	-70.266	18.563
2000	14.599	84.691	24.490	-69.927	-69.927	18.563
2100	14.626	85.404	25.097	-69.568	-69.568	18.563
2200	14.649	86.085	25.678	-69.185	-69.185	18.563
2300	14.670	86.736	26.230	-68.778	-68.778	18.563
2400	14.688	87.361	26.760	-68.348	-68.348	18.563
2500	14.704	87.961	27.266	-67.895	-67.895	18.563
2600	14.719	88.538	27.750	-67.419	-67.419	18.563
2700	14.732	89.094	28.210	-66.920	-66.920	18.563
2800	14.743	89.630	28.646	-66.400	-66.400	18.563
2900	14.754	90.147	29.059	-65.860	-65.860	18.563
3000	14.764	90.648	29.450	-65.300	-65.300	18.563
3100	14.772	91.132	29.820	-64.720	-64.720	18.563
3200	14.780	91.601	30.169	-64.120	-64.120	18.563
3300	14.787	92.056	30.500	-63.500	-63.500	18.563
3400	14.794	92.498	30.815	-62.860	-62.860	18.563
3500	14.800	92.926	31.115	-62.200	-62.200	18.563
3600	14.806	93.344	31.400	-61.520	-61.520	18.563
3700	14.811	93.749	31.670	-60.830	-60.830	18.563
3800	14.816	94.144	31.925	-60.130	-60.130	18.563
3900	14.820	94.529	32.165	-59.420	-59.420	18.563
4000	14.824	94.904	32.390	-58.700	-58.700	18.563
4100	14.828	95.271	32.600	-57.970	-57.970	18.563
4200	14.831	95.628	32.795	-57.230	-57.230	18.563
4300	14.835	95.977	32.975	-56.480	-56.480	18.563
4400	14.838	96.318	33.140	-55.720	-55.720	18.563
4500	14.841	96.651	33.290	-54.950	-54.950	18.563
4600	14.843	96.978	33.425	-54.170	-54.170	18.563
4700	14.846	97.297	33.545	-53.380	-53.380	18.563
4800	14.848	97.610	33.650	-52.580	-52.580	18.563
4900	14.851	97.916	33.740	-51.770	-51.770	18.563
5000	14.853	98.216	33.815	-50.950	-50.950	18.563
5100	14.855	98.510	33.885	-50.120	-50.120	18.563
5200	14.857	98.798	33.950	-49.280	-49.280	18.563
5300	14.859	99.081	34.000	-48.430	-48.430	18.563
5400	14.860	99.359	34.040	-47.580	-47.580	18.563
5500	14.862	99.632	34.075	-46.720	-46.720	18.563
5600	14.863	99.900	34.105	-45.850	-45.850	18.563
5700	14.865	100.163	34.130	-44.980	-44.980	18.563
5800	14.866	100.421	34.150	-44.100	-44.100	18.563
5900	14.867	100.675	34.165	-43.220	-43.220	18.563
6000	14.868	100.925	34.175	-42.340	-42.340	18.563

Dec. 31, 1962; Mar. 31, 1965

Boron Dibromide (BBr₂)
(Ideal Gas) Mol. Wt. = 170.652

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	9.000	∞	INFINITE	2.918	18.233	18.233	INFINITE
100	9.344	56.220	76.888	2.067	18.410	13.763	30.122
200	10.444	66.029	71.420	1.078	18.148	9.239	10.096
298	11.486	70.402	70.402	∞	15.000	5.276	3.867
300	11.503	70.473	70.402	∞	14.983	5.216	3.800
400	12.248	72.893	70.893	1.211	14.831	4.713	1.463
500	12.728	76.680	71.756	2.462	14.566	2.440	1.067
600	13.035	79.030	72.778	3.751	14.222	1.422	∞
700	13.242	81.056	73.819	5.066	13.798	∞	∞
800	13.368	82.743	74.871	6.414	13.293	∞	∞
900	13.488	84.114	75.931	7.781	12.718	∞	∞
1000	13.564	85.184	76.748	9.094	12.086	2.509	∞
1100	13.621	87.137	77.634	10.454	11.399	∞	∞
1200	13.666	88.225	78.476	11.818	10.657	∞	∞
1300	13.700	89.421	79.276	13.186	9.866	∞	∞
1400	13.725	90.430	80.038	14.558	9.030	2.116	∞
1500	13.752	91.384	80.763	15.932	8.185	7.111	1.036
1600	13.771	92.272	81.455	17.308	7.339	∞	∞
1700	13.786	93.108	82.116	18.686	6.495	∞	∞
1800	13.798	93.894	82.753	20.066	5.653	∞	∞
1900	13.811	94.649	83.355	21.446	4.811	10.449	1.213
2000	13.820	95.351	83.937	22.827	3.969	11.379	1.243
2100	13.829	96.026	84.497	24.210	3.125	12.195	1.269
2200	13.836	96.673	85.036	25.593	2.281	12.988	1.291
2300	13.842	97.298	85.556	26.977	1.436	13.759	1.309
2400	13.848	97.873	86.056	28.362	0.591	14.509	1.327
2500	13.853	98.439	86.540	29.747	∞	15.231	1.331
2600	13.857	98.982	87.008	31.132	∞	15.770	1.326
2700	13.861	99.505	87.462	32.518	2.146	16.299	1.319
2800	13.864	100.009	87.901	33.901	1.299	16.813	1.303
2900	13.867	100.496	88.327	35.281	2.679	17.327	1.287
3000	13.870	100.968	88.740	36.678	2.946	17.829	1.299
3100	13.873	101.421	89.142	38.065	3.215	18.321	1.292
3200	13.875	101.862	89.533	39.452	3.484	18.805	1.284
3300	13.877	102.297	89.918	40.838	3.753	19.279	1.276
3400	13.879	102.705	90.283	42.228	4.024	19.746	1.267
3500	13.881	103.103	90.644	43.616	4.296	20.204	1.262
3600	13.883	103.496	90.995	45.004	4.569	20.654	1.254
3700	13.884	103.877	91.338	46.392	4.842	21.100	1.246
3800	13.886	104.257	91.673	47.780	5.115	21.540	1.238
3900	13.887	104.608	92.000	49.169	5.392	21.963	1.231
4000	13.888	104.959	92.320	50.558	5.666	22.379	1.223
4100	13.889	105.302	92.632	51.947	5.940	22.788	1.216
4200	13.890	105.637	92.937	53.336	6.214	23.193	1.209
4300	13.891	105.966	93.233	54.726	6.488	23.594	1.202
4400	13.892	106.283	93.530	56.114	6.762	23.991	1.195
4500	13.893	106.595	93.817	57.503	7.036	24.385	1.188
4600	13.894	106.901	94.098	58.893	7.310	24.776	1.181
4700	13.895	107.207	94.373	60.282	7.584	25.163	1.174
4800	13.896	107.478	94.609	61.661	7.858	25.547	1.167
4900	13.897	107.748	94.890	63.041	8.132	25.928	1.160
5000	13.898	108.009	95.169	64.451	8.406	26.306	1.153
5100	13.897	108.334	95.425	65.840	8.680	26.682	1.146
5200	13.897	108.659	95.673	67.230	8.954	27.057	1.139
5300	13.898	108.969	95.915	68.620	9.228	27.430	1.132
5400	13.898	109.129	96.164	70.009	9.502	27.802	1.125
5500	13.899	109.384	96.402	71.399	9.776	28.173	1.118
5600	13.899	109.634	96.636	72.789	10.050	28.543	1.111
5700	13.899	109.884	96.865	74.179	10.324	28.912	1.104
5800	13.899	110.120	97.089	75.569	10.598	29.280	1.097
5900	13.900	110.360	97.316	76.959	10.872	29.647	1.090
6000	13.901	110.593	97.535	78.349	11.146	30.011	1.083
						33.301	1.213

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1964

BORON DIBROMIDE (BBr₂) (IDEAL GAS)

MOL. WT. = 170.652

BBr₂

Point Group [C_{2v}]
 $\Delta H_f^0 = [18.2 \pm 15] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [70.402] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{298.15} = [15.0 \pm 15] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight [2]

Vibrational Frequencies and Degeneracies

ΔE cm. ⁻¹
[600](1)
[150](1)
[830](1)

Bond Distance: [1.87] Å
 Bond Angle: [120°]

$\sigma = 2$

Product of the Moments of Inertia: $I_A I_B I_C = 7.26584 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation was estimated by analogy with BP₃, specifically the ratio

$$\Delta H_f(\text{BX}_3) \rightarrow \text{BX}_2 + \text{X} / \Delta H_f(\text{BX}_3) \rightarrow \text{B} + 3\text{X}$$

was taken as 0.347.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trihalide given by G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were $I_B = 1.4708 \times 10^{-39} \text{ g. cm.}^2$, $I_A = 69.5532 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 71.0240 \times 10^{-39} \text{ g. cm.}^2$

BBr₂

Boron Dibromide Chloride (BBr₂Cl)

(Ideal Gas) Mol. Wt. = 206.109

BBr₂Cl

BORON DIBROMIDE CHLORIDE (BBr₂Cl)

(IDEAL GAS)

MOL. WT. = 206.109

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	-3.607	-	61.359	-	INFINITE
100	10.827	62.411	89.591	-	61.359	-	140.261
200	19.932	70.977	78.209	-	61.359	-	72.921
298	19.781	78.909	78.909	-	61.359	-	50.371
300	19.810	77.007	76.016	.029	65.016	-	50.077
400	17.038	81.736	77.546	1.676	72.346	-	37.614
500	17.833	85.630	78.785	3.422	72.323	-	29.810
600	18.354	88.030	80.208	5.284	72.309	-	24.242
700	18.706	89.788	81.971	7.194	72.303	-	20.458
800	18.953	94.303	83.089	8.971	72.308	-	17.658
900	19.131	96.546	84.662	10.876	72.320	-	15.464
1000	19.262	98.569	85.773	12.796	72.332	-	13.707
1100	19.365	100.409	87.021	14.727	72.343	-	12.271
1200	19.440	102.098	88.397	16.668	72.347	-	11.058
1300	19.502	103.656	89.837	18.615	72.347	-	10.058
1400	19.551	105.103	90.412	20.568	72.346	-	9.168
1500	19.591	106.454	91.437	22.525	72.343	-	8.434
1600	19.624	107.719	92.416	24.486	72.340	-	7.773
1700	19.652	108.910	93.351	26.449	72.336	-	7.189
1800	19.675	110.034	94.247	28.416	72.330	-	6.670
1900	19.695	111.098	95.106	30.384	72.323	-	6.204
2000	19.712	112.109	95.931	32.355	73.003	-	5.785
2100	19.727	113.071	96.725	34.327	73.117	-	5.405
2200	19.740	113.989	97.489	36.300	73.239	-	5.059
2300	19.751	114.867	98.225	38.275	73.366	-	4.742
2400	19.761	115.707	98.936	40.250	73.499	-	4.451
2500	19.769	116.514	99.623	42.227	79.024	-	4.174
2600	19.777	117.290	100.288	44.204	79.159	-	3.908
2700	19.784	118.036	100.932	46.182	79.296	-	3.649
2800	19.790	118.756	101.556	48.161	79.436	-	3.432
2900	19.796	119.450	102.161	50.140	79.576	-	3.218
3000	19.801	120.122	102.748	52.120	79.718	-	3.018
3100	19.805	120.771	103.319	54.100	79.864	-	2.830
3200	19.809	121.400	103.878	56.081	80.015	-	2.652
3300	19.813	122.009	104.415	58.062	80.159	-	2.488
3400	19.817	122.601	104.941	60.044	80.309	-	2.332
3500	19.820	123.175	105.454	62.026	80.463	-	2.185
3600	19.823	123.734	105.954	64.008	80.618	-	2.045
3700	19.825	124.277	106.442	65.990	80.775	-	1.913
3800	19.828	124.806	106.918	67.973	80.934	-	1.787
3900	19.830	125.321	107.383	69.956	81.096	-	1.667
4000	19.832	125.823	107.838	71.939	81.262	-	1.547
4100	19.834	126.313	108.283	73.922	81.431	-	1.437
4200	19.836	126.791	108.718	75.905	81.602	-	1.337
4300	19.837	127.257	109.144	77.889	81.775	-	1.247
4400	19.839	127.713	109.560	79.873	81.950	-	1.167
4500	19.841	128.159	109.969	81.857	82.126	-	1.097
4600	19.842	128.595	110.369	83.841	82.303	-	1.037
4700	19.843	129.022	111.761	85.825	82.481	-	1.005
4800	19.844	129.440	113.146	87.810	82.660	-	1.005
4900	19.846	129.849	114.524	89.794	82.840	-	1.005
5000	19.847	130.250	115.894	91.778	83.020	-	1.005
5100	19.848	130.643	117.258	93.763	83.203	-	1.005
5200	19.849	131.028	118.615	95.748	83.387	-	1.005
5300	19.849	131.407	119.966	97.733	83.572	-	1.005
5400	19.850	131.778	121.311	99.718	83.758	-	1.005
5500	19.851	132.142	122.650	101.703	83.944	-	1.005
5600	19.852	132.499	123.984	103.688	84.131	-	1.005
5700	19.853	132.851	125.312	105.673	84.319	-	1.005
5800	19.853	133.196	126.634	107.658	84.508	-	1.005
5900	19.854	133.536	127.952	109.644	84.698	-	1.005
6000	19.855	133.869	129.264	111.630	84.889	-	1.005

Sept. 30, 1962; Dec. 31, 1964

Point Group C_{2v}

S_{298.15} = 76.909 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight [1]

ΔH_f⁰ = [-61.4 ± 10] kcal. mole⁻¹

ΔH_f⁰ 298.15 = [-65 ± 10] kcal. mole⁻¹

Vibrational Levels and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
925(1)	834(1)
344(1)	195(1)
166(1)	406(1)

Bond Distance: B-Br = 1.87 Å B-Cl = 1.75 Å

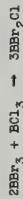
Bond Angle: Br-B-Br = [120°] Cl-B-Br = [120°]

Product of the Moments of Inertia: I_AI_BI_C = 2.55478 X 10⁻¹¹² g.³ cm.⁶

σ' = 2

Heat of Formation.

The heat of formation was estimated by assuming ΔH_f = 0 for the reaction



Heat Capacity and Entropy.

The vibrational frequencies have all been observed and assigned by L. P. Lindeman and M. K. Wilson, J. Chem. Phys., 24, 242 (1956). The bond lengths were reported by T. Wentink and V. H. Tiensau, J. Chem. Phys., 28, 826 (1958).

Bond angles were estimated by analogy with the other trihalides of boron. Individual moments of inertia are

I_B = 35.0754 X 10⁻³⁹ g. cm.², I_A = 69.5934 X 10⁻³⁹ g. cm.² and I_C = 104.6668 X 10⁻³⁹ g. cm.²

BBr₂Cl

Boron Dibromide Fluoride (BBr_2F)
(Ideal Gas) Mol. Wt. = 189.652

T, °K.	C_p°	$-\text{cal. mole}^{-1}\text{deg}^{-1}$	$S^\circ - (\text{F}^\circ - \text{H}_{298}^\circ)/T$	$\text{H}^\circ - \text{H}_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _F
0	<0.00	INFINITE	-	3.287	-119.181	INFINITE	
100	9.938	60.594	85.927	-2.533	-119.208	266.780	
200	12.998	68.496	83.373	-1.373	-119.792	136.193	
298	14.894	74.066	74.066	0.000	-123.000	92.792	
300	14.923	74.159	74.067	0.028	-123.017	92.236	
400	15.213	78.640	74.669	1.588	-130.404	69.005	
500	17.110	82.360	75.846	3.257	-130.434	54.754	
600	17.742	85.538	77.203	5.001	-130.469	45.251	
700	18.194	88.309	78.596	6.800	-130.505	38.462	
800	18.524	90.761	79.966	8.636	-130.543	33.368	
900	18.780	92.928	81.290	10.502	-130.579	29.406	
1000	18.956	94.846	82.557	12.388	-130.620	26.234	
1100	19.100	96.759	83.767	14.291	-130.669	23.639	
1200	19.214	98.426	84.920	16.207	-130.724	21.475	
1300	19.305	99.968	86.019	18.133	-130.788	19.643	
1400	19.379	101.411	87.066	20.068	-130.860	18.072	
1500	19.439	102.741	88.068	22.005	-130.944	16.710	
1600	19.489	103.997	89.025	23.955	-131.037	15.517	
1700	19.531	105.180	89.941	25.906	-131.140	14.464	
1800	19.566	106.297	90.819	27.861	-131.252	13.527	
1900	19.595	107.350	91.661	29.820	-131.371	12.688	
2000	19.623	108.362	92.471	31.789	-131.496	11.952	
2100	19.645	109.319	93.251	33.744	-131.627	11.247	
2200	19.665	110.234	94.002	35.700	-131.764	10.625	
2300	19.682	111.108	94.727	37.676	-131.906	10.055	
2400	19.697	111.945	95.434	39.674	-132.054	9.532	
2500	19.711	112.751	96.104	41.616	-132.204	9.042	
2600	19.723	113.524	96.760	43.588	-132.356	8.579	
2700	19.734	114.269	97.394	45.560	-132.489	8.150	
2800	19.744	114.986	98.000	47.534	-132.609	7.751	
2900	19.752	115.679	98.584	49.509	-132.714	7.380	
3000	19.760	116.349	99.188	51.485	-132.815	7.032	
3100	19.767	116.997	99.752	53.461	-132.912	6.707	
3200	19.773	117.625	100.301	55.438	-133.007	6.401	
3300	19.778	118.234	100.835	57.416	-133.100	6.114	
3400	19.784	118.824	101.355	59.394	-133.190	5.845	
3500	19.789	119.398	101.863	61.372	-133.279	5.588	
3600	19.794	119.955	102.357	63.352	-133.317	5.347	
3700	19.798	120.497	102.840	65.331	-133.483	5.118	
3800	19.805	121.046	103.312	67.311	-133.651	4.901	
3900	19.805	121.564	103.772	69.291	-133.811	4.695	
4000	19.809	122.041	104.223	71.272	-133.971	4.502	
4100	19.812	122.531	104.664	73.253	-134.114	4.324	
4200	19.815	123.008	105.095	75.235	-134.257	4.156	
4300	19.818	123.474	105.517	77.216	-134.400	4.000	
4400	19.820	123.934	105.935	79.197	-134.543	3.855	
4500	19.822	124.375	106.335	81.180	-134.686	3.719	
4600	19.824	124.811	106.732	83.162	-134.829	3.591	
4700	19.826	125.237	107.121	85.145	-134.972	3.470	
4800	19.828	125.654	107.507	87.128	-135.115	3.356	
4900	19.830	126.064	107.891	89.113	-135.258	3.248	
5000	19.832	126.464	108.266	91.094	-135.401	3.145	
5100	19.833	126.857	108.607	93.077	-135.544	3.047	
5200	19.835	127.242	108.961	95.060	-135.687	2.954	
5300	19.837	127.619	109.310	97.043	-135.830	2.866	
5400	19.839	127.991	109.659	99.028	-135.973	2.782	
5500	19.839	128.355	109.989	101.011	-136.116	2.702	
5600	19.840	128.712	110.320	102.995	-136.259	2.627	
5700	19.841	129.063	110.646	104.979	-136.402	2.556	
5800	19.843	129.408	110.968	106.963	-136.545	2.489	
5900	19.844	129.748	111.282	108.948	-136.688	2.425	
6000	19.844	130.081	111.593	110.932	-136.831	2.364	

Sept. 30, 1962; Dec. 31, 1964

BBr_2F

BORON DIBROMIDE FLUORIDE (BBr_2F) (IDEAL GAS)

MOL. WT. = 189.652

Point Group C_{2v}
 $\Delta H_f^\circ 0 = [-119.2 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-123 \pm 10] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [74.066] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies

ω , cm.^{-1}	ω , cm.^{-1}
1310 (1)	869 (1)
[418](1)	[283](1)
[183](1)	[496](1)

Bond Distance: B-Br = 1.87 Å B-Cl = 1.295 Å
 Bond Angle: Br-B-Br = [120°] Br-B-F = [120°]
 $\sigma = 2$

Product of the Moments of Inertia: $I_A I_B I_C = 8.72359 \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f^\circ = 0$ for the reaction $2\text{BBr}_3 + \text{BF}_3 \rightarrow 3\text{BBr}_2\text{F}$.

Heat Capacity and Entropy.

Two of the vibrational frequencies were observed and assigned by L. P. Lindeman and M. K. Wilson, J. Chem. Phys., 24, 242 (1956), the remaining frequencies were calculated by a normal coordinate treatment using force constants obtained by comparison with the other mixed trihalides. The bond distances were reported by T. Wentink and V. H. Flensburg, J. Chem. Phys., 28, 826 (1958). The bond angles were estimated by analogy with the other trihalides. The individual moments of inertia were $I_B = 14.8452 \times 10^{-59} \text{ g. cm.}^2$, $I_A = 69.5934 \times 10^{-59} \text{ g. cm.}^2$ and $I_C = 84.4386 \times 10^{-59} \text{ g. cm.}^2$

BBr_2F

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ cal. mole ⁻¹	ΔF° _f	Log K _P
0	4.000	INFINITE	3.017	20.854	INFINITE
100	8.525	76.889	21.462	21.462	21.462
200	12.726	69.617	25.000	20.897	21.015
300	12.757	69.896	25.021	20.928	21.802
400	14.209	73.776	32.578	30.022	16.403
500	15.247	77.065	42.952	32.747	12.635
600	16.006	79.915	52.886	28.673	10.444
700	16.589	82.428	62.047	27.958	8.759
800	17.054	84.675	70.126	27.228	7.438
900	17.434	86.706	77.345	26.483	6.431
1000	17.748	88.500	83.276	25.728	5.623
1100	18.011	90.264	88.443	24.966	4.960
1200	18.231	91.841	92.815	24.195	4.407
1300	18.418	93.308	96.468	23.419	3.937
1400	18.577	94.678	99.466	22.635	3.533
1500	18.713	95.965	101.849	21.849	3.183
1600	18.830	97.176	103.620	21.053	2.876
1700	18.931	98.321	104.828	20.252	2.604
1800	19.018	99.406	105.947	19.448	2.361
1900	19.095	100.436	106.981	18.632	2.143
2000	19.162	101.417	107.935	17.813	1.947
2100	19.221	102.354	108.828	16.992	1.768
2200	19.273	103.249	109.668	16.160	1.605
2300	19.319	104.107	110.458	15.324	1.456
2400	19.361	104.930	111.200	14.486	1.319
2500	19.398	105.721	111.900	13.648	1.192
2600	19.431	106.482	112.567	12.812	1.076
2700	19.461	107.216	113.200	11.976	0.970
2800	19.488	107.924	113.800	11.137	0.873
2900	19.512	108.609	114.375	10.296	0.785
3000	19.534	109.271	114.915	9.455	0.704
3100	19.555	109.911	115.418	8.614	0.629
3200	19.573	110.533	115.885	7.772	0.560
3300	19.590	111.135	116.315	6.929	0.496
3400	19.606	111.720	116.708	6.086	0.437
3500	19.620	112.289	117.064	5.243	0.382
3600	19.633	112.842	117.384	4.399	0.331
3700	19.646	113.380	117.666	3.555	0.283
3800	19.657	113.904	117.909	2.712	0.238
3900	19.668	114.415	118.113	1.869	0.196
4000	19.677	114.913	118.284	1.026	0.157
4100	19.686	115.399	118.418	0.183	0.121
4200	19.695	115.873	118.506	0.340	0.086
4300	19.703	116.337	118.550	0.497	0.052
4400	19.710	116.790	118.560	0.654	0.019
4500	19.717	117.233	118.534	0.811	0.000
4600	19.724	117.666	118.462	0.968	0.000
4700	19.730	118.090	118.342	1.125	0.000
4800	19.735	118.506	118.176	1.282	0.000
4900	19.741	118.913	117.964	1.439	0.000
5000	19.746	119.312	117.706	1.596	0.000
5100	19.751	119.703	117.402	1.753	0.000
5200	19.755	120.086	117.052	1.910	0.000
5300	19.759	120.463	116.657	2.067	0.000
5400	19.763	120.836	116.218	2.224	0.000
5500	19.767	121.199	115.735	2.381	0.000
5600	19.771	121.551	115.208	2.538	0.000
5700	19.774	121.901	114.636	2.695	0.000
5800	19.778	122.245	114.019	2.852	0.000
5900	19.781	122.584	113.356	3.009	0.000
6000	19.784	122.913	112.648	3.166	0.000

Mar. 31, 1966

Point Group C_{2v}
S°_{298.15} = [69.82] cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = [-21 ± 5] kcal. mole⁻¹
ΔH°_f 298.15 = [-25 ± 5] kcal. mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies		
ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
2600 (1)	1044 (1)	
[532](1)	775 (1)	
[158](1)	783 (1)	

Bond Distance : B-H = 1.20 Å B-Br = [1.87] Å
Bond Angle: Br-B-Br = 119.5 ± 2° Br-B-H = 120.3 ± 1°
Product of the Moments of Inertia: I_AI_BI_C = 1.08645 X 10⁻¹¹³ g.³ cm.⁶
σ = 2

Heat of Formation.
The value of ΔH°_f 298.15 (BBr₂H, g) was derived by assuming the B-H bond strength to be 92 kcal. mole⁻¹, the same as that in BCl₂H(g).

Heat Capacity and Entropy.

The molecular structure, B-H bond distance and bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. 41, 3165 (1964). The B-Br bond distance was taken from that in BBr₃(g) molecule. The vibrational frequencies adopted and corrected to the average isotopic species were assigned by O. Brioux de Mandirola and J. P. Westerkamp, Spectrochim. Acta, 21, 1101 (1965), from infrared spectrum. The values in brackets are calculated by the Wilson's FG-method. Infrared spectrum of BBr₂H(g) was also reported by S. K. Watson and R. P. Porter, J. Phys. Chem. 69, 2461 (1965), and three frequencies, ν₁, ν₂ and ν₃, were assigned. The three principal moments of inertia are: I_A = 6.87842 X 10⁻³⁸, I_B = 2.2244 X 10⁻³⁸ and I_C = 7.10086 X 10⁻³⁸ g. cm.²

Boron Tribromide (BB₃)

(Liquid) Mol. Wt. = 250.568

T, °K.	C _p ^o	$\int_0^T \frac{C_p^o}{T^2} dT$	$\int_0^T \frac{C_p^o}{T} dT$	$\int_0^T \frac{C_p^o}{T^2} dT$	$\int_0^T \frac{C_p^o}{T} dT$	$\int_0^T \frac{C_p^o}{T^2} dT$	Log K _p
0							
200	30.600	54.700	54.700	0.000	- 57.000	- 56.619	41.501
250	30.600	54.889	54.701	0.057	- 56.998	- 56.616	41.243
300	30.600	55.092	55.501	0.117	- 56.620	- 56.439	39.743
400	30.600	55.520	56.187	0.177	- 55.297	- 54.550	22.531
500	30.600	56.099	60.705	0.237	- 64.044	- 48.919	17.818
600	30.600	80.816	63.249	12.297	- 62.840	- 46.494	14.515
700	30.600	84.902	65.706	15.357	- 61.669	- 44.240	12.085
800	30.600	88.043	68.063	18.417	- 60.522	- 42.130	10.230
900	30.600	91.750	70.235	21.477	- 59.397	- 40.145	8.773

BORON TRIBROMIDE (BB₃)

(LIQUID)

$S_{298.15}^o = 54.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 227.2^\circ\text{K}$
 $T_b = 364.4^\circ\text{K}$
 $\Delta H_f^o = 7.30 \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = \text{Unknown}$
 $\Delta H_v^o = -57.0 \pm 0.2 \text{ kcal. mole}^{-1}$
 MOL. WT. = 250.568

Heat of Formation.

The heat of formation of boron tribromide liquid has been determined by H. A. Skinner and N. B. Smith, Trans. Farad. Soc. 51, 19 (1955) by hydrolysis to H₃BO₃ and HBr. The adopted heat of formation was calculated from Skinner's hydrolysis data using $\Delta H_f^o \text{ H}_3\text{BO}_3(\text{c})$ from these tables, $\Delta H_{\text{soln}}^o \text{ H}_3\text{BO}_3$ from L. G. Fessenden, National Research Corporation Special Report NMR-3608 (OO) June 2, 1964, with the dilution data of J. Smisko and L. S. Mason, J. Am. Chem. Soc. 72, 3679 (1950). The $\Delta H_f^o \text{ HBr}(\text{aq})$ was taken from W. H. Evans, Appendix III, Natl. Bureau of Standards Report 8504, 1 July 1964.

Heat Capacity and Entropy.

The heat capacity was estimated from that of the gas by K. K. Kelley USNM Bulletin 383. The entropy was back calculated from that of the gas by adjusting the free energy functions to give the best fit of the vapor pressure data.

Melting Data.

The temperature of melting was reported by J. Goubeau and H. Keller, Z. anorg. allgem. Chem. 267, 1 (1951) and A. Stock and E. Kuss, Ber. 47, 3113 (1914). This value was recently confirmed by the triple point measurement of 227.31°K by W. F. Barber, C. F. Boynton and P. E. Gallagher J. Chem. Eng. Data 9, 137 (1964).

Boiling Data.

The boiling point is from the data of Stock and Kuss, loc. cit. A second and third law analysis of the vapor pressure data of Stock and Kuss (1) and Barber et. al. (2) loc. cit. indicated that the data of Stock gave the best agreement as indicated below.

	Second Law	Third Law
ΔH_v	298.15 kcal. mole ⁻¹	$S_{298}^o = 54.26$
Ref. 1.	8.175 ± 0.03	8.222 (-0.02)
Ref. 2.	8.229 ± 0.03	8.203 (-0.44)
		8.361 (0.42)
		8.347 (0.00)

Ref. 1. had the first eight data points rejected due to a statistical test on the third law values. The values in parentheses are values of the third law drift measured as $\Delta(\Delta H) / \Delta T$. The second law entropy also confirmed the choice of the data of ref. 1 and an entropy of 54.7 cal. deg.⁻¹ mole⁻¹.

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	g° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	Log K _f
0	-0.000	0.000	INFINITE	-3.755	-43.475	INFINITE
100	11.544	62.344	90.633	-2.629	-47.852	10.576
200	14.474	71.364	78.018	-1.311	-44.075	56.777
298	16.108	77.487	77.487	0.000	-48.800	55.213
300	16.224	77.588	77.488	0.100	-48.825	40.549
400	17.578	82.348	78.488	0.910	-48.825	30.753
500	18.079	86.380	79.404	3.468	-50.786	23.569
600	18.545	89.720	80.652	5.321	-50.760	19.234
700	18.857	92.604	82.329	7.492	-50.745	16.125
800	19.120	95.137	83.775	9.880	-50.736	13.764
900	19.345	97.425	85.041	12.493	-50.736	11.511
1000	19.535	99.425	86.491	15.293	-50.740	10.550
1100	19.692	101.275	88.073	18.273	-50.758	9.343
1200	19.829	102.967	89.751	21.419	-50.785	8.353
1300	19.958	104.490	91.500	24.726	-50.823	7.519
1400	20.079	105.950	93.320	28.193	-50.873	6.827
1500	20.193	107.334	95.226	31.820	-50.934	6.174
1600	20.299	108.602	97.192	35.606	-50.005	5.628
1700	20.398	109.794	99.134	39.543	-50.086	5.145
1800	20.490	110.918	101.050	43.630	-50.180	4.711
1900	20.575	111.985	102.940	47.867	-50.280	4.331
2000	20.655	112.997	104.800	52.256	-50.388	3.984
2100	20.731	113.960	106.630	56.797	-50.500	3.669
2200	20.798	114.876	108.430	61.485	-50.618	3.383
2300	20.857	115.747	110.200	66.317	-50.742	3.126
2400	20.908	116.575	111.940	71.293	-50.872	2.896
2500	20.954	117.360	113.650	76.417	-51.009	2.690
2600	20.996	118.103	115.330	81.689	-51.152	2.499
2700	21.035	118.800	116.980	87.111	-51.300	2.321
2800	21.071	119.450	118.600	92.683	-51.452	2.155
2900	21.105	120.060	120.190	98.405	-51.608	2.002
3000	21.136	120.630	121.750	104.277	-51.768	1.867
3100	21.165	121.166	123.280	110.299	-51.932	1.746
3200	21.191	121.666	124.780	116.471	-52.100	1.636
3300	21.215	122.130	126.250	122.793	-52.272	1.536
3400	21.236	122.560	127.690	129.265	-52.448	1.444
3500	21.255	122.960	129.100	135.887	-52.628	1.359
3600	21.271	123.330	130.480	142.659	-52.812	1.280
3700	21.285	123.670	131.830	149.581	-53.000	1.207
3800	21.297	123.980	133.150	156.653	-53.192	1.139
3900	21.307	124.260	134.450	163.875	-53.388	1.075
4000	21.315	124.520	135.720	171.247	-53.588	1.015
4100	21.321	124.760	136.960	178.669	-53.792	0.958
4200	21.326	124.980	138.170	186.141	-54.000	0.904
4300	21.329	125.180	139.350	193.663	-54.212	0.852
4400	21.331	125.360	140.510	201.235	-54.428	0.802
4500	21.332	125.520	141.650	208.857	-54.648	0.754
4600	21.332	125.660	142.770	216.529	-54.872	0.708
4700	21.331	125.780	143.870	224.251	-55.100	0.664
4800	21.329	125.880	144.950	232.023	-55.332	0.621
4900	21.326	125.960	146.010	239.845	-55.568	0.580
5000	21.321	126.020	147.050	247.717	-55.808	0.540
5100	21.315	126.060	148.070	255.639	-56.052	0.500
5200	21.307	126.090	149.070	263.601	-56.300	0.461
5300	21.297	126.110	150.050	271.613	-56.552	0.423
5400	21.285	126.120	151.010	279.675	-56.808	0.386
5500	21.271	126.120	151.950	287.787	-57.068	0.350
5600	21.255	126.110	152.870	295.949	-57.332	0.315
5700	21.236	126.090	153.770	304.161	-57.600	0.280
5800	21.215	126.060	154.650	312.423	-57.872	0.246
5900	21.191	126.020	155.510	320.735	-58.148	0.213
6000	21.165	125.960	156.350	329.097	-58.428	0.180

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

Point Group D_{3h}
 $S_{298.15}^o = 77.487 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = -43.5 \pm 0.22 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = -48.8 \pm 0.22 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	$278 (1)$
	379 (1)
	827 (2)
	150 (2)

Bond Distance: B-Br = $1.87 \pm 0.02 \text{ \AA}$
 Bond Angle: Br-B-Br = $120^\circ \pm 6^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 6.74115 \times 10^{-112} \text{ g. cm.}^5$
 $\sigma = 8$

Heat of Formation.

ΔH_f^o 298 was obtained from the heat of formation of the liquid plus the heat of vaporization at 298°K, taken as 8.20 kcal. mole⁻¹ as the average second and third law value derived from the vapor pressures of A. Stock and E. Kuss, Ber. 47, 3113 (1914). See BBr₃(1) for details.

Heat Capacity and Entropy.

Vibrational frequencies were obtained from T. Wentink, Jr., and V. H. Tiensuu, J. Chem. Phys., 28, 825 (1958) modified for the natural isotopic abundances (B 10.16.8%, Br 81.17%) given by J. R. Bradford, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., 1958. B-Br bond distance was reported by T. Wentink, Jr., and V. H. Tiensuu, loc. cit. Br-B-Br angle was taken from L. E. Sutton (editor), "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. The individual moments of inertia were $I_A = I_B = 419.167 \times 10^{-39} \text{ g. cm.}^2$, $I_C = 838.375 \times 10^{-39} \text{ g. cm.}^2$.

BORON MONOCHLORIDE (BCl)
(IDEAL GAS)
MOL. WT. = 46.277
Ground State Configuration 1^2
 $\Delta H_f^0 = 33.1 \pm 4.0$ kcal mole $^{-1}$
 $\Delta H_f^{298.15} = 50.942$ cal deg $^{-1}$ mole $^{-1}$
 $S_{298.15}^0 = 33.6 \pm 4.0$ kcal mole $^{-1}$

Electronic Levels and Quantum Weight

s_i , cm $^{-1}$	g_i
0	1
$\omega_e x_e = 5.167$ cm $^{-1}$	$\sigma = 1$
$\omega_e = 843.65$ cm $^{-1}$	$\alpha_e = 0.00657$ cm $^{-1}$
$B_e = 0.6914$ cm $^{-1}$	$r_e = 1.7157$ Å

Heat of Formation

The dissociation energy (D_0^0) of BCl(g) has been reported by G. Herzberg¹, A. G. Gaydon² and R. F. Barrow³, respectively. Hence the corresponding values of ΔH_f^0 for BCl(g) were derived. The results are given as follows.

Investigator	e.v.	D_0^0	ΔH_f^0
Herzberg ¹	4.2	96.9	82.6
Gaydon ²	5.1 \pm 0.4	117.6 \pm 9.2	41.8 \pm 9.2
Barrow ³	---	127	33.8 \pm 4

1 G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950.

2 A. G. Gaydon, "Association Energies", Chapman and Hall Ltd., London, 1953.

3 R. F. Barrow, Trans. Faraday Soc. **56**, 952 (1960).

The last value of ΔH_f^0 298.15 listed in the above table is adopted. Using the bond energy, $D^0(B-Cl)$, obtained from BCl $_3$ (g) molecule, the heat of formation (ΔH_f^0 298.15) for BCl(g) was calculated as 37.8 kcal mole $^{-1}$ employing the same ratio of $D^0(B-X)$ /average bond energy of BX_3 as found in BF_3 (g) and BF_3 (g), which is within the uncertainty of the value evaluated from dissociation energy.

Heat Capacity and Entropy

The spectroscopic constants were obtained from G. Herzberg, loc. cit. and corrected to the average isotopic species. The principal moment of inertia (I) is 4.0514×10^{-39} g cm 2 .

Boron Monochloride (BCl)

(Ideal Gas) Mol. Wt. = 46.277

T, K	C_p^0	S^0	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0	0.000	0.000	INFINITE	- 2.118	33.071	33.071	INFINITE
100	6.950	43.155	57.466	- 1.423	33.409	31.962	- 31.508
200	7.140	46.013	57.619	- 0.721	33.671	29.202	- 31.008
298	7.267	50.842	50.842	0.000	33.800	26.974	- 15.772
300	7.575	50.988	50.942	0.014	33.802	26.932	- 19.619
400	7.967	53.224	51.244	1.762	33.843	24.633	- 13.458
500	8.248	55.034	51.827	1.604	33.815	22.333	- 9.761
600	8.442	56.556	52.491	2.439	33.740	20.043	- 7.300
700	8.579	57.868	53.168	3.280	33.637	17.769	- 5.347
800	8.678	59.020	53.829	4.153	33.512	15.510	- 4.237
900	8.752	60.047	54.464	5.025	33.372	13.267	- 3.222
1000	8.810	60.972	55.069	5.903	33.219	11.042	- 2.413
1100	8.856	61.814	55.645	6.766	33.049	8.832	- 1.755
1200	8.894	62.566	56.191	7.674	32.868	6.659	- 1.209
1300	8.926	63.300	56.711	8.565	32.674	4.460	- 0.750
1400	8.954	63.962	57.206	9.459	32.469	2.298	- 0.359
1500	8.978	64.581	57.677	10.356	32.252	0.149	- 0.022
1600	9.000	65.161	58.127	11.255	32.024	- 1.083	0.271
1700	9.020	65.707	58.557	12.156	31.785	- 2.300	0.527
1800	9.038	66.223	58.968	13.059	31.538	- 3.525	0.753
1900	9.054	66.712	59.363	13.963	31.283	- 4.754	0.954
2000	9.070	67.177	59.742	14.869	31.023	- 6.000	1.133
2100	9.085	67.620	60.107	15.777	30.758	- 7.264	1.294
2200	9.099	68.043	60.458	16.686	30.488	- 8.544	1.439
2300	9.112	68.448	60.797	17.597	30.214	- 9.833	1.570
2400	9.125	68.836	61.124	18.509	29.936	- 11.133	1.689
2500	9.138	69.209	61.440	19.422	29.656	- 12.444	1.788
2600	9.150	69.567	61.746	20.336	29.368	- 13.764	1.869
2700	9.162	69.913	62.042	21.242	29.071	- 15.094	1.943
2800	9.174	70.246	62.329	22.149	28.766	- 16.433	2.011
2900	9.185	70.568	62.607	23.057	28.452	- 17.781	2.074
3000	9.196	70.880	62.878	24.006	28.132	- 19.132	2.132
3100	9.207	71.182	63.141	24.926	27.804	- 20.486	2.186
3200	9.218	71.474	63.397	25.847	27.468	- 21.844	2.235
3300	9.229	71.758	63.646	26.770	27.124	- 23.204	2.281
3400	9.240	72.034	63.889	27.693	26.774	- 24.564	2.323
3500	9.250	72.302	64.125	28.618	26.418	- 25.924	2.363
3600	9.261	72.562	64.356	29.543	26.054	- 27.284	2.400
3700	9.271	72.816	64.581	30.470	25.681	- 28.644	2.435
3800	9.281	73.064	64.801	31.397	25.298	- 30.004	2.467
3900	9.292	73.305	65.016	32.326	24.904	- 31.364	2.497
4000	9.302	73.540	65.226	33.256	24.500	- 32.724	2.528
4100	9.312	73.770	65.432	34.186	24.086	- 34.084	2.558
4200	9.322	73.995	65.633	35.118	23.662	- 35.444	2.588
4300	9.332	74.214	65.830	36.051	23.234	- 36.804	2.618
4400	9.342	74.429	66.023	36.984	22.800	- 38.164	2.648
4500	9.352	74.639	66.212	37.919	22.356	- 39.524	2.678
4600	9.361	74.844	66.398	38.855	21.902	- 40.884	2.708
4700	9.371	75.046	66.579	39.791	21.442	- 42.244	2.738
4800	9.381	75.243	66.758	40.729	20.974	- 43.604	2.768
4900	9.391	75.437	66.933	41.668	20.500	- 44.964	2.798
5000	9.401	75.627	67.105	42.607	20.016	- 46.324	2.828
5100	9.410	75.813	67.274	43.548	19.522	- 47.684	2.858
5200	9.420	75.996	67.440	44.489	19.018	- 49.044	2.888
5300	9.430	76.175	67.603	45.432	18.504	- 50.404	2.918
5400	9.439	76.351	67.763	46.375	17.979	- 51.764	2.948
5500	9.448	76.525	67.921	47.320	17.444	- 53.124	2.978
5600	9.459	76.695	68.076	48.265	16.899	- 54.484	3.008
5700	9.468	76.863	68.229	49.211	16.344	- 55.844	3.038
5800	9.478	77.027	68.379	50.159	15.779	- 57.204	3.068
5900	9.488	77.189	68.527	51.107	15.204	- 58.564	3.098
6000	9.497	77.349	68.673	52.056	14.619	- 59.924	3.128

Boron Monochloride Unipositive Ion (BCl⁺)

(Ideal Gas) GFW = 46.2634

T, °K	C _p ^o	S ^o - (C _p ^o - H _{298.15})/T	H ^o - H _{298.15}	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100	7.563	52.347	52.346	.000	295.000	286.268
200						
300	7.571	52.347	52.347	.014	295.010	286.213
400	7.563	52.428	52.428	.752	295.548	283.198
500	7.543	52.436	52.431	1.603	296.017	280.056
600	7.508	52.395	52.395	2.437	296.439	276.833
700	7.467	52.329	52.329	3.268	296.831	273.522
800	7.422	52.232	52.232	4.151	297.202	270.166
900	7.376	52.107	52.107	5.082	297.559	266.785
1000	7.331	51.962	51.962	6.069	297.902	263.395
1100	7.286	51.800	51.800	7.102	298.229	259.992
1200	7.241	51.623	51.623	8.180	298.544	256.580
1300	7.196	51.432	51.432	9.303	298.845	253.150
1400	7.151	51.228	51.228	10.469	299.136	249.703
1500	7.106	51.012	51.012	11.678	299.415	246.239
1600	7.061	50.785	50.785	12.929	299.683	242.760
1700	7.016	50.548	50.548	14.221	299.940	239.267
1800	6.971	50.301	50.301	15.554	300.188	235.760
1900	6.926	50.044	50.044	16.938	300.429	232.239
2000	6.881	49.778	49.778	18.372	300.665	228.703
2100	6.836	49.503	49.503	19.856	300.898	225.153
2200	6.791	49.219	49.219	21.390	301.121	221.589
2300	6.746	48.926	48.926	22.974	301.342	218.012
2400	6.701	48.624	48.624	24.608	301.559	214.423
2500	6.656	48.313	48.313	26.292	301.772	210.823
2600	6.611	48.000	48.000	28.026	301.981	207.213
2700	6.566	47.678	47.678	29.809	302.186	203.593
2800	6.521	47.354	47.354	31.642	302.387	199.963
2900	6.476	47.021	47.021	33.526	302.584	196.323
3000	6.431	46.688	46.688	35.460	302.777	192.673
3100	6.386	46.354	46.354	37.444	302.966	189.013
3200	6.341	46.021	46.021	39.478	303.151	185.343
3300	6.296	45.688	45.688	41.562	303.332	181.663
3400	6.251	45.354	45.354	43.696	303.510	177.973
3500	6.206	45.021	45.021	45.880	303.685	174.273
3600	6.161	44.688	44.688	48.114	303.857	170.563
3700	6.116	44.354	44.354	50.400	304.026	166.843
3800	6.071	44.021	44.021	52.736	304.191	163.113
3900	6.026	43.688	43.688	55.122	304.352	159.373
4000	5.981	43.354	43.354	57.558	304.510	155.623
4100	5.936	43.021	43.021	60.044	304.665	151.863
4200	5.891	42.688	42.688	62.580	304.817	148.093
4300	5.846	42.354	42.354	65.166	304.966	144.313
4400	5.801	42.021	42.021	67.802	305.112	140.523
4500	5.756	41.688	41.688	70.488	305.255	136.723
4600	5.711	41.354	41.354	73.224	305.395	132.913
4700	5.666	41.021	41.021	76.010	305.532	129.093
4800	5.621	40.688	40.688	78.846	305.666	125.263
4900	5.576	40.354	40.354	81.732	305.797	121.423
5000	5.531	40.021	40.021	84.668	305.926	117.573
5100	5.486	39.688	39.688	87.654	306.052	113.713
5200	5.441	39.354	39.354	90.690	306.175	109.843
5300	5.396	39.021	39.021	93.776	306.296	105.963
5400	5.351	38.688	38.688	96.912	306.414	102.073
5500	5.306	38.354	38.354	100.100	306.529	98.173
5600	5.261	38.021	38.021	103.338	306.641	94.263
5700	5.216	37.688	37.688	106.626	306.750	90.343
5800	5.171	37.354	37.354	110.064	306.856	86.413
5900	5.126	37.021	37.021	113.652	306.959	82.473
6000	5.081	36.688	36.688	117.290	307.059	78.523

June 30, 1968

BCl⁺

(IDEAL GAS)

GFW = 42.2634

ΔH₀^o = [294.3 ± 10] kcal/mol

ΔH_{298.15}^o = [295 ± 10] kcal/mol

Ground State Configuration [2²]

S_{298.15}^o = [52.3 ± 0.5] gibbs/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	[2]
[28000]	[4]

ω_x = [845] cm⁻¹
B₀ = [0.68] cm⁻¹
ω_e = [5] cm⁻¹
α_e = [0.0056] cm⁻¹
r_e = [1.73] Å

Heat of Formation

Several values of the appearance potential of BCl⁺ from BCl₃ have been reported. Oberghaus (1) gave 19.2eV, Harriott and Craggs (2) reported 18.54 ± 0.07eV, and Koski et al. (3) obtained two values of 17.2 ± 0.2eV and 20 ± 0.2eV. We make the presumption that the higher values, 19.2 and 20, refer to the reaction BCl₃(g) + e⁻ → BCl + 2Cl(g) + 2e⁻ and the other values to BCl₃(g) + e⁻ → BCl + Cl₂(g) + 2e⁻. Using the lower value in each case to help eliminate any excess kinetic energy, we obtain ΔH_{f,298}^o(BCl⁺, g) = 289 and 300 kcal/mol, respectively. We adopt an average value of ΔH_{f,298}^o(BCl⁺, g) = 295 ± 10 kcal/mol, which corresponds to an ionization potential for BCl(g) of 11.3 ± 0.3eV.

Heat Capacity and Entropy

BCl⁺ is isoelectronic with BaCl and the ground state configuration and electronic levels are estimated by comparison with BaCl. The bond length, frequency and anharmonicity constant are estimated between the values for BCl and BCl₂; the rotational constant is calculated from the bond length and atomic masses, and α_e is obtained from the above constants assuming a Morse potential function.

The enthalpy at 0°K is -2.118 kcal/mol.

References

1. O. Oberghaus, Z. Phys. 120, 368 (1950).
2. J. Harriott and J. D. Craggs, J. Electron. Contr. 3, 194 (1957).
3. W. S. Koski, J. J. Kaufman and C. F. Pachuki, J. Am. Chem. Soc. 81, 1326 (1959).

Boron Chloride Fluoride (BClF)
(Ideal Gas) Mol. Wt. = 65.277

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH° _f	ΔF°	Log K _P
0	+0.00	+0.00	INFINITE	-	2.631	-	75.187	-	INFINITE
100	8.253	53.326	71.628	-	1.890	-	75.000	-	166.353
200	9.258	59.362	64.130	-	.954	-	75.000	-	84.344
298	10.169	63.229	63.229	-	.000	-	75.000	-	57.369
300	10.186	63.292	63.292	-	.019	-	75.001	-	57.030
400	11.025	66.341	63.640	-	1.081	-	75.061	-	43.367
500	11.688	68.876	64.440	-	2.218	-	75.167	-	35.150
600	12.181	71.053	65.365	-	3.412	-	75.298	-	29.680
700	12.602	72.859	66.317	-	4.590	-	75.451	-	25.758
800	12.959	74.352	67.355	-	5.750	-	75.621	-	22.512
900	13.268	75.652	68.163	-	6.899	-	75.751	-	20.515
1000	13.555	77.551	69.034	-	8.518	-	75.917	-	18.673
1100	13.278	78.812	69.866	-	9.840	-	76.094	-	17.184
1200	13.445	81.042	70.678	-	11.573	-	76.278	-	15.902
1300	13.465	82.404	71.462	-	13.523	-	76.459	-	14.812
1400	13.506	82.043	72.142	-	15.861	-	76.679	-	13.913
1500	13.555	82.977	72.834	-	18.624	-	76.895	-	13.114
1600	13.596	83.653	73.465	-	21.572	-	77.122	-	12.413
1700	13.638	84.181	74.059	-	24.739	-	77.359	-	11.792
1800	13.680	84.568	74.737	-	28.209	-	77.600	-	11.242
1900	13.695	85.197	75.321	-	32.065	-	77.860	-	10.762
2000	13.706	86.900	75.882	-	36.426	-	78.120	-	10.293
2100	13.724	87.569	76.423	-	41.339	-	78.386	-	9.886
2200	13.741	88.181	76.934	-	46.859	-	78.659	-	9.515
2300	13.755	88.619	77.409	-	53.045	-	78.931	-	9.175
2400	13.767	89.404	77.933	-	59.957	-	79.219	-	8.861
2500	13.778	89.967	78.404	-	67.649	-	84.895	-	8.563
2600	13.789	90.507	78.859	-	76.169	-	85.181	-	8.277
2700	13.798	91.030	79.298	-	85.561	-	85.472	-	8.011
2800	13.805	91.540	79.728	-	95.875	-	85.757	-	7.761
2900	13.812	92.014	80.143	-	107.165	-	86.048	-	7.532
3000	13.818	92.443	80.547	-	119.489	-	86.341	-	7.316
3100	13.824	92.936	80.939	-	132.809	-	86.635	-	7.113
3200	13.830	93.391	81.321	-	147.182	-	86.932	-	6.922
3300	13.834	93.800	81.693	-	162.659	-	87.231	-	6.741
3400	13.839	94.213	82.055	-	179.292	-	87.531	-	6.571
3500	13.843	94.615	82.408	-	197.139	-	87.835	-	6.410
3600	13.846	95.005	82.753	-	216.259	-	88.139	-	6.258
3700	13.849	95.378	83.097	-	236.722	-	88.443	-	6.113
3800	13.853	95.753	83.437	-	258.599	-	88.756	-	5.973
3900	13.856	96.113	83.758	-	281.954	-	89.067	-	5.844
4000	13.858	96.464	84.052	-	306.869	-	89.378	-	5.721
4100	13.861	96.806	84.359	-	333.409	-	89.689	-	5.602
4200	13.863	97.140	84.659	-	361.649	-	89.999	-	5.491
4300	13.865	97.467	84.953	-	391.669	-	90.306	-	5.382
4400	13.867	97.785	85.241	-	423.549	-	90.616	-	5.273
4500	13.869	98.097	85.524	-	457.369	-	90.921	-	5.166
4600	13.871	98.407	85.800	-	493.209	-	91.231	-	5.061
4700	13.873	98.700	86.068	-	531.149	-	91.541	-	4.956
4800	13.874	98.992	86.336	-	571.269	-	91.851	-	4.851
4900	13.876	99.278	86.599	-	613.649	-	92.161	-	4.746
5000	13.877	99.559	86.855	-	658.369	-	92.471	-	4.641
5100	13.878	99.834	87.107	-	705.509	-	92.781	-	4.536
5200	13.880	100.103	87.355	-	754.649	-	93.091	-	4.431
5300	13.881	100.368	87.597	-	805.889	-	93.401	-	4.326
5400	13.882	100.627	87.836	-	859.229	-	93.711	-	4.221
5500	13.883	100.882	88.071	-	914.669	-	94.021	-	4.116
5600	13.884	101.132	88.302	-	972.209	-	94.331	-	4.011
5700	13.885	101.376	88.527	-	1031.849	-	94.641	-	3.906
5800	13.886	101.619	88.753	-	1093.589	-	94.951	-	3.801
5900	13.887	101.857	88.973	-	1157.429	-	95.261	-	3.696
6000	13.887	102.090	89.190	-	1223.369	-	95.571	-	3.591

Mer. 31, 1961; Dec. 31, 1964

BORON CHLORIDE FLUORIDE (BClF) (IDEAL GAS)

MOL. WT. = 65.277

Point Group C_{2v}
 $\Delta H_f^0 = [-75.2 \pm 7.0] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [63.229] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{298.15} = [-75.0 \pm 7.0] \text{ kcal. mole}^{-1}$
Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω_e , cm. ⁻¹
[920] (1)
[360] (1)
[1220] (1)

Bond Distance: B-Cl = [1.73] Å B-F = [1.295] Å
Bond Angle: F-B-Cl = [120]°
Product of the Moments of Inertia: I_AI_BI_C = [1.81165 X 10⁻¹¹⁵] g.³ cm.⁶

σ = 1

Heat of Formation.

The value of $\Delta H_f^{298.15}$ for BClF(g) was estimated based on an assumption that $\Delta H_f^{298.15} = 0$ for the reaction $\text{BCl}_2(\text{g}) + \text{BF}_2(\text{g}) = 2\text{BClF}(\text{g})$. The values of $\Delta H_f^{298.15}$ of $\text{BCl}_2(\text{g})$ and $\text{BF}_2(\text{g})$, used for calculation, are -20 and -130 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy.

The ground state quantum weight and bond angle were assumed to be the same as those for $\text{BF}_2(\text{g})$. The bond distances of B-Cl and B-F were estimated by comparison with those in $\text{BCl}_3(\text{g})$ and $\text{PF}_3(\text{g})$ molecules, respectively. The vibrational frequencies were estimated from the corresponding values for $\text{BCl}_2(\text{g})$ and $\text{BF}_2(\text{g})$. The three principal moments of inertia are: I_A = 1.48569 X 10⁻³⁸, I_B = 7.7980 X 10⁻⁴⁰ and I_C = 1.56367 X 10⁻³⁸ g.² cm.²

BClF

Boron Chloride Difluoride (BCIF₂)

(Ideal Gas) Mol. Wt. = 84.277

BORON CHLORIDE DIFLUORIDE (BCIF₂) (IDEAL GAS) MOL. WT. = 84.277

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	INFINITE	-	2.945	-	211.046	-	INFINITE
100	8.428	54.323	75.737	2.141	-	211.046	-	211.046
200	10.902	60.893	65.769	1.179	-	211.046	-	459.783
298	13.018	65.662	65.662	∞.000	-	211.046	-	228.820
300	13.052	65.742	65.662	∞.24	-	211.046	-	152.732
400	14.637	69.726	66.194	1.413	-	211.046	-	151.774
500	15.814	73.125	67.249	2.538	-	211.046	-	113.230
600	16.683	76.089	68.480	4.565	-	211.046	-	90.089
700	17.357	78.111	69.759	6.267	-	211.046	-	74.653
800	17.857	80.000	71.000	8.000	-	211.046	-	59.621
900	18.171	83.177	72.261	9.825	-	211.046	-	48.904
1000	18.451	85.107	73.450	11.656	-	211.046	-	43.749
1100	18.670	86.876	74.592	13.513	-	212.417	-	39.530
1200	18.844	88.484	75.689	15.389	-	212.417	-	36.012
1300	18.993	90.032	77.289	17.289	-	212.417	-	32.481
1400	19.097	91.433	77.730	19.185	-	212.417	-	28.267
1500	19.150	92.754	78.688	21.099	-	212.417	-	26.328
1600	19.268	93.995	79.606	23.022	-	212.417	-	23.095
1700	19.389	95.272	80.486	24.860	-	212.417	-	21.732
1800	19.437	96.272	82.148	26.830	-	212.417	-	20.505
1900	19.478	97.322	83.322	28.830	-	212.417	-	19.394
2000	19.478	98.320	84.032	30.776	-	212.417	-	17.459
2100	19.513	99.271	84.688	32.726	-	213.640	-	16.358
2200	19.571	101.046	85.121	34.534	-	213.640	-	15.394
2300	19.595	101.883	85.502	36.534	-	213.640	-	14.428
2400	19.595	101.883	85.502	38.534	-	213.640	-	13.428
2500	19.617	102.683	86.462	40.533	-	213.640	-	12.428
2600	19.635	103.453	87.100	42.516	-	219.870	-	15.083
2700	19.652	104.193	87.621	44.460	-	219.870	-	13.762
2800	19.668	104.900	88.321	46.360	-	220.221	-	13.168
2900	19.681	105.599	88.905	48.414	-	220.400	-	12.615
3000	19.694	106.267	89.473	50.383	-	220.582	-	12.097
3100	19.705	106.913	90.025	52.352	-	220.766	-	11.610
3200	19.714	107.543	90.562	54.263	-	220.953	-	11.161
3300	19.724	108.159	91.085	56.125	-	221.134	-	10.721
3400	19.733	108.734	91.597	58.268	-	221.314	-	10.315
3500	19.740	109.306	92.094	60.242	-	221.530	-	9.930
3600	19.748	109.863	92.580	62.216	-	221.727	-	9.566
3700	19.750	110.411	93.051	64.141	-	221.928	-	9.221
3800	19.750	110.931	93.501	66.014	-	222.134	-	8.894
3900	19.756	111.444	93.971	67.833	-	222.338	-	8.584
4000	19.771	111.945	94.414	70.000	-	222.538	-	8.294
4100	19.776	112.433	94.848	72.098	-	222.738	-	8.007
4200	19.783	112.903	95.268	74.094	-	222.938	-	7.715
4300	19.785	113.375	95.668	76.094	-	223.134	-	7.428
4400	19.789	113.830	96.095	78.032	-	223.334	-	7.135
4500	19.792	114.275	96.494	80.011	-	223.530	-	6.842
4600	19.796	114.710	96.885	81.991	-	223.727	-	6.549
4700	19.796	115.135	97.266	83.971	-	223.928	-	6.256
4800	19.802	115.552	97.626	85.951	-	224.134	-	5.963
4900	19.805	115.961	97.931	87.931	-	224.334	-	5.670
5000	19.807	116.361	98.178	89.912	-	224.530	-	5.377
5100	19.810	116.753	98.735	91.892	-	224.727	-	5.084
5200	19.815	117.135	99.299	93.873	-	224.928	-	4.791
5300	19.815	117.515	99.854	95.854	-	225.134	-	4.498
5400	19.817	117.895	99.768	97.836	-	225.334	-	4.205
5500	19.819	118.249	100.100	99.818	-	225.530	-	3.912
5600	19.821	118.606	100.428	101.800	-	225.727	-	3.619
5700	19.824	118.956	100.756	103.782	-	225.928	-	3.326
5800	19.826	119.302	101.076	105.764	-	226.134	-	3.033
5900	19.827	119.641	101.378	107.747	-	226.334	-	2.740
6000	19.827	119.974	101.686	109.730	-	226.530	-	2.447

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1964

Point Group = C_{2v}S_{298.15} = 65.66 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
1250 (1)	1430 (1)
697 (1)	366 (1)
429 (1)	608 (1)

Bond Distances: B-Cl = [1.73] Å B-F = [1.295] Å

Bond Angle: F-B-Cl = [120°] F-B-F = [120°]

Product of the Moments of Inertia: I_AI_BI_C = 3567.6 X 10⁻¹¹⁷ g.³ cm.⁶

σ = 2

Heat of Formation.

The values for BCl₂F and BClF₂ of ΔH_f^o 298.15 = -154 and ΔH_f^o 298.15 = -211.6 kcal. mole⁻¹, respectively, are obtained from the average bond energies of BF₃ and BCl₃. The calculated values were each made less negative by about 0.8 kcal. mole⁻¹ in order to make them consistent with the equilibrium measurements of T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw, and A. J. Roscow, J. Chem. Phys. 23, 1544 (1955) and S. R. Gunn and R. H. Sanborn, J. Chem. Phys. 33, 955 (1960) for the reaction



Values for the heat of reaction are ΔH_r^o 298.15 = +1.68 kcal. mole⁻¹ and ΔH_r^o 298.15 = 1.1 (uncertainty of -0.5 to +0.6) kcal. mole⁻¹, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of ΔH_r^o 298.15 = 1.6 kcal. mole⁻¹ fixes the sum of the heats of formation of BCl₂F and BClF₂ as -385.6 kcal. mole⁻¹, but it does not determine the individual values. Thus, the selected heats of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be ± 5 kcal. mole⁻¹.

Heat Capacity and Entropy.

The observed frequencies of L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956), were adjusted to the normal isotopic composition of 81.2% ¹⁰B and 18.8% ¹¹B. The bond angles were assumed to be 120° and the bond lengths were taken to be the same as in the respective trihalides. As a result, the principal moments of inertia are I_A = 17.6044 X 10⁻³⁹, I_B = 7.335 X 10⁻³⁹, and I_C = 25.5394 X 10⁻³⁹ g. cm.².

Boron Oxide Chloride (BOCl)
(Ideal Gas) Mol. Wt. = 62.277

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	(^o H ₂₉₈ - H ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	7.384	46.962	65.292	-1.833	-75.709	-75.709	-75.709	∞.000
200	9.382	52.692	57.662	-.995	-75.720	-76.072	-76.072	166.247
298	10.765	56.770	56.770	-.000	-75.662	-76.443	-76.443	89.520
300	10.785	56.786	56.786	.020	-75.599	-76.851	-76.851	55.983
400	11.662	60.015	57.154	1.144	-75.567	-77.275	-77.275	42.219
500	12.241	62.681	58.001	2.340	-75.577	-77.701	-77.701	33.961
600	12.703	64.935	58.075	3.288	-75.615	-78.122	-78.122	28.455
700	13.081	66.844	58.104	4.000	-75.635	-78.542	-78.542	24.565
800	13.393	68.707	60.647	5.109	-75.735	-79.000	-79.000	21.565
900	13.599	70.295	61.908	7.548	-75.804	-79.339	-79.339	19.265
1000	13.790	71.738	62.820	8.818	-75.880	-79.727	-79.727	17.423
1100	13.965	73.060	63.462	10.395	-75.965	-80.108	-80.108	15.915
1200	14.127	74.270	63.944	11.308	-76.060	-80.484	-80.484	14.660
1300	14.276	75.409	65.318	13.138	-76.158	-80.845	-80.845	13.591
1400	14.426	76.463	66.671	14.941	-76.267	-81.201	-81.201	12.675
1500	14.536	77.450	66.803	15.971	-76.386	-81.551	-81.551	11.861
1600	14.598	78.377	67.497	17.407	-76.515	-81.889	-81.889	11.185
1700	14.620	79.251	68.083	18.683	-76.653	-82.212	-82.212	10.572
1800	14.635	80.079	68.602	20.297	-76.801	-82.540	-82.540	10.012
1900	14.643	80.864	69.417	21.749	-76.956	-82.860	-82.860	9.531
2000	14.568	81.610	70.008	23.204	-77.117	-83.166	-83.166	9.088
2100	14.597	82.321	70.577	24.662	-77.284	-83.463	-83.463	8.666
2200	14.623	83.062	71.157	26.127	-77.456	-83.756	-83.756	8.266
2300	14.645	83.652	71.657	27.587	-77.633	-84.048	-84.048	7.886
2400	14.666	84.275	72.160	29.052	-77.823	-84.309	-84.309	7.577
2500	14.683	84.874	72.666	30.522	-78.020	-84.567	-84.567	7.384
2600	14.699	85.451	73.147	31.989	-78.222	-84.808	-84.808	7.103
2700	14.714	86.002	73.605	33.450	-78.429	-85.039	-85.039	6.845
2800	14.727	86.531	74.035	34.933	-78.641	-85.262	-85.262	6.606
2900	14.738	87.038	74.435	36.405	-78.857	-85.478	-85.478	6.374
3000	14.749	87.558	74.831	37.879	-79.076	-85.691	-85.691	6.162
3100	14.758	88.082	75.346	39.355	-79.299	-85.896	-85.896	5.964
3200	14.765	88.596	75.834	40.830	-79.526	-86.093	-86.093	5.782
3300	14.770	89.096	76.314	42.308	-79.757	-86.282	-86.282	5.601
3400	14.782	89.466	76.528	43.786	-79.990	-86.465	-86.465	5.436
3500	14.789	89.835	76.902	45.264	-80.226	-86.648	-86.648	5.279
3600	14.795	90.251	77.257	46.744	-80.464	-86.825	-86.825	5.130
3700	14.801	90.657	77.631	48.221	-80.704	-86.997	-86.997	4.986
3800	14.806	91.052	77.972	49.706	-80.948	-87.164	-87.164	4.848
3900	14.811	91.436	78.312	51.185	-81.195	-87.326	-87.326	4.715
4000	14.816	91.811	78.645	52.666	-81.444	-87.483	-87.483	4.587
4100	14.820	92.177	78.970	54.148	-81.694	-87.635	-87.635	4.464
4200	14.825	92.534	79.293	55.630	-81.946	-87.782	-87.782	4.346
4300	14.827	92.883	79.601	57.113	-82.199	-87.925	-87.925	4.232
4400	14.831	93.224	79.907	58.596	-82.453	-88.064	-88.064	4.122
4500	14.834	93.557	80.207	60.079	-82.708	-88.200	-88.200	4.016
4600	14.837	93.883	80.500	61.562	-82.964	-88.331	-88.331	3.911
4700	14.840	94.203	80.793	63.046	-83.220	-88.458	-88.458	3.806
4800	14.842	94.515	81.071	64.530	-83.476	-88.581	-88.581	3.701
4900	14.845	94.821	81.349	66.015	-83.732	-88.700	-88.700	3.596
5000	14.847	95.121	81.621	67.499	-83.987	-88.815	-88.815	3.491
5100	14.849	95.415	81.889	68.984	-84.243	-88.926	-88.926	3.386
5200	14.852	95.703	82.154	70.468	-84.499	-89.033	-89.033	3.281
5300	14.853	95.986	82.410	71.956	-84.755	-89.136	-89.136	3.176
5400	14.855	96.264	82.664	73.440	-85.011	-89.235	-89.235	3.071
5500	14.857	96.537	82.914	74.926	-85.266	-89.330	-89.330	2.966
5600	14.859	96.804	83.159	76.411	-85.521	-89.421	-89.421	2.861
5700	14.860	97.067	83.391	77.895	-85.776	-89.508	-89.508	2.756
5800	14.862	97.326	83.639	79.378	-86.031	-89.591	-89.591	2.651
5900	14.863	97.580	83.873	80.870	-86.286	-89.670	-89.670	2.546
6000	14.865	97.830	84.104	82.356	-86.541	-89.745	-89.745	2.441

Dec. 31, 1960; Sept. 30, 1963; Mar. 31, 1965

BC10

BORON OXIDE CHLORIDE (BOCl) (IDEAL GAS) MOL. WT. = 62.277

Point Group [C_{∞v}]
S_{298.15}^o = [56.72] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

ΔH_f^o 0 = -74.8 ± 7.0 kcal. mole⁻¹
ΔH_f^o 298.15 = -75.6 ± 7.0 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
[690] (1)
[400] (2)
[1850] (1)

Bond Distance: Cl-B = [1.75] Å B-O [1.20] Å

Bond Angle: Cl-B-O = [180]°

Rotational Constant: B₀ = [0.16504] cm.⁻¹

σ = 1

Heat of Formation.

The vapor-phase equilibria existing in the B₂O₃ + BCl₃ system were determined by an effusion method in the temperature range 1234-1389°K. by J. Blauer and M. Farber, Trans. Faraday Soc. 50, 301 (1964). Based on the equilibrium constants reported for the reaction 1/3 B₂O₃(l) + 1/3 BCl₃(g) = BCl(g), the second and third law values of ΔH_f^o 298.15 were evaluated as 57.7 and 56.3 kcal. mole⁻¹, respectively. The third law value for ΔH_f^o 298.15 was adopted for the calculation of the heat of formation (ΔH_f^o 298.15) for BCl(g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The vibrational frequencies (ω) were estimated from the values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, k₁ = 5.2 X 10⁵, k₂ = 16.7 X 10⁵ dynes cm.⁻¹ and k₃ = 0.40 X 10¹¹ dynes cm. rad.⁻¹. The B-O and B-Cl bond distances were assumed to be the same as those in B₂O₃(g) and BCl₃(g), respectively. The moment of inertia is 1.6958 X 10⁻³⁸ g. cm.².

BC10

Boron Dichloride (BCl₂)

(Ideal Gas) Mol. Wt. = 81.734

BORON DICHLORIDE (BCl₂) (IDEAL GAS)

MOL. WT. = 81.734

Point Group [C_{2v}]
S_{298.15} = [84.956] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight [2]
ΔH_f⁰ = [-20.3 ± 15] kcal. mole⁻¹
ΔH_f^{298.15} = [-20 ± 15] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹
[720](1)
[240](1)
[980](1)

Bond Distance: B-Cl = [1.75] Å
Bond Angle: Cl-B-Cl = [120°]
Product of the Moments of Inertia: I_AI_BI_C = [9.48841 × 10⁻¹¹⁵] g.³ cm.⁶
σ = 2

Heat of Formation.

The heat of formation was estimated by analogy with BF₃, specifically the ratio

$$\Delta H_f(\text{BX}_3) \rightarrow \text{BX}_2 + \text{X} / \Delta H_f(\text{BX}_3) \rightarrow \text{B} + 3\text{X}$$

was taken as 0.547.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trichloride given by O. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trichlorides and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were I_B = 1.1661 × 10⁻³⁹ g. cm.², I_A = 26.4189 × 10⁻³⁹ g. cm.² and I_C = 27.5851 × 10⁻³⁹ g. cm.²

T. °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-	2.775	- 20.289	- 20.289	INFINITE	
100	8.756	54.374	73.050	- 1.958	- 20.179	- 21.089	46.086	
200	9.898	60.810	65.023	- 1.023	- 20.045	- 22.058	24.102	
298	10.919	64.956	64.956	- 0.000	- 20.000	- 23.060	16.903	
300	10.937	65.024	64.957	- 0.020	- 20.000	- 23.080	16.813	
400	12.331	70.978	66.289	1.367	- 20.019	- 23.055	10.980	
500	12.331	70.978	66.282	2.363	- 20.075	- 23.122	10.980	
600	12.721	73.263	67.235	3.617	- 20.165	- 26.122	9.515	
700	12.990	75.246	68.241	4.904	- 20.272	- 27.107	8.463	
800	13.161	76.953	69.256	6.153	- 20.394	- 28.076	7.670	
900	13.320	78.353	70.282	7.358	- 20.524	- 29.026	7.080	
1000	13.424	79.663	71.088	8.475	- 20.667	- 29.966	6.540	
1100	13.503	81.247	71.954	10.222	- 20.821	- 30.889	6.137	
1200	13.565	82.424	72.778	11.575	- 20.987	- 31.796	5.791	
1300	13.613	83.512	73.562	12.524	- 21.164	- 32.691	5.496	
1400	13.656	84.510	74.316	13.170	- 21.351	- 33.574	5.246	
1500	13.685	85.466	75.022	13.665	- 21.551	- 34.438	5.017	
1600	13.711	86.350	75.703	17.035	- 21.762	- 35.289	4.820	
1700	13.734	87.182	76.394	18.407	- 21.984	- 36.126	4.644	
1800	13.756	87.967	77.077	19.781	- 22.216	- 36.952	4.486	
1900	13.776	88.711	77.756	21.156	- 22.456	- 37.764	4.344	
2000	13.782	89.418	78.190	22.535	- 22.701	- 38.563	4.214	
2100	13.794	90.090	78.703	23.914	- 22.952	- 39.349	4.095	
2200	13.804	90.732	79.235	25.293	- 23.211	- 40.124	3.986	
2300	13.813	91.346	79.749	26.674	- 23.474	- 40.887	3.885	
2400	13.821	91.934	80.246	28.054	- 23.744	- 41.637	3.791	
2500	13.828	92.498	80.723	29.438	- 24.006	- 42.268	3.695	
2600	13.834	93.041	81.186	30.821	- 24.278	- 42.779	3.596	
2700	13.839	93.563	81.635	32.205	- 24.552	- 43.276	3.493	
2800	13.844	94.069	82.070	33.589	- 24.829	- 43.764	3.386	
2900	13.848	94.562	82.492	34.972	- 25.106	- 44.243	3.275	
3000	13.853	95.022	82.902	36.359	- 30.788	- 44.714	3.257	
3100	13.856	95.476	83.301	37.744	- 31.072	- 45.173	3.185	
3200	13.860	95.916	83.688	39.130	- 31.358	- 45.623	3.116	
3300	13.863	96.345	84.055	40.516	- 31.647	- 46.064	3.051	
3400	13.866	96.757	84.419	41.902	- 31.937	- 46.496	2.981	
3500	13.868	97.159	84.770	43.290	- 32.231	- 46.924	2.930	
3600	13.870	97.549	85.139	44.676	- 32.528	- 47.334	2.873	
3700	13.873	97.929	85.480	46.064	- 32.826	- 47.741	2.820	
3800	13.876	98.300	85.812	47.452	- 33.127	- 48.131	2.769	
3900	13.876	98.660	86.137	48.838	- 33.431	- 48.506	2.719	
4000	13.878	99.011	86.454	50.226	- 154.916	- 46.772	2.555	
4100	13.880	99.354	86.765	51.614	- 154.992	- 44.070	2.349	
4200	13.881	99.688	87.069	53.002	- 155.070	- 41.359	2.152	
4300	13.883	99.999	87.366	54.390	- 155.148	- 38.646	1.962	
4400	13.884	100.334	87.657	55.779	- 155.232	- 35.940	1.789	
4500	13.885	100.646	87.942	57.167	- 155.317	- 33.232	1.614	
4600	13.886	100.951	88.222	58.556	- 155.401	- 30.516	1.450	
4700	13.887	101.250	88.496	59.944	- 155.489	- 27.799	1.293	
4800	13.888	101.542	88.765	61.332	- 155.576	- 25.082	1.142	
4900	13.889	101.826	89.037	62.722	- 155.668	- 22.365	1.007	
5000	13.890	102.109	89.287	64.111	- 155.760	- 19.640	0.886	
5100	13.891	102.384	89.541	65.500	- 155.853	- 16.914	0.725	
5200	13.891	102.654	89.791	66.889	- 155.947	- 14.190	0.596	
5300	13.892	102.919	89.997	68.278	- 156.043	- 11.469	0.473	
5400	13.893	103.178	90.197	69.667	- 156.140	- 8.748	0.356	
5500	13.893	103.433	90.514	71.057	- 156.238	- 6.000	0.238	
5600	13.894	103.684	90.747	72.446	- 156.338	- 3.279	0.128	
5700	13.895	103.930	90.976	73.835	- 156.441	- 0.546	0.021	
5800	13.896	104.171	91.202	75.224	- 156.544	- 0.183	-	
5900	13.896	104.400	91.423	76.613	- 156.647	- 0.183	-	
6000	13.896	104.642	91.642	78.004	- 156.754	- 0.183	-	

Dec. 31, 1960; Mar. 31, 1963; Dec. 31, 1964

Boron Dichloride Unipositive Ion (BCl₂⁺)

(Ideal Gas) GFW = 81.71645

T, °K	C _p ^a	S ^b	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	kcal/mol ΔH ^c	ΔG ^c	Log Kp
0							
100	12.661	61.590	61.590	.000	148.000	144.456	-105.889
200							
250	12.678	61.668	61.590	.023	148.012	144.434	-105.220
300	13.402	65.423	62.097	1.330	146.664	143.141	-76.209
400	13.866	66.465	63.076	2.695	149.260	141.691	-61.933
500							
600	14.128	71.017	64.193	4.094	149.812	140.125	-51.040
700	14.313	73.209	65.328	5.517	150.337	138.460	-43.232
800	14.441	75.159	66.435	6.955	150.841	136.737	-37.355
900	14.532	76.836	67.468	8.404	151.331	134.945	-32.769
1000	14.599	78.371	68.510	9.861	151.806	133.098	-29.069
1100	14.650	79.764	69.571	11.323	152.264	131.205	-26.048
1200	14.689	81.081	70.362	12.790	152.709	129.272	-23.584
1300	14.720	82.218	71.248	14.261	153.140	127.300	-21.401
1400	14.745	83.310	72.071	15.734	153.559	125.298	-19.560
1500	14.765	84.328	72.855	17.210	153.965	123.263	-17.959
1600	14.781	85.281	73.602	18.687	154.358	121.204	-16.556
1700	14.795	86.178	74.315	20.166	154.740	119.122	-15.314
1800	14.807	87.024	74.998	21.646	155.110	117.013	-14.207
1900	14.818	87.825	75.652	23.127	155.473	114.890	-13.245
2000	14.827	88.585	76.280	24.609	155.828	112.745	-12.320
2100	14.836	89.309	76.883	26.093	156.179	110.580	-11.508
2200	14.844	89.999	77.484	27.577	156.522	108.401	-10.769
2300	14.853	90.659	78.023	29.061	156.858	106.206	-10.092
2400	14.861	91.281	78.563	30.547	157.190	103.999	-9.470
2500	14.870	91.898	79.095	32.034	157.529	101.884	-8.907
2600	14.879	92.481	79.589	33.521	157.858	99.867	-8.395
2700	14.889	93.043	80.077	35.009	158.185	97.840	-7.920
2800	14.899	93.585	80.549	36.497	158.511	95.798	-7.477
2900	14.911	94.108	81.008	37.989	158.834	93.747	-7.065
3000	14.923	94.614	81.453	39.481	159.157	91.680	-6.679
3100	14.936	95.103	81.886	40.974	159.478	89.604	-6.317
3200	14.950	95.577	82.306	42.468	159.797	87.522	-5.977
3300	14.965	96.038	82.715	43.964	159.715	85.429	-5.658
3400	14.981	96.485	83.114	45.461	159.631	83.326	-5.356
3500	14.997	96.919	83.502	46.960	159.546	81.209	-5.071
3600	15.015	97.342	83.881	48.461	159.461	79.089	-4.801
3700	15.033	97.754	84.250	49.963	159.374	76.955	-4.546
3800	15.052	98.155	84.611	51.467	159.287	74.817	-4.303
3900	15.072	98.546	84.963	52.973	159.199	72.668	-4.072
4000	15.092	98.928	85.307	54.482	159.111	70.516	-3.857
4100	15.113	99.301	85.644	55.992	159.024	68.369	-3.657
4200	15.134	99.665	85.974	57.504	158.937	66.224	-3.476
4300	15.156	100.021	86.296	59.019	158.850	64.079	-3.303
4400	15.178	100.370	86.612	60.535	158.763	61.933	-3.145
4500	15.200	100.711	86.922	62.054	158.676	59.787	-3.001
4600	15.222	101.046	87.225	63.575	158.589	57.641	-2.869
4700	15.245	101.373	87.523	65.099	158.502	55.495	-2.747
4800	15.267	101.695	87.815	66.624	158.415	53.349	-2.635
4900	15.290	102.010	88.101	68.152	158.328	51.203	-2.532
5000	15.313	102.319	88.382	69.681	158.241	49.057	-2.438
5100	15.335	102.622	88.659	71.215	158.154	46.911	-2.353
5200	15.358	102.920	88.930	72.749	158.067	44.765	-2.277
5300	15.380	103.213	89.197	74.286	157.980	42.619	-2.209
5400	15.402	103.501	89.459	75.825	157.893	40.473	-2.149
5500	15.424	103.783	89.717	77.367	157.806	38.327	-2.095
5600	15.446	104.062	89.970	78.910	157.719	36.181	-2.047
5700	15.467	104.335	90.220	80.456	157.632	34.035	-2.004
5800	15.488	104.604	90.469	82.003	157.545	31.889	-1.966
5900	15.509	104.869	90.708	83.553	157.458	29.743	-1.932
6000	15.530	105.130	90.946	85.105	157.371	27.597	-1.902

June 30, 1968



(IDEAL GAS)

BORON DICHLORIDE UNIPosITIVE ION (BCl₂⁺)

Point Group [D_{∞h}]

S_{298.15} = [61.6 ± 2] gibbs/mol

ΔH_f⁰ = 147.4 ± 5 kcal/mol

ΔH_f⁰ = 147.4 ± 5 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i , cm ⁻¹	g_i
1 _g ⁺	0	1
1 _g ⁻		
1 _u ⁺	[16000]	1
1 _u ⁻		
1 _g ⁺	[35000]	1
1 _g ⁻		

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
[500] (1)
[150] (2)
[800] (1)

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [180°]

Rotational Constant: B₀ = [0.0785] cm⁻¹

Heat of Formation

The appearance potential (AP) of the positive ion fragment BCl₂⁺ from BCl₃(g) was determined mass spectrometrically by Oberghaus (1), Marriott (2), and Koski (3) as 13.2 ± 0.5, 13.01 ± 0.02, and 11.8 ± 0.2 eV, respectively. From the reaction BCl₃ + e⁻ = BCl₂⁺ + Cl + 2e⁻, the corresponding values of ΔH_f⁰ for BCl₂⁺(g) are derived to be 180.4 ± 11.5, 176.0 ± 0.5, and 148.1 ± 4.6 kcal/mol, using ΔH_f⁰ = -96.078 and 28.520 kcal/mol for BCl₃(g) and Cl(g). The value of ΔH_f⁰ for BCl₂⁺(g) is adopted as 148 ± 5 kcal/mol, since the lowest value is likely to have the least excess kinetic energy in the fragments.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) predictions for 16 valence electron XY₂ molecules. The electronic states, levels and vibrational frequencies are estimated by comparison with those for CO₂(g). The B-Cl bond distance is estimated using the method of Krasnov (5). The moment of inertia is 3.564 × 10⁻³⁸ g cm². The enthalpy at 0°K is -3.07 kcal/mol.

References

1. O. Oberghaus, Z. Phys. 128, 366 (1950).
2. J. Marriott and J. D. Craggs, J. Electron. Contr. 3, 194 (1957).
3. W. S. Koski, J. J. Kaufman, and C. F. Pachucki, J. Am. Chem. Soc. 81, 1376 (1959).
4. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
6. K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).



Boron Dichloride Uninegative Ion (BCl₂⁻)GF_W = 81.71755

(Ideal Gas)

Point Group [C_{2v}] $\Delta H_f^\circ = [-26 \pm 30] \text{ kcal/mol}$ $S_{298.15}^\circ = [63.5 \pm 2] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-26 \pm 30] \text{ kcal/mol}$

Electronic Levels and Quantum Weights			
ϵ_i , cm ⁻¹	g_i		
0	1		
[4000]	3		
[20000]	1		

Vibrational Frequencies and Degeneracies

 ω , cm⁻¹

[740] (1)

[245] (1)

[990] (1)

Bond Distance: B-Cl = [1.74] Å

Bond Angle: Cl-B-Cl = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [8.798 \times 10^{-115}] \text{ g}^3 \text{ cm}^6$ $\sigma = 2$

Heat of Formation

The electron captured by BCl₂ should go into a non-bonding orbital according to the correlation diagrams of Walsh (1), thus one expects a small electron affinity. In fact one reasonable estimate of the dissociation energy yields a negative electron affinity (EA). Consider the isoelectronic reactions $\text{BCl}_2^- \rightarrow \text{B}^+ + 2\text{Cl}$ and $\text{CCl}_2 \rightarrow \text{C} + 2\text{Cl}$, if we make the assumption that these binding energies are the same then $\Delta H_{298}^\circ(\text{BCl}_2^-) = -32 \text{ kcal}$. Another possible estimate is obtained from the isoelectronic reactions $\text{BCl}_2^- + \text{B} + \text{Cl}^- \rightarrow \text{BClAr} + \text{B} + \text{Ar}$, although the latter reaction is unknown we expect a zero bond strength; applying this to the first reaction yields $\Delta H_{298}^\circ(\text{BCl}_2^-) = -22 \text{ kcal/mol}$ or $\text{EA}(\text{BCl}_2^-) = 2 \text{ kcal}$.

In consideration of the above arguments we choose $\text{EA}(\text{BCl}_2^-) = \text{EA}(\text{B}, g) = 6 \text{ kcal}$ (2) which gives $\Delta H_{298}^\circ(\text{BCl}_2^-) = -26 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular structure is assumed to be bent using the correlations of A. D. Walsh (3) for 18 valence electron XY₂ molecules. The B-Cl bond distance is estimated using the method of Krasnov (3). The Cl-B-Cl bond angle is taken as 120°. The electronic levels, quantum weights and vibrational frequencies are estimated by comparison with those for CF₂(4) and other related isoelectronic molecules. The three principal moments of inertia are $I_A = 1.179 \times 10^{-39}$, $I_B = 2.873 \times 10^{-38}$ and $I_C = 2.791 \times 10^{-38} \text{ g cm}^2$. The enthalpy at 0°K is -2.76 kcal/mol .

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8528, 1 January 1965.
3. K. S. Krasnov, Zh. Strukt. Khim. 1, 209 (1960).
4. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.

June 30, 1968; Dec. 31, 1968

Boron Dichloride Fluoride
(Ideal Gas)

Mol. Wt. = 100.734



MOL. WT. = 100.734

BORON DICHLORIDE FLUORIDE (BCl₂F)

(IDEAL GAS)

Point Group = C_{2v}

$$\Delta H_f^0 = -154 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -154 \pm 5 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = 1

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₃₀₀)/T	H°-H° ₃₀₀	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	INFINITE
100	9.4078	56.2480	70.785	0.7350	1.519	153.630	-153.630	-153.630	INFINITE
200	17.7895	100.0000	125.810	1.2581	3.135	153.604	-153.604	-153.604	110.634
298	14.117	68.732	68.732	0.000	0.000	154.000	-154.000	-154.000	110.634
300	14.1149	68.819	68.732	0.026	0.026	154.001	-154.001	-154.001	109.958
400	15.616	73.103	69.306	1.519	1.519	154.045	-154.045	-154.045	81.909
500	16.651	76.705	70.435	3.135	3.135	154.099	-154.099	-154.099	65.073
600	17.385	79.810	71.745	4.839	4.839	154.155	-154.155	-154.155	53.846
700	17.912	82.532	73.066	6.605	6.605	154.208	-154.208	-154.208	45.823
800	18.297	84.950	74.429	8.417	8.417	154.260	-154.260	-154.260	39.805
900	18.584	87.122	75.721	10.261	10.261	154.310	-154.310	-154.310	35.122
1000	18.801	89.092	76.961	12.131	12.131	154.362	-154.362	-154.362	31.374
1100	18.970	90.892	78.147	14.020	14.020	154.420	-154.420	-154.420	28.307
1200	19.103	92.549	79.279	15.924	15.924	154.483	-154.483	-154.483	25.750
1300	19.209	94.082	80.359	17.840	17.840	154.555	-154.555	-154.555	23.585
1400	19.295	95.509	81.391	19.765	19.765	154.634	-154.634	-154.634	21.720
1500	19.365	96.842	82.377	21.698	21.698	154.724	-154.724	-154.724	20.119
1600	19.424	98.094	83.321	23.638	23.638	154.822	-154.822	-154.822	18.710
1700	19.473	99.273	84.225	25.582	25.582	154.931	-154.931	-154.931	17.465
1800	19.515	100.388	85.082	27.532	27.532	155.048	-155.048	-155.048	16.359
1900	19.550	101.444	85.925	29.485	29.485	155.172	-155.172	-155.172	15.367
2000	19.581	102.447	86.726	31.442	31.442	155.303	-155.303	-155.303	14.474
2100	19.607	103.403	87.498	33.401	33.401	155.438	-155.438	-155.438	13.666
2200	19.630	104.316	88.242	35.363	35.363	155.581	-155.581	-155.581	12.931
2300	19.650	105.189	88.966	37.327	37.327	155.729	-155.729	-155.729	12.258
2400	19.668	106.026	89.663	39.293	39.293	155.883	-155.883	-155.883	11.641
2500	19.684	106.829	90.325	41.260	41.260	156.043	-156.043	-156.043	11.064
2600	19.698	107.601	90.974	43.230	43.230	156.208	-156.208	-156.208	10.521
2700	19.710	108.345	91.604	45.200	45.200	156.388	-156.388	-156.388	10.016
2800	19.721	109.062	92.215	47.172	47.172	156.571	-156.571	-156.571	9.550
2900	19.731	109.754	92.808	49.144	49.144	156.766	-156.766	-156.766	9.114
3000	19.741	110.423	93.384	51.118	51.118	156.972	-156.972	-156.972	8.707
3100	19.749	111.070	93.944	53.092	53.092	157.189	-157.189	-157.189	8.325
3200	19.756	111.698	94.489	55.068	55.068	157.416	-157.416	-157.416	7.967
3300	19.763	112.306	95.020	57.044	57.044	157.652	-157.652	-157.652	7.630
3400	19.769	112.896	95.537	59.020	59.020	157.897	-157.897	-157.897	7.313
3500	19.775	113.469	96.041	60.997	60.997	158.151	-158.151	-158.151	7.014
3600	19.781	114.026	96.533	62.975	62.975	158.414	-158.414	-158.414	6.730
3700	19.785	114.568	97.013	64.944	64.944	158.686	-158.686	-158.686	6.462
3800	19.790	115.096	97.482	66.932	66.932	158.967	-158.967	-158.967	6.208
3900	19.794	115.610	97.940	68.911	68.911	159.256	-159.256	-159.256	5.967
4000	19.798	116.111	98.388	70.891	70.891	159.553	-159.553	-159.553	5.732
4100	19.801	116.600	98.826	72.871	72.871	159.857	-159.857	-159.857	5.502
4200	19.805	117.077	99.255	74.851	74.851	160.168	-160.168	-160.168	5.280
4300	19.808	117.543	99.675	76.832	76.832	160.484	-160.484	-160.484	5.067
4400	19.811	117.999	100.087	78.813	78.813	160.806	-160.806	-160.806	4.862
4500	19.813	118.444	100.490	80.794	80.794	161.133	-161.133	-161.133	4.666
4600	19.816	118.879	100.885	82.776	82.776	161.466	-161.466	-161.466	4.477
4700	19.818	119.306	101.272	84.757	84.757	161.804	-161.804	-161.804	4.293
4800	19.821	119.723	101.652	86.739	86.739	162.147	-162.147	-162.147	4.114
4900	19.823	120.131	102.025	88.721	88.721	162.494	-162.494	-162.494	3.940
5000	19.825	120.532	102.391	90.704	90.704	162.846	-162.846	-162.846	3.772
5100	19.827	120.925	102.751	92.686	92.686	163.202	-163.202	-163.202	3.608
5200	19.828	121.310	103.104	94.669	94.669	163.562	-163.562	-163.562	3.450
5300	19.830	121.687	103.451	96.652	96.652	163.926	-163.926	-163.926	3.298
5400	19.831	122.058	103.792	98.635	98.635	164.294	-164.294	-164.294	3.150
5500	19.833	122.422	104.128	100.618	100.618	164.666	-164.666	-164.666	3.006
5600	19.834	122.779	104.458	102.602	102.602	165.042	-165.042	-165.042	2.866
5700	19.836	123.130	104.782	104.585	104.585	165.422	-165.422	-165.422	2.730
5800	19.837	123.475	105.101	106.569	106.569	165.806	-165.806	-165.806	2.598
5900	19.838	123.814	105.416	108.553	108.553	166.194	-166.194	-166.194	2.470
6000	19.839	124.148	105.725	110.536	110.536	166.586	-166.586	-166.586	2.346

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1961; Dec. 31, 1964

MOL. WT. = 100.734

BORON DICHLORIDE FLUORIDE (BCl₂F)

(IDEAL GAS)

Point Group = C_{2v}

$$\Delta H_f^0 = -154 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -154 \pm 5 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies	$\bar{\nu}$, cm ⁻¹	$\bar{\nu}$, cm ⁻¹
1320 (1)	1000 (1)	
[554] (1)	[339] (1)	
[266] (1)	528 (1)	

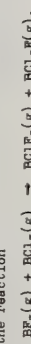
Bond Distance: B-Cl = [1.73] Å B-F = [1.295] Å

Bond Angle: Cl-B-Cl = [120°] F-B-Cl = [120°]

Product of the Moments of Inertia: I_AI_BI_C = 12020 X 10⁻¹¹⁷ g.³ cm.⁶

Heat of Formation.

The values for BCl₂F and BClF₂ of ΔH_f⁰ 298.15 = -154 and ΔH_f⁰ 298.15 = -211.6 kcal. mole⁻¹, respectively, are obtained from the average bond energies of BF₃ and BCl₃. The calculated values were each made less negative by about 0.6 kcal. mole⁻¹ in order to make them consistent with the equilibrium measurements of T. H. S. Higgins, E. C. Leisegang, C. J. G. Haw, and A. J. Rossouw, J. Chem. Phys. 22, 1544 (1955) and S. R. Gunn and R. H. Sanborn, J. Chem. Phys. 33, 955 (1960) for the reaction



Values for the heat of reaction are ΔH_{298.15} = +1.68 kcal. mole⁻¹ and ΔH_{298.15} = 1.1 (uncertainty of -0.5 to +0.8) kcal. mole⁻¹, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of ΔH_{298.15} = 1.6 kcal. mole⁻¹ fixes the sum of the heats of formation of BClF₂ and BCl₂F as -365.6 kcal. mole⁻¹, but it does not determine the individual values. Thus, the selected heats of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be ± 5 kcal. mole⁻¹.

Heat Capacity and Entropy.

The spectroscopic constants are based on the work of L. P. Lindeman and M. K. Wilson, J. Chem. Phys. 24, 242 (1956), who observed ν₁, ν₂, and ν₃ and calculated ν₁, ν₂, ν₃, and ν₄. The frequencies were adjusted to the normal isotopic composition of 61.8% ¹⁰B and 38.2% ¹¹B. The bond angles were taken to be 120° while the bond lengths were assumed to be the same as in the respective trihalides. As a result, the principal moments of inertia are I_A = 11.8748 X 10⁻³⁹, I_B = 28.4368 X 10⁻³⁹, and I_C = 36.3016 X 10⁻³⁹ g. cm.².



T, °K	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _f
0	8.000	INFINITE	2.807	-58.609	-58.609	INFINITE
100	8.521	53.399	73.385	-58.887	-58.887	127.809
200	10.035	59.744	65.118	-59.066	-59.066	63.394
298	11.865	64.092	4.000	-59.300	-57.450	42.112
300	11.898	64.165	64.092	-59.305	-57.439	41.844
400	13.499	67.818	64.579	-59.530	-56.783	31.025
500	14.686	70.964	65.549	-59.733	-56.071	24.509
600	15.564	73.723	66.686	-59.913	-55.321	20.151
700	16.236	76.175	67.870	-60.066	-54.747	17.563
800	16.719	78.377	69.092	-60.202	-54.263	15.523
900	17.108	80.380	70.197	-60.312	-53.854	13.854
1000	17.551	82.210	71.309	-60.412	-53.507	12.388
1100	17.843	83.897	72.377	-60.506	-53.273	10.187
1200	18.098	85.491	73.403	-60.584	-53.050	8.335
1300	18.326	86.997	74.388	-60.652	-52.837	6.835
1400	18.529	88.429	75.331	-60.713	-52.634	5.606
1500	18.717	89.789	76.238	-60.769	-52.441	4.673
1600	18.885	91.074	77.108	-60.821	-52.258	3.918
1700	19.035	92.284	77.945	-60.869	-52.086	3.318
1800	19.170	93.419	78.752	-60.913	-51.924	2.841
1900	19.293	94.481	79.528	-60.953	-51.772	2.467
2000	19.406	95.479	80.276	-60.989	-51.630	2.167
2100	19.510	96.413	80.999	-61.023	-51.496	1.926
2200	19.606	97.287	81.697	-61.053	-51.370	1.738
2300	19.695	98.102	82.371	-61.079	-51.251	1.597
2400	19.777	98.859	83.029	-61.102	-51.139	1.498
2500	19.853	99.563	83.663	-61.123	-51.034	1.424
2600	19.923	100.223	84.279	-61.141	-50.936	1.360
2700	19.987	100.846	84.873	-61.157	-50.844	1.303
2800	20.046	101.431	85.445	-61.171	-50.757	1.253
2900	20.100	101.986	86.000	-61.183	-50.674	1.209
3000	20.150	102.521	86.541	-61.193	-50.596	1.171
3100	20.196	103.036	87.067	-61.202	-50.522	1.137
3200	20.239	103.531	87.578	-61.209	-50.453	1.106
3300	20.279	104.006	88.074	-61.214	-50.389	1.077
3400	20.316	104.461	88.556	-61.218	-50.330	1.050
3500	20.350	104.896	89.024	-61.221	-50.276	1.024
3600	20.381	105.311	89.478	-61.223	-50.226	1.000
3700	20.409	105.706	89.918	-61.224	-50.180	0.976
3800	20.434	106.081	90.344	-61.224	-50.137	0.953
3900	20.457	106.436	90.756	-61.223	-50.097	0.930
4000	20.478	106.771	91.154	-61.221	-50.060	0.907
4100	20.496	107.086	91.539	-61.218	-50.026	0.884
4200	20.512	107.381	91.911	-61.214	-50.000	0.861
4300	20.526	107.656	92.269	-61.209	-49.971	0.838
4400	20.539	107.911	92.614	-61.202	-49.946	0.815
4500	20.550	108.146	92.946	-61.193	-49.924	0.792
4600	20.560	108.361	93.266	-61.183	-49.904	0.769
4700	20.569	108.556	93.574	-61.171	-49.886	0.746
4800	20.576	108.731	93.871	-61.157	-49.869	0.723
4900	20.582	108.886	94.156	-61.141	-49.853	0.700
5000	20.587	109.021	94.429	-61.123	-49.837	0.677
5100	20.591	109.136	94.691	-61.102	-49.822	0.654
5200	20.594	109.231	94.936	-61.079	-49.807	0.631
5300	20.596	109.306	95.166	-61.053	-49.792	0.608
5400	20.598	109.361	95.381	-61.023	-49.777	0.585
5500	20.599	109.396	95.584	-61.000	-49.762	0.562
5600	20.599	109.411	95.776	-60.974	-49.747	0.539
5700	20.599	109.416	95.956	-60.946	-49.732	0.516
5800	20.599	109.411	96.124	-60.913	-49.717	0.493
5900	20.598	109.396	96.281	-60.877	-49.702	0.470
6000	20.597	109.371	96.426	-60.838	-49.687	0.447

Mar. 31, 1966

BCl₂H

Point Group C_{2v}
S_{298.15} = [64.1] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[2610](1)	1091 (1)
744 (1)	[894](1)
[287](1)	788 (1)

Bond Distances: B-H = 1.13 ± 0.2 Å B-Cl = [1.75] Å

Bond Angle: Cl-B-H = 119.7 ± 3° Cl-B-Cl = 120.15 ± 1.5°

Product of the Moments of Inertia: I_AI_BI_C = 1.39215 X 10⁻¹¹⁴ g. cm.⁶

Heat of Formation

The chemical equilibria for the following two reactions: (A) BCl₃(g) + H₂(g) = BCl₂(g) + HCl(g), and (B) 5BCl₂(g) = B₂H₆(g) + 4BCl₃(l, g) were investigated by (1) J. H. Muris, D. Horvitz, and C. A. Bonecutter, Ind. Eng. Chem. Prod. Res. Develop. **3**, 275 (1963); (2) F. H. Mook, G. R. Salier, and E. R. Watson, "Process Development, Preplot and Pilot Plant Investigations - High Energy Boron Fuels," ASDR 62-7-558 A, Vol. IV, March 1962; and (3) L. Lynds and C. D. Bass, Inorg. Chem. **3**, 1147 (1964). Using the reported equilibrium constants, the corresponding enthalpy changes and the respective ΔH°_f 298.15 values were evaluated. The results obtained are presented as follows.

Reaction	Temperature, °K.	Third Law Value	Second Law Value	ΔH° _f 298.15 ^a , kcal. mole ⁻¹	Reference
A	873 - 973	16.19	15.57 ± 0.8	-58.06 ± 0.5	(1)
A	1073 - 1273	13.91	13.50 ± 3.0	-60.3 ± 0.7	(2)
B	273	-17.85	—	-59.6	(1)
B	288	-19.09	—	-59.4	(3)

^aBased on the third law value of ΔH°_f 298.15°

The value of ΔH°_f 298.15 for BCl₂(g) is selected as -59.3 ± 1 kcal. mole⁻¹.

Heat Capacity and Entropy

The molecular structure, B-H bond distance and Cl-B-Cl bond angle were obtained from L. Lynds and C. D. Bass, J. Chem. Phys. **40**, 1590 (1964). The B-Cl bond distance was assumed to be the same as that in BCl₃(g). The vibrational frequencies adopted were reported by C. D. Bass, L. Lynds, T. Wolfram, and R. E. DeWames, J. Chem. Phys. **40**, 3611 (1964), and corrected to the average isotopic species. It has been pointed out that the complete assignment of the infrared spectra of BCl₂(g) is quite difficult due to the unavoidable presence of BCl₃(g). The adopted frequencies were obtained using the Green's function and partitioning techniques, taking HBCl₂ as an "isotopic" species of BCl₃. An excellent agreement between the calculated and observed spectra reported by L. Lynds and C. D. Bass, loc. cit. was claimed. Spectra of the mixture of BCl₃, HBCl₂ and BCl₂ are quite complex and have been observed by L. Lynds and D. R. Stern, J. Am. Chem. Soc. **81**, 5006 (1959), H. G. Nadeau and D. M. Oaka, Jr., Anal. Chem. **32**, 1481 (1961), and H. W. Myers and R. F. Putnam, Inorg. Chem. **2**, 655 (1963) and only three bands were correlated with HBCl₂. Analysis of infrared data from previous works, according to the conventional Wilson's method of symmetry coordinates, has been undertaken by O. B. de Mandirola and J. P. Westerkamp, Spectrochim. Acta, **20**, 1635 (1964). Based on four observed frequencies, a set of six frequencies was derived and assigned. The three principal moments of inertia are: I_A = 2.6980 X 10⁻³⁸, I_B = 1.7957 X 10⁻³⁵ and I_C = 2.8755 X 10⁻³⁸ g. cm.²

Boron Trichloride (BCl₃)

(Ideal Gas) Mol. Wt. = 117.191

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔG _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	9.725	56.006	-3.351	-96.078	-96.078	INFINITE
200	12.866	63.783	-2.510	-96.108	-96.108	207.849
298	14.912	69.328	-0.000	-96.316	-96.316	102.612
300	14.944	69.420	0.028	-96.310	-92.730	67.969
400	16.335	73.926	0.933	-96.310	-92.708	67.534
500	17.298	77.683	1.116	-96.307	-91.500	65.471
600	17.935	80.897	1.246	-96.329	-89.103	62.434
700	18.273	83.642	1.343	-96.366	-86.692	58.542
800	18.684	86.172	1.417	-96.386	-84.268	54.095
900	18.910	88.411	1.477	-96.412	-81.841	49.095
1000	19.079	90.388	1.528	-96.442	-79.414	43.646
1100	19.208	92.122	1.571	-96.467	-76.987	37.751
1200	19.308	93.643	1.608	-96.482	-74.560	31.401
1300	19.388	95.007	1.640	-96.492	-72.133	24.691
1400	19.452	96.276	1.667	-96.503	-69.706	17.621
1500	19.504	97.482	1.691	-96.507	-67.279	10.291
1600	19.547	98.640	1.715	-96.508	-64.852	2.621
1700	19.589	99.761	1.738	-96.511	-62.425	-5.049
1800	19.624	100.853	1.761	-96.514	-60.000	-12.574
1900	19.654	101.919	1.783	-96.517	-57.575	-20.049
2000	19.682	102.965	1.806	-96.521	-55.150	-27.474
2100	19.708	103.993	1.828	-96.526	-52.725	-34.849
2200	19.731	104.997	1.850	-96.531	-50.300	-42.174
2300	19.751	105.981	1.871	-96.536	-47.875	-49.449
2400	19.768	106.947	1.891	-96.541	-45.450	-56.674
2500	19.783	107.897	1.911	-96.546	-43.025	-63.849
2600	19.797	108.833	1.930	-96.551	-40.600	-70.974
2700	19.809	109.757	1.948	-96.556	-38.175	-78.049
2800	19.819	110.671	1.966	-96.561	-35.750	-85.074
2900	19.827	111.575	1.983	-96.566	-33.325	-92.049
3000	19.833	112.470	1.999	-96.571	-30.900	-98.974
3100	19.838	113.356	2.015	-96.576	-28.475	-105.849
3200	19.842	114.233	2.030	-96.581	-26.050	-112.674
3300	19.845	115.102	2.045	-96.586	-23.625	-119.449
3400	19.847	115.963	2.059	-96.591	-21.200	-126.174
3500	19.849	116.816	2.073	-96.596	-18.775	-132.849
3600	19.850	117.663	2.087	-96.601	-16.350	-139.474
3700	19.851	118.504	2.099	-96.606	-13.925	-146.049
3800	19.852	119.340	2.112	-96.611	-11.500	-152.574
3900	19.853	120.171	2.125	-96.616	-9.075	-159.049
4000	19.854	120.997	2.137	-96.621	-6.650	-165.474
4100	19.855	121.819	2.149	-96.626	-4.225	-171.849
4200	19.856	122.637	2.161	-96.631	-1.800	-178.174
4300	19.857	123.452	2.173	-96.636	0.725	-184.449
4400	19.858	124.263	2.185	-96.641	3.150	-190.674
4500	19.859	125.070	2.197	-96.646	5.575	-196.849
4600	19.860	125.873	2.209	-96.651	7.999	-202.974
4700	19.861	126.673	2.221	-96.656	10.424	-209.049
4800	19.862	127.469	2.233	-96.661	12.849	-215.124
4900	19.863	128.262	2.245	-96.666	15.274	-221.199
5000	19.864	129.052	2.257	-96.671	17.699	-227.224
5100	19.865	129.839	2.269	-96.676	20.124	-233.249
5200	19.866	130.623	2.281	-96.681	22.549	-239.274
5300	19.867	131.404	2.293	-96.686	24.974	-245.299
5400	19.868	132.182	2.305	-96.691	27.399	-251.324
5500	19.869	132.957	2.317	-96.696	29.824	-257.349
5600	19.870	133.731	2.329	-96.701	32.249	-263.374
5700	19.871	134.502	2.341	-96.706	34.674	-269.399
5800	19.872	135.271	2.353	-96.711	37.099	-275.424
5900	19.873	136.037	2.365	-96.716	39.524	-281.449
6000	19.874	136.801	2.377	-96.721	41.949	-287.474

Dec. 31, 1960 Dec. 31, 1964

BORON TRICHLORIDE (BCl₃)

(IDEAL GAS)

MOL. WT. = 117.191

Point Group D_{3h}

ΔH_f⁰ = -96.08 ± 0.50 kcal. mole⁻¹

ΔH_f⁰ 298.15 = -96.31 ± 0.50 kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

λ, cm. ⁻¹	Δλ, cm. ⁻¹
471.0 (1)	986.3 (2)
470.6 (1)	243.0 (2)

Bond Distance: B-Cl = 1.75 Å

Bond Angle: Cl-B-Cl = 120°

Product of the Moments of Inertia: I_AI_BI_C = 3.95517 X 10⁻¹¹³ g.³ cm.³

σ⁻ = 6

Heat of Formation.

The enthalpy change (ΔH_f⁰ 298.15) of the reaction B(amorph) + 3/2 Cl₂(g) = BCl₃(g) has been determined in a calorimeter by W. H. Johnson, R. G. Miller and E. J. Prosen, *J. Res. Natl. Bur. Std.* 62, 213 (1959). From the reported value, ΔH_f⁰ 298.15 = -97.51 ± 0.32 kcal. mole⁻¹, the heat of formation (ΔH_f⁰ 298.15) for BCl₃(g) was derived as -96.31 ± 0.50 kcal. mole⁻¹, using ΔH_f⁰ 298.15 = 1.20 ± 0.40 kcal. mole⁻¹ for the reaction B(c) = B(amorph). Some other related heats of reaction reported by previous investigators are presented as follows.

Investigator	Reaction	ΔH _f ⁰ 298.15, kcal. mole ⁻¹	ΔH _f ⁰ 298.15, kcal. mole ⁻¹
Gail'chenko, et al. ¹	B(am.) + 3/2 Cl ₂ (g) = BCl ₃ (g)	-97.4 ± 0.7	-96.2 ± 0.8
	B(am.) + 3/2 Cl ₂ (g) = BCl ₃ (g)	-103.3 ± 0.6	-96.5 ± 0.7
J. R. Lacher, et al. ²	B ₂ H ₆ (g) + 6 Cl ₂ (g) = 2 BCl ₃ (g) + 6 HCl(g)	-342.9	-100.4 ± 5.0
Skinner and Smith ³	BCl ₃ (l) + (n+3)H ₂ O(l) = (H ₂ BO ₃ +3HCl)·n H ₂ O (Sol.)	-69.2 ± 1.0	-97.2 ± 1.0
Gunn and Green ⁴	BCl ₃ (l) + 2403 H ₂ O(l) = (H ₂ BO ₃ +3HCl)·2400H ₂ O (Sol.)	-68.68 ± 0.06	-96.3 ± 0.2
Passolunghi ⁵	BCl ₃ (l) + 593 H ₂ O(l) = (H ₂ BO ₃ +3HCl)·590 H ₂ O (Sol.)	-69.12 ± 0.11	-95.44 ± 0.39

¹ G. L. Gail'chenko, B. I. Timofeev and S. M. Skuratov, *Russ. J. Inorg. Chem.* 5, 1279 (1960). ΔH_f⁰ 298.15 were derived from ΔH_f⁰ 298.15 using ΔH_f⁰ = -1.2 ± 0.4 kcal. mole⁻¹ for B(am.) = B(c) and ΔH_f⁰ 298.15(BCl₃, l) = 5.6 kcal. mole⁻¹.

² J. R. Lacher, R. E. Scruby and J. D. Park, *J. Am. Chem. Soc.* 74, 5292 (1952). The ΔH_f⁰ 298.15 value was calculated based on ΔH_f⁰ 298.15 = 9.60 kcal. mole⁻¹ for B₂H₆(g).

³ H. A. Skinner and E. J. Prosen, *Trans. Faraday Soc.* 49, 601 (1953), where n = 4978, average value of seven sets of measurement.

⁴ S. R. Gunn and L. G. Green, *J. Phys. Chem.* 64, 61 (1960).

⁵ L. G. Passolunghi, "Heat of Formation of Boron Trichloride", NMR-3508(OO) National Research Corporation, Massachusetts, July 15, 1964.

The heats of formation for BCl₃(l) derived from the heats of hydrolysis reported by other investigators were reviewed by W. H. Johnson, R. G. Miller and E. J. Prosen, *loc. cit.*

Heat Capacity and Entropy.

The bond distance of B and Cl atoms has been reported to be 1.73 ± 0.02, 1.76 ± 0.02 and 1.75 Å by H. A. Levy and L. O. Brockway, *J. Am. Chem. Soc.* 59, 2085 (1937), A. H. Gregg, O. C. Hampton and G. I. Jenkins, *P. L. F. Jena* and L. E. Sutton, *Trans. Faraday Soc.* 53, 952 (1957), and C. Spencer and W. N. Lipscomb, *J. Chem. Phys.* 28, 355 (1958), respectively. The last value is adopted. The values of vibrational frequencies were used were reported by L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.* 24, 242 (1956). The vibrational frequencies were also determined by A. B. D. Cassie, *Proc. Roy. Soc. A145*, 87 (1935), T. F. Anderson, E. N. Lassettre and D. M. Yost, *J. Chem. Phys.* 5, 703 (1936), and R. E. Scruby, J. R. Lacher and J. D. Park, *J. Chem. Phys.* 19, 386 (1951). The molecular structure was given by H. A. Levy, et al., *loc. cit.* The three principal moments of inertia are: I_A = I_B = 2.7042 X 10⁻³⁸ and I_C = 5.4085 X 10⁻³⁸ g. cm.²

Boron Monofluoride (BF)
(Ideal Gas)

BORON MONOFLUORIDE (BF)

(IDEAL GAS)

MOL. WT. = 29.82

Mol. Wt. = 29.82

Ground State Configuration $1\Sigma^+$

$\Delta H_f^\circ = -28.4 \pm 3.3$ kcal. mole $^{-1}$

$\Delta H_f^\circ = 47.890$ cal. deg. $^{-1}$ mole $^{-1}$

$\Delta H_f^\circ = -27.7 \pm 3.3$ kcal. mole $^{-1}$

Electronic Levels and Quantum Weight

ϵ_1 , cm. $^{-1}$
0
 $\omega_e = 11.99$ cm. $^{-1}$
 $\omega_e x_e = 11.99$ cm. $^{-1}$
 $\omega_e = 1.265$ Å

Heat of Formation

The equilibria of the reaction $2/5 \text{ B(c)} + 1/5 \text{ BF}_3(\text{g}) = \text{BF(g)}$ were studied by J. Blauer, M. A. Greenbaum and M. Farber¹, by means of transpiration at pressures below 300 μ . The values of $\log K_p$ at 1375 and 1476°K. were reported as -3.99 ± 0.02 and -3.30 ± 0.05 , respectively. By the third law method the value of ΔH_f° 298.15 for the reaction was derived to be 61.38 kcal. mole $^{-1}$, yielding ΔH_f° 298.15 = -28.7 ± 2.6 kcal. mole $^{-1}$ for BF(g). The system B + CaF₂ was studied mass spectrometrically in a graphite Knudsen cell by D. L. Hildenbrand. The equilibria involving BF(g) were observed. Intensity measurements were made at temperatures, 1583–1734°K. From the third law value, ΔH_f° 298.15 = 12.2 ± 0.3 kcal. mole $^{-1}$, for the reaction $\text{BF}_3(\text{g}) + \text{Ca(g)} = \text{BF(g)} + \text{CaF}_2(\text{g})$, the value of ΔH_f° 298.15 for BF(g) was derived as -26.7 ± 2 kcal. mole $^{-1}$. The dissociation energy (D_0°) of BF(g) molecule has been reported by G. Herzberg², A. G. Gaydon³ and R. F. Barrow⁴, respectively. Hence the corresponding values of ΔH_f° 298.15 for BF(g) were derived. The results are compared with those obtained from equilibrium data as follows.

Investigator	Reaction	ΔH_f° 298.15, kcal. mole $^{-1}$	ΔH_f° 298.15, kcal. mole $^{-1}$
Farber, et al. ¹	$2/5 \text{ B(c)} + 1/5 \text{ BF}_3(\text{g}) = \text{BF(g)}$	61.38	-28.7 ± 2.6
Herzberg ²	$\text{BF(g)} = \text{B(g)} + \text{F(g)}$	100.2	+51.5
Gaydon ³	$\text{BF(g)} = \text{B(g)} + \text{F(g)}$	197.0	-45.3 ± 11.5
Barrow ⁴	$\text{BF(g)} = \text{B(g)} + \text{F(g)}$	186.0	-34.3
Gross, et al. ⁵	$2/5 \text{ B(c)} + 1/5 \text{ BF}_3(\text{g}) = \text{BF(g)}$	—	-28 ± 3
Hildenbrand ⁶	$\text{BF}_3(\text{g}) + \text{Ca(g)} = \text{BF(g)} + \text{CaF}_2(\text{g})$	12.2	-26.7 ± 2

1 J. Blauer, M. A. Greenbaum and M. Farber, J. Phys. Chem. 69, 2332 (1964).

2 G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, New York, 1950. ΔH_f° 298.15 was calculated based on $D_0^\circ = 4.3$ e.v.

3 A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. ΔH_f° 298.15 was derived from $D_0^\circ = 8.5 \pm 0.5$ e.v.

4 R. F. Barrow, Trans. Faraday Soc. 56, 952 (1960). ΔH_f° 298.15 was calculated based on $D_0^\circ = 185$ kcal. mole $^{-1}$.

5 F. Gross, C. Hayman, D. L. Levi and R. H. Lewin, "Stability of Lower Boron Halides", Final Technical Report, August 22, 1963, Polymer Research Institute Limited, England. The reported value, ΔH_f° 298.15 = -28 ± 3 kcal. mole $^{-1}$, is a preliminary estimated one.

6 D. L. Hildenbrand, "Thermodynamic Properties of Propellant Combustion Products", QLR-65-3, Philco Corporation, California.

The value of ΔH_f° 298.15 adopted is the average of the first and last ΔH_f° 298.15 values listed in the above table.

Heat Capacity and Entropy

The spectroscopic constants used were obtained from R. Onaka, J. Chem. Phys. 27, 374 (1957) and corrected to the average isotopic species. Spectroscopic constants for BF(g) were also reported by G. Herzberg, loc. cit. The moment of inertia (I) is 1.6321×10^{-39} g. cm. 2

Dec. 31, 1960; Dec. 31, 1964

T, °K.	C _p cal. mole $^{-1}$ deg. $^{-1}$	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole $^{-1}$	ΔH_f°	Log K _p
0	.000	INFINITE	-2.078	-28.431	INFINITE
100	6.957	40.269	1.384	-28.074	65.724
200	6.968	48.593	.688	-27.824	35.153
298	7.073	47.890	.000	-27.700	25.169
300	7.076	47.934	.013	-27.699	25.044
400	7.309	50.000	.732	-27.687	20.002
500	7.581	51.660	1.476	-27.759	16.974
600	7.832	53.065	2.247	-27.879	14.940
700	8.042	54.286	3.041	-28.027	12.993
800	8.211	55.374	3.854	-28.192	11.493
900	8.348	56.349	4.682	-28.368	10.336
1000	8.457	57.234	5.523	-28.555	10.847
1100	8.545	58.045	6.378	-28.754	10.376
1200	8.620	58.795	7.231	-28.964	9.934
1300	8.681	59.484	8.087	-29.184	9.516
1400	8.732	60.129	8.942	-29.414	9.041
1500	8.776	60.733	9.803	-29.655	8.734
1600	8.814	61.301	10.722	-29.906	8.463
1700	8.848	61.836	11.695	-30.167	8.222
1800	8.877	62.343	12.682	-30.436	8.005
1900	8.903	62.824	13.681	-30.712	7.810
2000	8.927	63.281	14.672	-30.993	7.633
2100	8.949	63.717	15.645	-31.279	7.471
2200	8.969	64.134	16.602	-31.570	7.322
2300	8.987	64.533	17.540	-31.865	7.185
2400	9.004	64.916	17.859	-32.164	7.058
2500	9.020	65.283	18.761	-32.466	6.931
2600	9.035	65.638	19.643	-32.771	6.803
2700	9.049	65.979	20.567	-33.082	6.684
2800	9.062	66.308	21.473	-33.394	6.572
2900	9.075	66.626	22.380	-33.708	6.467
3000	9.088	66.934	23.288	-34.024	6.369
3100	9.100	67.232	24.197	-34.344	6.276
3200	9.111	67.521	25.108	-34.664	6.189
3300	9.122	67.802	26.020	-34.984	6.106
3400	9.133	68.075	26.932	-35.304	6.027
3500	9.143	68.339	27.846	-35.624	5.952
3600	9.154	68.597	28.761	-35.944	5.881
3700	9.164	68.848	29.677	-36.264	5.813
3800	9.173	69.093	30.594	-36.584	5.749
3900	9.183	69.331	31.512	-36.904	5.687
4000	9.192	69.564	32.430	-37.224	5.617
4100	9.202	69.791	33.350	-37.544	5.549
4200	9.211	70.013	34.271	-37.864	5.485
4300	9.220	70.229	35.192	-38.184	5.423
4400	9.229	70.441	36.115	-38.504	5.363
4500	9.238	70.649	37.038	-38.824	5.307
4600	9.246	70.852	37.962	-39.144	5.254
4700	9.255	71.051	38.887	-39.464	5.202
4800	9.264	71.246	39.813	-39.784	5.150
4900	9.272	71.437	40.740	-40.104	5.100
5000	9.280	71.624	41.668	-40.424	5.051
5100	9.289	71.808	42.596	-40.744	5.003
5200	9.297	71.989	43.525	-41.064	4.956
5300	9.305	72.166	44.456	-41.384	4.910
5400	9.313	72.340	45.386	-41.704	4.865
5500	9.322	72.511	46.318	-42.024	4.821
5600	9.330	72.679	47.251	-42.344	4.778
5700	9.338	72.844	48.184	-42.664	4.735
5800	9.346	73.007	49.118	-42.984	4.693
5900	9.354	73.166	50.053	-43.304	4.651
6000	9.362	73.324	50.989	-43.624	4.610

Boron Oxide Fluoride (BOF)

(Ideal Gas) Mol. Wt. = 45.82

BORON OXIDE FLUORIDE (BOF)

MOL. WT. = 45.82

(IDEAL GAS)

T, °K.	C _p ^o	S ^o - (R°·H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	+0.00	INFINITE	- 2.374	- 143.990	- 143.990	INFINITE
100	44.736	41.505	- 1.677	- 144.002	- 144.002	315.477
200	8.505	54.562	- .901	- 143.997	- 143.997	190.127
298	9.798	53.705	- .000	- 144.000	- 144.000	106.331
300	9.819	53.766	53.705	- 144.000	- 144.000	105.681
400	10.792	56.730	54.103	- 144.030	- 145.073	79.454
500	11.540	59.222	54.884	- 144.094	- 145.770	63.713
600	12.130	61.380	55.791	- 144.178	- 146.097	53.213
700	12.578	63.195	56.728	- 144.271	- 146.509	45.709
800	12.915	64.695	57.691	- 144.369	- 146.986	39.684
900	13.275	66.051	58.659	- 144.466	- 147.519	34.654
1000	13.515	67.192	59.459	- 144.567	- 147.770	32.184
1100	13.710	68.250	60.263	- 144.675	- 147.536	29.311
1200	13.870	69.225	61.008	- 144.788	- 147.791	26.915
1300	14.000	70.125	61.698	- 144.905	- 148.042	24.915
1400	14.109	72.607	62.562	- 145.035	- 148.272	23.195
1500	14.200	73.584	63.244	- 145.171	- 148.500	21.635
1600	14.277	74.503	63.938	- 145.316	- 148.716	20.313
1700	14.338	75.368	64.598	- 145.471	- 148.923	19.164
1800	14.386	76.192	65.226	- 145.636	- 149.118	18.174
1900	14.427	76.971	65.806	- 145.804	- 149.311	17.316
2000	14.467	77.713	66.363	- 145.980	- 149.491	16.535
2100	14.504	78.421	66.900	- 146.162	- 149.662	15.875
2200	14.538	79.095	67.416	- 146.350	- 149.826	15.320
2300	14.568	79.745	67.907	- 146.542	- 150.000	14.863
2400	14.600	80.366	68.399	- 146.744	- 150.122	13.670
2500	14.631	80.963	68.896	- 146.944	- 150.151	13.126
2600	14.651	81.537	69.458	- 147.141	- 150.050	12.613
2700	14.669	82.085	70.000	- 147.336	- 150.000	12.138
2800	14.685	82.605	70.530	- 147.536	- 150.000	11.690
2900	14.699	83.100	70.792	- 147.736	- 149.736	11.284
3000	14.712	83.639	71.212	- 147.936	- 149.618	10.899
3100	14.724	84.121	71.620	- 148.136	- 149.488	10.538
3200	14.735	84.576	72.016	- 148.336	- 149.353	10.200
3300	14.745	85.002	72.406	- 148.536	- 149.218	9.883
3400	14.754	85.403	72.784	- 148.736	- 149.083	9.591
3500	14.762	85.810	73.153	- 148.936	- 148.948	9.296
3600	14.770	86.236	73.513	- 149.136	- 148.813	9.029
3700	14.778	86.680	73.866	- 149.336	- 148.678	8.775
3800	14.783	87.125	74.212	- 149.536	- 148.543	8.530
3900	14.789	87.500	74.545	- 149.736	- 148.408	8.296
4000	14.795	87.884	74.874	- 149.936	- 148.273	8.063
4100	14.800	88.249	75.196	- 150.136	- 148.138	7.830
4200	14.805	88.594	75.511	- 150.336	- 148.003	7.602
4300	14.809	88.925	75.819	- 150.536	- 147.868	7.379
4400	14.813	89.245	76.122	- 150.736	- 147.733	7.156
4500	14.817	89.628	76.418	- 150.936	- 147.598	6.933
4600	14.821	89.994	76.709	- 151.136	- 147.463	6.710
4700	14.825	90.355	77.000	- 151.336	- 147.328	6.487
4800	14.828	90.585	77.274	- 151.536	- 147.193	6.264
4900	14.831	90.800	77.549	- 151.736	- 147.058	6.041
5000	14.834	91.130	77.819	- 151.936	- 146.923	5.818
5100	14.836	91.484	78.084	- 152.136	- 146.788	5.595
5200	14.839	91.774	78.345	- 152.336	- 146.653	5.372
5300	14.841	92.035	78.600	- 152.536	- 146.518	5.149
5400	14.844	92.332	78.852	- 152.736	- 146.383	4.926
5500	14.846	92.604	79.100	- 152.936	- 146.248	4.703
5600	14.848	92.872	79.343	- 153.136	- 146.113	4.480
5700	14.850	93.112	79.581	- 153.336	- 145.978	4.257
5800	14.852	93.393	79.819	- 153.536	- 145.843	4.034
5900	14.854	93.647	80.051	- 153.736	- 145.708	3.811
6000	14.855	93.867	80.280	- 153.936	- 145.573	3.588

Point Group [C_{2v}]

S_{298.15} = [53.7] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

Wavenumber (cm. ⁻¹)	Degeneracy
[1050] (1)	1
[500] (2)	2
[1900] (1)	1

Bond Distance: B-P = [1.30] Å B-O = [1.20] Å

Bond Angle: O-B-P = [180°]

B₀ = [0.30399] cm.⁻¹

Heat of Formation

The equilibrium constants for the reaction B₂O₃(l) + BF₃(g) = 3BOF(g) in the temperature range 1054-1253°K. were determined by M. Perber and J. Blauer, Trans. Faraday Soc. 59, 2050 (1962), using the so-called Molecular Flow Reaction Method. The value of ΔH_f^o for this reaction was evaluated by both the second and third law methods, using the equilibrium constants corrected for the trimer and correcting K_p at 1200°K. from 9.6 X 10⁻¹¹ to 9.6 X 10⁻¹⁰. D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. 39, 1973 (1963) analyzed the vapor above mixture of MgF₂ and B₂O₃ contained in a Knudsen cell with a mass spectrometer and found that in the temperature range 980-1230°K. the vapor is composed of BF₃(g), (BOF)₂(g) and BOF(g) species. From the reported temperature dependence of appropriate ion intensities the enthalpy change of the reaction (BOF)₂(g) = 3BOF(g) was derived by the second law method as 127.9 kcal. mole⁻¹ at 1115°K. or 129.75 kcal. mole⁻¹ at 298.15°K. The results obtained are presented as follows, using JANAP free energy functions and auxiliary data.

Investigator	Reaction	Second law value	Third law value	ΔH _f ^o 298.15 ⁻¹ kcal. mole ⁻¹
Perber and Blauer	B ₂ O ₃ (l) + BF ₃ (g) = 3BOF(g)	150.2 ± 16.6	149.0	-140.1 ± 6*
Hildenbrand, et al.	(BOF) ₂ (g) = 3BOF(g)	129.8 ± 3	—	-145.2 ± 1.5

*Calculation based on the third law value and one point rejected due to statistical test.

The adopted value of ΔH_f^o 298.15 for BOF(g) is the weighted average of the two ΔH_f^o 298.15 values listed above.

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The vibrational frequencies (W) were estimated from the W values calculated by the valence force method described by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., 1945, using estimated force constants, k₁ = 10 X 10⁵ dynes cm.⁻¹ and k₂ = 25.6 X 10⁵ dynes cm.⁻¹ and k₃ = 0.47 X 10⁻¹¹ dynes cm. rad.⁻¹. The B-O and B-P bond distances were assumed to be the same as those in BO(g) and BF₃(g) molecules. The moment of inertia is 9.0464 X 10⁻³⁹ g. cm.².

BORON DIFLUORIDE (BF₂)

MOL. WT. = 48.82

(IDEAL GAS)

Point Group C_{2v}

$$\Delta H_f^0 = -130 \pm 6 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [58.996] \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = -130 \pm 6 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	Deg.
[1120] (1)	[470] (1)
[1450] (1)	

Bond Distance: B-F = [1.295] Å

Bond Angle: F-B-F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = 3.96532 \times 10^{-116} \text{ g.}^3 \text{ cm.}^6$

$$\sigma = 2$$

Heat of Formation.

The heat of formation (ΔH_f^0 298.15) was obtained from J. L. Margrave, J. Phys. Chem. **66**, 1209 (1962), from appearance potentials.

Heat Capacity and Entropy.

The bond distance and angle were assumed to be the same as those in BF₃(g) molecule. The vibrational frequencies were calculated using force constants transferred from those for BF₃(g) given by G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., 1945. The three principal moments of inertia are: $I_A = 7.8278 \times 10^{-39}$, $I_B = 5.8710 \times 10^{-40}$ and $I_C = 8.5149 \times 10^{-39} \text{ g. cm.}^2$

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1964

Boron Difluoride Unipositive Ion (BF₂⁺)

(Ideal Gas) GFW = 48.80725

T, °K	Cp°	$\frac{\text{gibbs/mol}}{T}$	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	10.586	53.785	53.785	.000	84.000	81.340	- 59.624
300							
400	10.605	53.850	53.785	.070	84.010	81.322	- 59.243
500	11.513	57.032	54.213	1.120	84.523	80.349	- 43.901
600	12.211	59.675	55.048	2.315	84.987	79.250	- 34.640
700							
800	12.747	61.955	56.014	3.564	85.426	78.062	- 28.434
900	13.126	63.732	57.090	4.860	85.750	76.800	- 23.420
1000	13.456	65.052	57.990	6.196	86.000	75.578	- 18.420
1100	13.713	65.931	58.640	7.552	86.184	74.305	- 13.420
1200	13.902	66.786	59.653	8.933	87.092	72.685	- 8.420
1300							
1400	14.052	70.119	60.227	10.331	87.491	71.225	- 3.420
1500	14.266	73.485	61.358	11.727	87.748	69.800	1.580
1600	14.349	73.345	63.120	14.566	88.639	68.201	4.560
1700	14.414	74.538	63.648	16.034	89.002	66.644	7.540
1800							
1900	14.470	75.470	64.546	17.478	89.355	65.060	10.479
2000	14.556	76.179	65.456	18.569	90.031	63.482	13.420
2100	14.644	76.930	66.339	20.381	90.359	61.911	16.360
2200	14.686	77.665	67.182	21.639	90.680	60.340	19.300
2300	14.703	81.390	69.736	23.299	90.965	58.762	22.240
2400	14.718	81.990	70.218	24.762	91.000	57.185	25.180
2500	14.732	82.568	70.636	26.052	91.031	55.608	28.120
2600	14.756	83.660	71.140	30.052	91.065	54.031	31.060
2700	14.766	84.178	71.581	35.052	91.097	52.454	34.000
2800	14.775	84.679	72.009	38.011	91.128	50.877	36.940
2900							
3000	14.784	85.164	72.426	39.489	91.151	49.300	39.880
3100	14.800	86.089	73.026	42.467	91.166	47.723	42.820
3200	14.808	86.531	73.611	43.927	91.181	46.146	45.760
3300	14.815	86.960	73.986	45.409	91.196	44.569	48.700
3400							
3500	14.822	87.377	74.352	46.890	90.004	42.992	51.640
3600	14.829	87.784	74.710	48.373	90.266	41.415	54.580
3700	14.836	88.181	75.060	49.856	90.528	39.838	57.520
3800	14.843	88.565	75.400	51.340	90.790	38.261	60.460
3900	14.850	88.941	75.734	52.825	91.052	36.684	63.400
4000							
4100	14.857	89.307	76.061	54.310	91.314	35.107	66.340
4200	14.872	89.651	76.381	55.795	91.576	33.530	69.280
4300	14.872	90.015	76.691	57.283	91.838	31.953	72.220
4400	14.880	90.357	77.000	58.771	92.100	30.376	75.160
4500	14.888	90.692	77.301	60.259	92.362	28.799	78.100
4600							
4700	14.897	91.019	77.595	61.748	92.624	27.222	81.040
4800	14.914	91.453	77.888	63.239	92.886	25.645	83.980
4900	14.921	91.861	78.174	64.721	93.148	24.068	86.920
5000	14.933	92.263	78.420	66.208	93.410	22.491	89.860
5100	14.943	92.558	78.688	67.696	93.672	20.914	92.800
5200	14.965	92.843	78.934	69.184	93.934	19.337	95.740
5300	14.985	93.113	79.176	70.676	94.196	17.760	98.680
5400	14.976	93.413	79.766	73.666	94.458	16.183	101.620
5500	14.987	93.688	80.017	75.194	94.720	14.606	104.560
5600							
5700	14.999	93.959	80.263	76.693	94.982	13.029	107.500
5800	15.023	94.425	81.184	78.184	95.244	11.452	110.440
5900	15.035	94.742	80.680	81.168	95.506	9.875	113.380
6000	15.048	94.995	81.211	82.702	95.768	8.298	116.320

June 30, 1968



(IDEAL GAS)

BORON DIFLUORIDE UNIPOSITIVE ION (BF₂⁺)

Point Group [D_{∞h}]

S°_{298.15} = [53.8 ± 2] gibbs/mol

GFW = 48.80725

ΔHf°₀ = 83.9 ± 2 kcal/mol

ΔHf°_{298.15} = 84.0 ± 2 kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i , cm ⁻¹	$\frac{g_i}{g_0}$
1 _g ⁺	0	1
1 _{B₂}	[25000]	1

Vibrational Frequencies and Degeneracies

$\frac{\omega_e}{\text{cm}^{-1}}$
[900] (1)
[370] (2)
[1550] (1)

Bond Distance: B-F = [1.31] Å

Bond Angle: F-B-F = [180°]

Rotational Constant: B₀ = [0.2885] cm⁻¹

σ = 2

Heat of Formation

The electron impact reaction at low pressure in BF₃(g) has been studied with a mass spectrometer by Osberg (1), Law (2), and Harriott (3). From the reported appearance potentials 17.0 ± 0.5, 16.2 ± 0.2, and 16.7 ± 0.05 eV and assumed process BF₃⁺ + e = BF₂⁺ + F + 2e, we calculate the corresponding values of ΔHf°₂₉₈ (BF₂⁺, g) as 102.8 ± 11.5, 84.4 ± 4.6, and 83.7 ± 1.2 kcal/mol, using ΔHf° = 270.977 and 18.357 kcal/mol for BF₃(g) and F(g). The adopted value of ΔHf° for BF₂⁺(g) is 84 ± 2 kcal/mol, since the lower values are likely to have the least excess kinetic energy in the fragments.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (4) prediction for 16 valence electron XY₂ molecules. The electronic states and levels, and vibrational frequencies are estimated by comparison with those for CO₂(g). The B-F bond distance is calculated by the method recommended by Krasnov (5). The moment of inertia is 1.083 × 10⁻³⁸ g cm². The enthalpy at 0°K is -2.54 kcal/mol.

References

1. O. Osberg, *Z. Phys.*, **128**, 366 (1950).
2. R. W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956).
3. J. Harriott and J. D. Craggs, *J. Electron. Contr.*, **3**, 194 (1957).
4. A. D. Walsh, *J. Chem. Soc.*, **1953**, 2266 (1953).
5. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1966.
6. K. S. Krasnov, *Zh. Strukt. Khim.*, **1**, 209 (1960).



GFW = 48.80835

(IDEAL GAS)

BORON DIFLUORIDE UNINEGATIVE ION (BF₂⁻) $\Delta H_f^\circ = [-136 \pm 30] \text{ kcal/mol}$ Point Group [C_{2v}] $\Delta H_f^\circ = [-136 \pm 30] \text{ kcal/mol}$ $S_{298.15}^\circ = [57.5 \pm 2] \text{ gibbs/mol}$

Electronic Levels and Quantum Heights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	1
[6000]	3
[28000]	1

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	g_e
[1000] (1)	1
[5701] (1)	1
[11000] (1)	1

Bond Distance: B-F = [1.301] Å

Bond Angle: F-B-F = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [4.054 \times 10^{-116}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

The electron captured by BF₂ should go into a non-bonding orbital according to the correlation diagrams of Walsh (1), thus we would expect a small electron affinity. Two estimates of the dissociation energy of BF₂⁻ indicate a negative electron affinity (EA); consider the isoelectronic reactions BF₂⁻ + B⁺ + 2F + C + 2F if we make the reasonable assumption that the atomization energies are the same then $\Delta H_f^\circ(\text{BF}_2^-)$, g) = -86 kcal/mol, or EA(BF₂⁻) = -44 kcal. Another approach is to consider the isoelectronic reactions BF₂⁻ + BF + F⁻ and BNe + BF + Ne, although the latter reaction is unknown we would expect zero bond strength, and if used in the first reaction this yields $\Delta H_f^\circ(\text{BF}_2^-)$, g) = -90 kcal/mol, or EA(BF₂⁻) = -40 kcal.

In consideration of the above we choose EA(BF₂⁻) = EA(B, g) = 6 kcal (2), which gives $\Delta H_f^\circ(\text{BF}_2^-)$, g) = -136 kcal/mol.

Heat Capacity and Entropy

The molecular structure and B-F bond distance are assumed to be the same as those for the BF₂(g) molecule. The electronic levels, quantum heights and vibrational frequencies are estimated by comparison with those for CF₂(3) which is isoelectronic with BF₂⁻. The three principal moments of inertia are: $I_A = 5.904 \times 10^{-40}$, $I_B = 7.997 \times 10^{-39}$ and $I_C = 8.587 \times 10^{-39} \text{ g cm}^2$. The enthalpy at 0°K is -2.52 kcal/mol.

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. G. Herzberg, "Electronic Spectra of Polyatomic Molecules", D. Van Nostrand Co., Inc., New York, 1966.

Boron Difluoride Uninegative Ion (BF₂⁻)

GFW = 48.80835

(Ideal Gas)

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	kcal/mol ΔH _f ^o	ΔG _f ^o	Log K _p
0						
100						
200						
298	9.702	57.489	57.489	1.000	-136.790	100.270
300	9.722	57.549	57.489	1.018	-136.010	99.655
400	10.728	60.489	57.483	1.042	-136.575	74.838
500	11.550	62.970	58.659	2.156	-137.178	59.684
600	12.058	65.119	59.561	3.335	-137.803	49.869
700	12.461	67.010	60.492	4.562	-138.439	42.683
800	12.762	68.694	61.414	5.824	-139.085	37.268
900	13.000	70.211	62.309	7.112	-139.736	33.037
1000	13.204	71.592	63.169	8.423	-140.392	29.638
1100	13.393	72.859	63.993	9.753	-141.055	26.881
1200	13.579	74.033	64.781	11.101	-141.720	24.500
1300	13.767	75.127	65.536	12.468	-142.386	22.510
1400	13.959	76.154	66.258	13.855	-143.050	20.796
1500	14.155	77.124	66.950	15.260	-143.714	19.304
1600	14.351	78.044	67.615	16.686	-144.373	17.992
1700	14.543	78.919	68.254	18.130	-145.029	16.829
1800	14.729	79.756	68.870	19.594	-145.678	15.792
1900	14.905	80.557	69.464	21.076	-146.320	14.859
2000	15.069	81.326	70.038	22.575	-146.954	14.015
2100	15.218	82.065	70.594	24.089	-147.582	13.249
2200	15.351	82.776	71.131	25.618	-148.203	12.549
2300	15.467	83.461	71.653	27.159	-148.818	11.908
2400	15.567	84.121	72.158	28.711	-149.431	11.317
2500	15.650	84.759	72.650	30.272	-150.049	10.763
2600	15.717	85.374	73.127	31.840	-150.631	10.239
2700	15.769	85.968	73.592	33.415	-151.208	9.752
2800	15.808	86.542	74.044	34.994	-151.782	9.309
2900	15.834	87.097	74.485	36.576	-152.357	8.874
3000	15.848	87.634	74.914	38.160	-152.931	8.477
3100	15.853	88.154	75.333	39.745	-153.508	8.105
3200	15.849	88.657	75.742	41.330	-154.089	7.754
3300	15.838	89.145	76.140	42.915	-154.668	7.423
3400	15.820	89.618	76.530	44.498	-155.243	7.110
3500	15.797	90.076	76.910	46.079	-155.816	6.814
3600	15.770	90.520	77.282	47.657	-156.387	6.533
3700	15.739	90.952	77.646	49.233	-156.956	6.267
3800	15.705	91.371	78.002	50.805	-157.523	6.014
3900	15.669	91.779	78.350	52.373	-158.089	5.773
4000	15.631	92.175	78.690	53.938	-158.654	5.542
4100	15.592	92.561	79.024	55.500	-159.227	5.325
4200	15.552	92.936	79.351	57.057	-159.798	5.104
4300	15.512	93.301	79.671	58.610	-160.366	4.881
4400	15.472	93.658	79.985	60.159	-160.931	4.664
4500	15.432	94.005	80.293	61.705	-161.493	4.452
4600	15.393	94.344	80.594	63.246	-162.052	4.244
4700	15.354	94.674	80.890	64.783	-162.608	4.040
4800	15.316	94.997	81.181	66.317	-163.161	3.840
4900	15.278	95.312	81.466	67.846	-163.711	3.644
5000	15.242	95.621	81.746	69.372	-164.258	3.452
5100	15.207	95.922	82.021	70.895	-164.802	3.264
5200	15.172	96.217	82.291	72.414	-165.343	3.080
5300	15.139	96.506	82.557	73.929	-165.881	2.900
5400	15.107	96.789	82.818	75.442	-166.416	2.724
5500	15.076	97.065	83.074	76.951	-166.948	2.552
5600	15.046	97.337	83.327	78.457	-167.478	2.384
5700	15.017	97.603	83.575	79.960	-167.995	2.220
5800	14.989	97.864	83.819	81.460	-168.509	2.060
5900	14.963	98.120	84.059	82.958	-169.020	1.904
6000	14.937	98.371	84.296	84.453	-169.528	1.752

June 30, 1968; Dec. 31, 1968

Di fluoroborane (BF₂)

(Ideal Gas) Mol. wt. = 49.81577

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	∞	∞	∞	2.550	-174.536	-174.536	INFINITE
100	7.998	48.830	48.830	1.755	-174.621	-174.621	381.149
200	8.765	54.360	54.360	.924	-175.072	-175.072	190.026
298	10.124	58.300	58.300	.000	-175.400	-175.400	127.002
300	10.152	58.363	58.363	.019	-175.407	-175.407	126.210
400	11.677	61.494	61.494	1.111	-175.754	-175.754	94.236
500	13.027	64.249	64.249	2.348	-176.086	-176.086	75.015
600	14.134	66.726	66.726	3.708	-176.383	-176.383	62.177
800	15.026	68.076	68.076	5.468	-176.641	-176.641	52.995
1000	15.632	68.919	68.919	6.593	-176.863	-176.863	46.905
1200	16.082	69.324	69.324	7.465	-177.058	-177.058	40.724
1400	16.412	69.665	69.665	8.313	-177.230	-177.230	36.423
1600	16.657	69.957	69.957	9.170	-177.387	-177.387	32.900
1800	16.821	70.209	70.209	10.042	-177.522	-177.522	29.962
2000	16.906	70.424	70.424	10.926	-177.638	-177.638	27.340
2200	16.961	70.601	70.601	11.819	-177.731	-177.731	25.000
2400	16.995	70.744	70.744	12.719	-177.805	-177.805	22.888
2600	17.013	70.861	70.861	13.624	-177.863	-177.863	21.868
2800	17.021	70.954	70.954	14.533	-177.900	-177.900	20.936
3000	17.023	71.026	71.026	15.445	-177.920	-177.920	19.995
3200	17.020	71.078	71.078	16.359	-177.927	-177.927	19.065
3400	17.014	71.111	71.111	17.274	-177.921	-177.921	18.138
3600	17.006	71.128	71.128	18.189	-177.903	-177.903	17.216
3800	16.996	71.131	71.131	19.104	-177.873	-177.873	16.300
4000	16.984	71.121	71.121	20.019	-177.831	-177.831	15.384
4200	16.970	71.100	71.100	20.934	-177.778	-177.778	14.468
4400	16.954	71.068	71.068	21.849	-177.713	-177.713	13.552
4600	16.936	71.026	71.026	22.764	-177.638	-177.638	12.640
4800	16.916	70.974	70.974	23.679	-177.553	-177.553	11.728
5000	16.894	70.912	70.912	24.594	-177.458	-177.458	10.816
5200	16.870	70.840	70.840	25.509	-177.353	-177.353	9.904
5400	16.844	70.758	70.758	26.424	-177.238	-177.238	9.000
5600	16.817	70.666	70.666	27.339	-177.113	-177.113	8.100
5800	16.789	70.564	70.564	28.254	-176.978	-176.978	7.200
6000	16.760	70.452	70.452	29.169	-176.833	-176.833	6.300
6200	16.730	70.330	70.330	30.084	-176.678	-176.678	5.400
6400	16.699	70.198	70.198	31.000	-176.513	-176.513	4.500
6600	16.667	70.056	70.056	31.915	-176.338	-176.338	3.600
6800	16.634	69.904	69.904	32.830	-176.153	-176.153	2.700
7000	16.599	69.742	69.742	33.745	-175.958	-175.958	1.800
7200	16.564	69.570	69.570	34.660	-175.753	-175.753	0.900
7400	16.528	69.388	69.388	35.575	-175.538	-175.538	0.000
7600	16.491	69.196	69.196	36.490	-175.313	-175.313	-0.900
7800	16.453	68.994	68.994	37.405	-175.078	-175.078	-1.800
8000	16.415	68.782	68.782	38.320	-174.833	-174.833	-2.700
8200	16.376	68.560	68.560	39.235	-174.578	-174.578	-3.600
8400	16.337	68.328	68.328	40.150	-174.313	-174.313	-4.500
8600	16.297	68.086	68.086	41.065	-174.038	-174.038	-5.400
8800	16.257	67.834	67.834	41.980	-173.753	-173.753	-6.300
9000	16.216	67.572	67.572	42.895	-173.458	-173.458	-7.200
9200	16.174	67.300	67.300	43.810	-173.153	-173.153	-8.100
9400	16.131	67.018	67.018	44.725	-172.838	-172.838	-9.000
9600	16.088	66.726	66.726	45.640	-172.513	-172.513	-9.900
9800	16.044	66.424	66.424	46.555	-172.178	-172.178	-10.800
10000	16.000	66.112	66.112	47.470	-171.833	-171.833	-11.700
10200	15.955	65.790	65.790	48.385	-171.478	-171.478	-12.600
10400	15.909	65.458	65.458	49.300	-171.113	-171.113	-13.500
10600	15.863	65.116	65.116	50.215	-170.738	-170.738	-14.400
10800	15.816	64.764	64.764	51.130	-170.353	-170.353	-15.300
11000	15.769	64.402	64.402	52.045	-169.958	-169.958	-16.200
11200	15.722	64.030	64.030	52.960	-169.553	-169.553	-17.100
11400	15.675	63.648	63.648	53.875	-169.138	-169.138	-18.000
11600	15.628	63.256	63.256	54.790	-168.713	-168.713	-18.900
11800	15.580	62.854	62.854	55.705	-168.278	-168.278	-19.800
12000	15.532	62.442	62.442	56.620	-167.833	-167.833	-20.700
12200	15.484	62.020	62.020	57.535	-167.378	-167.378	-21.600
12400	15.436	61.588	61.588	58.450	-166.913	-166.913	-22.500
12600	15.388	61.146	61.146	59.365	-166.438	-166.438	-23.400
12800	15.339	60.694	60.694	60.280	-165.953	-165.953	-24.300
13000	15.290	60.232	60.232	61.195	-165.458	-165.458	-25.200
13200	15.241	59.760	59.760	62.110	-164.953	-164.953	-26.100
13400	15.192	59.278	59.278	63.025	-164.438	-164.438	-27.000
13600	15.143	58.786	58.786	63.940	-163.913	-163.913	-27.900
13800	15.094	58.284	58.284	64.855	-163.378	-163.378	-28.800
14000	15.045	57.772	57.772	65.770	-162.833	-162.833	-29.700
14200	14.996	57.250	57.250	66.685	-162.278	-162.278	-30.600
14400	14.947	56.718	56.718	67.590	-161.713	-161.713	-31.500
14600	14.897	56.176	56.176	68.495	-161.138	-161.138	-32.400
14800	14.848	55.624	55.624	69.400	-160.553	-160.553	-33.300
15000	14.798	55.062	55.062	70.305	-159.958	-159.958	-34.200
15200	14.748	54.490	54.490	71.210	-159.353	-159.353	-35.100
15400	14.698	53.908	53.908	72.115	-158.738	-158.738	-36.000
15600	14.648	53.316	53.316	73.020	-158.113	-158.113	-36.900
15800	14.597	52.714	52.714	73.925	-157.478	-157.478	-37.800
16000	14.547	52.102	52.102	74.830	-156.833	-156.833	-38.700
16200	14.496	51.480	51.480	75.735	-156.178	-156.178	-39.600
16400	14.445	50.848	50.848	76.640	-155.513	-155.513	-40.500
16600	14.394	50.206	50.206	77.545	-154.838	-154.838	-41.400
16800	14.343	49.554	49.554	78.450	-154.153	-154.153	-42.300
17000	14.292	48.892	48.892	79.355	-153.458	-153.458	-43.200
17200	14.241	48.220	48.220	80.260	-152.753	-152.753	-44.100
17400	14.189	47.538	47.538	81.165	-152.038	-152.038	-45.000
17600	14.138	46.846	46.846	82.070	-151.313	-151.313	-45.900
17800	14.086	46.144	46.144	82.975	-150.578	-150.578	-46.800
18000	14.035	45.432	45.432	83.880	-149.833	-149.833	-47.700
18200	13.983	44.700	44.700	84.785	-149.078	-149.078	-48.600
18400	13.931	43.958	43.958	85.690	-148.313	-148.313	-49.500
18600	13.879	43.206	43.206	86.595	-147.538	-147.538	-50.400
18800	13.827	42.444	42.444	87.500	-146.753	-146.753	-51.300
19000	13.775	41.672	41.672	88.405	-145.958	-145.958	-52.200
19200	13.723	40.890	40.890	89.310	-145.153	-145.153	-53.100
19400	13.671	40.098	40.098	90.215	-144.338	-144.338	-54.000
19600	13.619	39.296	39.296	91.120	-143.513	-143.513	-54.900
19800	13.567	38.484	38.484	92.025	-142.678	-142.678	-55.800
20000	13.515	37.662	37.662	92.930	-141.833	-141.833	-56.700
20200	13.463	36.830	36.830	93.835	-140.978	-140.978	-57.600
20400	13.411	35.988	35.988	94.740	-140.113	-140.113	-58.500
20600	13.359	35.136	35.136	95.645	-139.238	-139.238	-59.400
20800	13.307	34.274	34.274	96.550	-138.353	-138.353	-60.300
21000	13.255	33.402	33.402	97.455	-137.458	-137.458	-61.200
21200	13.203	32.520	32.520	98.360	-136.553	-136.553	-62.100
21400	13.151	31.628	31.628	99.265	-135.638	-135.638	-63.000
21600	13.099	30.726	30.726	100.170	-134.713	-134.713	-63.900
21800	13.047	29.814	29.814	101.075	-133.778	-133.778	-64.800
22000	12.995	28.892	28.892	101.980	-132.833	-132.833	-65.700
22200	12.943	27.960	27.960	102.885	-131.878	-131.878	-66.600
22400	12.891	27.018	27.018	103.790	-130.913	-130.913	-67.500
22600	12.839	26.066	26.066	104.695	-129.938	-129.938	-68.400
22800	12.787	25.104	25.104	105.600	-128.953	-128.953	-69.300
23000	12.735	24.132	24.132	106.505	-127.958	-127.958	-70.200
23200	12.683	23.150	23.150	107.410	-126.953	-126.953	-71.100
23400	12.631	22.158	22.158	108.315	-125.938	-125.938	-72.000
23600	12.579	21.156	21.156	109.220	-124.913	-124.913	-72.900
23800	12.527	20.144	20.144	110.125	-123.878	-123.878	-73.800
24000	12.475	19.122	19.122	111.030	-122.833	-122.833	-74.700
24200	12.423	18.090	18.090	111.935	-121.778	-121.778	-75.600
24400	12.371	17.048	17.048	112.840	-120.713	-120.713	-76.500
24600	12.319	16.006	16.006	113.745	-119.638	-119.638	-77.400
24800	12.267	14.954	14.954</				

Point Group C_{2v}
S°_{298.15} = [64.31] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1
ΔH°_{f, 0} = [-257 ± 5] kcal. mole⁻¹
ΔH°_{f, 298.15} = [-259 ± 5] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[3680](1)	[888](1)
[1463](1)	[698](1)
[1420](1)	[480](1)
[1250](1)	[480](1)

Bond Distance: B-F = [1.30] Å B-O = [1.36] Å O-H = [0.96] Å
Bond Angle: F-B-F = [120]° F-B-O = [120]° B-O-H = [105]°
Product of the Moments of Inertia: I_AI_BI_C = [1.05094 X 10⁻¹¹⁴] g.³ cm.⁶
σ⁻ = 1

Heat of Formation.

The value of heat of formation (ΔH°_{f, 298.15}) was calculated based on an assumption that ΔH°_{f, 298.15} = 0 for the reaction 2/3 BF₃(g) + 1/3 B(OH)₃(g) = BOHF₂(g).

Heat Capacity and Entropy.

The vibrational frequencies were obtained from J. S. Gordon, Astrosystems International, Inc., private communication, November 2, 1962. The B-F and O-H bond distances were assumed to be the same as those in BF₃(g) and H₂O(g) molecules, respectively. The B-O bond distance and the bond angles were estimated from related molecules. The three principal moments of inertia are: I_A = 7.6114 X 10⁻³⁹, I_B = 8.3333 X 10⁻³⁹ and I_C = 1.61447 X 10⁻³⁸ g. cm.²

Boron Oxide Difluoride (BOF₂)

(Ideal Gas) GFW = 64.8072

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	9.114	53.574	173.172	2.757	-199.317	-199.317	INFINITE
200	9.843	59.653	65.017	1.960	-199.568	-199.568	434.430
298	11.498	63.969	63.969	0	-199.809	-199.809	216.246
300	12.036	64.063	63.989	-0.022	-200.003	-196.910	144.339
400	13.900	67.792	64.485	1.323	-200.150	-195.830	143.435
500	15.307	71.053	65.479	2.787	-200.272	-194.737	106.997
600	16.330	73.030	66.453	4.371	-200.372	-193.619	85.119
700	17.018	74.115	67.115	5.664	-200.452	-192.486	70.526
800	17.618	74.632	67.632	6.908	-200.510	-191.338	60.686
900	18.026	75.032	70.307	9.563	-200.555	-190.182	52.273
1000	18.337	75.448	71.467	11.381	-200.660	-189.032	46.185
1100	18.577	75.808	72.582	13.288	-200.729	-187.886	41.313
1200	18.767	76.123	73.752	15.262	-200.769	-186.748	37.326
1300	18.919	76.414	74.679	17.293	-200.782	-185.615	34.188
1400	19.042	76.683	75.663	19.448	-200.770	-184.489	31.775
1500	19.143	76.905	76.607	20.787	-200.739	-183.368	29.663
1600	19.227	77.073	77.512	22.706	-200.686	-182.252	27.797
1700	19.298	77.198	78.388	24.582	-200.614	-181.148	26.152
1800	19.358	77.276	79.217	26.595	-200.523	-179.951	24.652
1900	19.409	77.305	80.022	28.500	-200.419	-178.666	23.297
2000	19.453	77.280	80.797	30.347	-200.302	-177.297	22.050
2100	19.492	77.201	81.545	32.384	-200.172	-175.837	20.899
2200	19.527	77.067	82.264	34.643	-200.028	-174.284	19.800
2300	19.557	76.878	82.964	37.259	-199.870	-172.643	18.741
2400	19.585	76.639	83.640	40.216	-199.698	-170.914	17.710
2500	19.611	76.360	84.293	43.519	-199.512	-169.100	16.710
2600	19.635	76.049	84.927	47.179	-199.312	-167.212	15.741
2700	19.658	75.706	85.542	51.200	-199.098	-165.258	14.824
2800	19.680	75.333	86.138	55.597	-198.870	-163.238	13.974
2900	19.701	74.937	86.718	60.374	-198.628	-161.152	13.174
3000	19.723	74.515	87.282	65.550	-198.373	-159.000	12.412
3100	19.744	74.068	87.831	71.129	-198.105	-156.782	11.688
3200	19.766	73.598	88.365	77.199	-197.825	-154.500	11.007
3300	19.788	73.106	88.886	83.762	-197.532	-152.157	10.377
3400	19.810	72.594	89.393	90.817	-197.226	-149.752	9.795
3500	19.834	72.061	89.888	98.374	-196.908	-147.284	9.250
3600	19.858	71.507	90.372	106.440	-196.578	-144.752	8.746
3700	19.882	70.934	90.842	115.016	-196.232	-142.157	8.274
3800	19.908	70.344	91.306	124.100	-195.871	-139.500	7.834
3900	19.935	69.739	91.757	133.699	-195.495	-136.782	7.424
4000	19.962	69.119	92.199	143.817	-195.105	-134.000	7.037
4100	19.990	68.486	92.631	154.454	-194.700	-131.157	6.674
4200	20.019	67.840	93.046	165.710	-194.280	-128.252	6.334
4300	20.049	67.178	93.446	177.586	-193.845	-125.284	6.017
4400	20.079	66.500	93.835	189.990	-193.395	-122.252	5.724
4500	20.110	65.806	94.213	202.924	-192.930	-119.157	5.454
4600	20.142	65.096	94.586	216.390	-192.450	-116.000	5.207
4700	20.174	64.374	94.946	230.396	-191.955	-112.782	4.984
4800	20.206	63.644	95.294	244.940	-191.445	-109.500	4.784
4900	20.239	62.900	95.624	260.024	-190.920	-106.157	4.604
5000	20.273	62.146	95.939	275.648	-190.380	-102.752	4.444
5100	20.306	61.386	96.244	291.812	-189.825	-99.284	4.304
5200	20.340	60.616	96.544	308.516	-189.255	-95.752	4.184
5300	20.374	59.836	96.834	325.760	-188.670	-92.157	4.084
5400	20.407	59.046	97.114	343.544	-188.070	-88.500	4.004
5500	20.441	58.246	97.384	361.868	-187.455	-84.782	3.944
5600	20.475	57.436	97.644	380.732	-186.825	-81.000	3.894
5700	20.508	56.616	97.894	399.146	-186.180	-77.157	3.854
5800	20.541	55.786	98.134	418.110	-185.520	-73.252	3.824
5900	20.574	54.946	98.364	437.624	-184.845	-69.284	3.794
6000	20.606	54.096	98.584	457.688	-184.155	-65.252	3.774

Dec. 31, 1965; Dec. 31, 1966

BORON OXIDE DIFLUORIDE (BOF₂)

(IDEAL GAS)

GFW = 64.8072

Point Group C_{2v}

S_{298,15}° = [64] gibbs/mol

ΔH_f⁰ = [-199 ± 15] kcal/mol

ΔH_f⁰_{298,15} = [-200 ± 15] kcal/mol

Electronic Levels and Quantum Weights

$\frac{e, \text{ cm}^{-1}}{0}$	$\frac{g_i}{[2]}$
17171	[2]
22390	[2]

Vibrational Frequencies and Degeneracies

$\frac{w, \text{ cm}^{-1}}{1377 (1)}$	$\frac{w, \text{ cm}^{-1}}{(850) (1)}$
856 (1)	[1100] (1)
491 (1)	[500] (1)

Bond Distance : B-F = 1.30 ± 0.05 Å

Bond Angle : F-B-O = 117 ± 5°

Product of the Moments of Inertia: $I_A I_B I_C = 9.9464 \times 10^{-115} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The molecule BF₂O(g) is similar to BO₂(g) in that both have an extra electron. Based on an assumption that D₀(P₂B-O) = D₀(OB-O) = 10 = 134.3 kcal/mol, where the quantity -10 kcal/mol is estimated as the resonance stabilization energy in BO₂(g), the heat of formation (ΔH_f⁰_{298,15}) for BF₂O(g) is calculated to be -206 kcal/mol.

Assuming D₀(P₂BO-H) = D₀(HO-H) = 118 kcal/mol, the value of ΔH_f⁰_{298,15}(P₂BO,g) is evaluated as -131.6 kcal/mol, using ΔH_f⁰ = 51.63 and -257.35 kcal/mol for H(g) and P₂BOH(g), respectively.

The value of ΔH_f⁰_{298,15} for BOF₂(g) is tentatively adopted as -200 ± 15 kcal/mol.

Heat Capacity and Entropy

The 4465-Å emission spectrum was observed in a discharge through BF₃ and O₂ by C. W. Mathews, J. Mol. Spectry, **19**, 203 (1966). The emitter of the discharge was shown to be either the planar BOF₂ molecule or molecule-ion BOF₂⁺. No experimental evidence has been found to distinguish between them. The molecular structure, bond distances and angles were reported by Mathews, based on a rotational analysis of the emission spectrum. These values are adopted here.

Three vibrational frequencies for both 11P₁BO₂ and 10P₁BO₂ molecules (or ions) were determined by vibrational analysis of the 5800 - Å bands of the emission spectrum by C. W. Mathews and K. K. Innes, J. Mol. Spectry, **15**, 199 (1965). These values are corrected to the average isotopic species and adopted. The last three frequencies are estimated from values calculated by the valence-force method, using force constants transferred from COF₂(g).

The ground state quantum weight is taken as 2 because of the extra electron. The other two electronic levels are estimated from the band systems at 5800 and 4465 Å, assuming that the two systems have a common lower state, i.e. the ground state.

The three principal moments of inertia are: I_A = 8.4647 × 10⁻³⁹, I_B = 7.4045 × 10⁻³⁹ and I_C = 1.5869 × 10⁻³⁸ g cm².

Boron Trifluoride (BF₃) (Ideal Gas) GFW = 67.8062

Point Group D_{3h}
S_{298.15} = 60.77 ± 0.01 gibbs/mol
Ground State Quantum Weight = 1
ΔH_{f,0}^o = -270.7 ± 0.4 kcal/mol
ΔH_{f,298.15}^o = -271.42 ± 0.4 kcal/mol

T, °K	C _p ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	8.147	50.215	70.075	-270.747	-270.747	-270.747	INFINITE
200	10.030	56.372	61.006	-270.998	-269.907	-269.907	589.680
298	12.057	60.766	54.766	-271.420	-269.722	-269.722	593.646
300	12.092	60.841	54.766	-271.424	-269.722	-269.722	593.646
400	13.753	64.556	51.262	-271.605	-266.068	-266.068	194.621
500	15.044	67.770	48.249	-271.786	-264.664	-264.664	115.684
600	16.300	70.405	45.410	-271.953	-263.223	-263.223	85.879
700	17.374	72.734	43.022	-272.103	-261.755	-261.755	61.923
800	18.244	74.813	40.934	-272.240	-260.269	-260.269	41.102
900	18.979	76.683	39.112	-272.363	-258.765	-258.765	22.637
1000	19.587	78.374	37.595	-272.480	-257.247	-257.247	56.221
1100	19.983	81.116	36.255	-272.586	-255.719	-255.719	50.807
1200	20.299	82.723	35.031	-272.672	-254.178	-254.178	46.202
1300	20.566	84.218	33.904	-272.742	-252.629	-252.629	42.471
1400	20.795	85.614	32.866	-272.800	-251.070	-251.070	39.194
1500	20.991	86.922	31.900	-272.846	-249.502	-249.502	36.352
1600	21.157	88.153	31.000	-272.882	-247.926	-247.926	33.845
1700	21.299	89.315	30.166	-272.909	-246.339	-246.339	31.649
1800	21.420	90.414	29.390	-272.926	-244.748	-244.748	29.716
1900	21.522	91.457	28.666	-272.936	-243.144	-243.144	27.968
2000	21.608	92.450	27.990	-272.940	-241.530	-241.530	26.393
2100	21.678	93.396	27.366	-272.940	-239.912	-239.912	24.968
2200	21.734	94.301	26.792	-272.936	-238.286	-238.286	23.671
2300	21.778	95.167	26.266	-272.926	-236.646	-236.646	22.487
2400	21.811	95.997	25.790	-272.912	-235.002	-235.002	21.400
2500	21.835	96.790	25.366	-272.896	-233.352	-233.352	20.390
2600	21.850	97.547	24.990	-272.878	-231.692	-231.692	19.448
2700	21.857	98.267	24.666	-272.856	-229.926	-229.926	18.578
2800	21.856	98.944	24.386	-272.830	-228.156	-228.156	17.767
2900	21.847	99.573	24.150	-272.800	-226.376	-226.376	17.007
3000	21.831	100.156	23.956	-272.766	-224.586	-224.586	16.302
3100	21.808	100.694	23.800	-272.728	-222.778	-222.778	15.641
3200	21.778	101.193	23.686	-272.686	-220.952	-220.952	15.021
3300	21.742	101.656	23.610	-272.640	-219.110	-219.110	14.436
3400	21.699	102.083	23.570	-272.590	-217.256	-217.256	13.889
3500	21.650	102.483	23.560	-272.536	-215.386	-215.386	13.371
3600	21.596	102.856	23.580	-272.470	-213.500	-213.500	12.882
3700	21.537	103.197	23.630	-272.400	-211.600	-211.600	12.412
3800	21.474	103.507	23.700	-272.326	-209.686	-209.686	11.979
3900	21.406	103.786	23.790	-272.250	-207.756	-207.756	11.562
4000	21.334	104.036	23.900	-272.170	-205.800	-205.800	11.168
4100	21.258	104.253	24.030	-272.086	-203.826	-203.826	10.810
4200	21.178	104.436	24.180	-272.000	-201.836	-201.836	10.479
4300	21.094	104.586	24.340	-271.910	-199.830	-199.830	10.170
4400	21.006	104.706	24.510	-271.816	-197.806	-197.806	9.882
4500	20.914	104.796	24.690	-271.718	-195.766	-195.766	9.616
4600	20.818	104.856	24.880	-271.616	-193.710	-193.710	9.374
4700	20.719	104.886	25.080	-271.510	-191.636	-191.636	9.156
4800	20.617	104.886	25.290	-271.400	-189.546	-189.546	8.962
4900	20.512	104.856	25.510	-271.286	-187.440	-187.440	8.792
5000	20.404	104.796	25.740	-271.166	-185.316	-185.316	8.646
5100	20.293	104.636	25.980	-271.040	-183.176	-183.176	8.522
5200	20.179	104.386	26.230	-270.910	-181.020	-181.020	8.418
5300	20.062	104.156	26.490	-270.776	-178.846	-178.846	8.334
5400	19.942	103.946	26.760	-270.636	-176.656	-176.656	8.268
5500	19.818	103.766	27.040	-270.490	-174.446	-174.446	8.222
5600	19.691	103.616	27.330	-270.340	-172.216	-172.216	8.196
5700	19.561	103.486	27.630	-270.186	-169.976	-169.976	8.188
5800	19.428	103.376	27.940	-270.126	-167.726	-167.726	8.196
5900	19.292	103.286	28.260	-270.060	-165.466	-165.466	8.222
6000	19.154	103.216	28.590	-270.000	-163.196	-163.196	8.268

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1964; Sept. 30, 1965; June 30, 1969

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
888 (1)
696.7 (1)
1463.3 (2)
480.7 (2)

Bond Distance: B-F = 1.307 ± 0.002 Å
Bond Angle: F-B-F = 120°
Products of the Moments of Inertia: I_AI_BI_C = 1.0563 × 10⁻¹¹⁴ g³ cm⁶ σ = 6

Heat of Formation

The adopted heat of formation was selected by a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, g table 12-31-60). The data which were considered relating directly to BF₃ were as follows.
A. NF₃(g) + B(C, β) + BF₃(g) + 0.5 N₂ ΔH_{f,298}^o = -231.46 ± 1.2 kcal/mol
Ludwig and Cooper (1) report the above value after correction for 0.44 percent impurities in the boron. As much as 5 percent unburned boron was determined by analysis.

B. 1.5 F₂(g) + B(C, β) + BF₃(g)

Wise et al. (2) originally reported ΔH_{f,298}^o = -270.1 ± 0.24 kcal/mol but later reanalysis (3) of the impurities and due allowance for their effect changed this to -271.6 ± 0.9 kcal/mol. Johnson et al. (3) using zone refined boron obtained ΔH_{f,298}^o = -271.65 ± 0.22 kcal/mol after correction for 0.12 percent impurities. Domalski and Armstrong (4) obtained ΔH_{f,298}^o = -271.03 ± 0.51 kcal/mol from a combustion in the presence of Teflon, the boron contained 0.32 percent impurities and corrections were included. The above reaction constituted about 0.35 of the total energy measured. The measurements of Gross et al. (5), although on a zone refined sample, did not include a complete purity analysis and their data were not included since probable impurities could introduce serious errors.

C. 3HF(50 H₂O) + B(C, β) + 0.75 O₂(g) + BF₃(g) + 1.5 H₂O(l)

From the measurements of Gunn (6) on the reaction of BF₃(g) + 15.67 HF(3.747 H₂O) + [solution] and Good and Månsson (7) for the reaction B(C, β) + 0.75 O₂(g) + 18.57 HF(3.065 H₂O) + [solution] + 1.5 H₂O(l), where the resulting solutions have the same composition, we obtain ΔH_{f,298}^o = -142.77 ± 0.5 kcal/mol. Further details of the simultaneous solution are given by Syverud (8).

Heat Capacity and Entropy

The fundamental frequencies were selected from the measurements of Lindeman and Wilson (9), McKean (10), Nielsen (11), Anderson et al. (12) and Yost et al. (13). The bond lengths and structure are those reported by Gin et al. (14) which are in agreement with those of Kuchitsu and Konaka (15) from gas phase electron diffraction. These measurements disagree with the earlier determinations of Nielsen (11) and Levy and Brockway (16) but are considerably more precise and are adopted.
The individual moments of inertia are I_A = I_B = 8.083 × 10⁻³⁹ g cm² and I_C = 16.166 × 10⁻³⁹ g cm².

References

1. J. R. Ludvig and W. J. Cooper, J. Chem. Eng. Data **8**, 76 (1963).
2. S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. **65**, 2157 (1961).
3. G. K. Johnson, H. M. Feder and W. N. Hubbard, J. Phys. Chem. **70**, 1 (1966).
4. E. S. Domalski and G. T. Armstrong, J. Res. Natl. Bur. Std. **71A**, 195 (1967).
5. P. Gross, C. Hayman, D. L. Levi and M. C. Stuart, Fulmer Research Institute Report R.146/4/23 Nov. 1960.
6. S. R. Gunn, J. Phys. Chem. **69**, 1010 (1965).
7. W. D. Good and M. Månsson, J. Phys. Chem. **70**, 97 (1966).
8. A. N. Syverud, AFPL-TR-65-70, January 1969.
9. L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).
10. D. C. McKean, J. Chem. Phys. **24**, 1002 (1956).
11. A. H. Nielsen, J. Chem. Phys. **22**, 659 (1954).
12. T. F. Anderson, E. N. Lasette and D. M. Yost, J. Chem. Phys. **4**, 703 (1936).
13. D. M. Yost, D. DeVault, T. F. Anderson, and E. N. Lasette, J. Chem. Phys. **5**, 424 (1938).
14. S. G. W. Gln, J. K. Kanney and J. Overend, J. Chem. Phys. **45**, 4342 (1966).
15. K. Kuchitsu and S. Konaka, J. Chem. Phys. **45**, 1571 (1966).
16. H. Levy and L. O. Brockway, J. Amer. Chem. Soc. **59**, 2085 (1937).

GFW = 125.907

(CRYSTAL)

POTASSIUM TETRAFLUOROBORATE (KBF₄)

Potassium Tetrafluoroborate (KBF₄) (Crystal)

GFW = 125.907

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	27.362	32.000	32.000	.000	-451.000	-426.625	312.774
300	27.433	32.170	32.001	.051	-450.995	-426.474	310.696
400	31.266	40.565	33.122	2.985	-451.937	-414.237	226.514
500	35.125	47.977	35.367	6.305	-450.687	-410.047	179.231
600	37.962	53.430	38.469	13.176	-446.681	-402.250	146.519
700	35.019	45.748	41.994	16.626	-444.165	-394.884	123.248
800	36.075	40.490	42.245	20.180	-445.600	-387.599	105.897
900	37.131	34.800	46.310	23.841	-444.969	-380.385	92.370
1000	38.188	28.767	51.160	27.606	-444.280	-373.246	81.573
1100	39.244	22.456	53.840	31.476	-462.433	-365.155	72.550
1200	40.301	15.916	56.370	35.455	-461.366	-356.356	64.901
1300	41.357	9.183	58.769	39.538	-460.220	-347.652	58.446
1400	42.413	2.287	61.054	43.727	-458.989	-339.037	52.926
1500	43.470	95.249	63.235	48.021	-457.675	-330.514	48.156

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

ΔHf° = Unknown

ΔHf°_{298.15} = -451.0 ± 1 kcal/mol

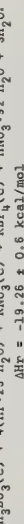
ΔHt° = 3.36 ± 0.04 kcal/mol

ΔHm° = 4.22 ± 0.04 kcal/mol

ΔHs°_{298.15} = [80] kcal/mol

Heat of Formation

Bills and Cotton (1) measured the enthalpies of several reactions at 25°C which led to the following result:



$$\Delta H_r = -19.26 \pm 0.6 \text{ kcal/mol}$$

Combining this result with the following heat of formation data,

$$\Delta H_f^\circ(\text{H}_2\text{BO}_3, \text{c}) = -261.47 \pm 0.2 \text{ kcal/mol (2)}$$

$$\Delta H_f^\circ(\text{HF} \cdot 23 \text{H}_2\text{O}) = -76.75 \pm 0.1 \text{ kcal/mol (3)}$$

$$\Delta H_f^\circ(\text{KNO}_3, \text{c}) = -118.22 \text{ kcal/mol (4)}$$

$$\Delta H_f^\circ(\text{HNO}_3 \cdot 92 \text{H}_2\text{O}) = -49.44 \text{ kcal/mol (5)}$$

$$\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) = -68.315 \text{ kcal/mol (5)}$$

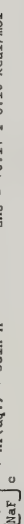
$$\Delta H_f^\circ(\text{KBF}_4, \text{c}) = -451.6 \pm 1.2 \text{ kcal/mol}$$

We derive, ΔHf°(KBF₄, c) = -451.6 ± 1.2 kcal/mol.

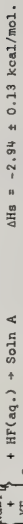
Gross, Hayman, and Joël (6) recently measured the following heats of reaction:



$$\Delta H_r = -32.04 \pm 0.12 \text{ kcal/mol}$$



$$\Delta H_s = +8.14 \pm 0.18 \text{ kcal/mol}$$



$$\Delta H_s = -2.34 \pm 0.13 \text{ kcal/mol.}$$

These data combine to give, ΔHr = -43.13 ± 0.22 kcal/mol, for the reaction



Combining this result with the following heats of formation,

$$\Delta H_f^\circ(\text{KF}, \text{c}) = -135.9 \pm 0.1 \text{ kcal/mol (7)}$$

$$\Delta H_f^\circ(\text{BF}_3, \text{g}) = -271.42 \pm 0.4 \text{ kcal/mol (7)}$$

We derive, ΔHf°(KBF₄, c) = -450.5 ± 0.7 kcal/mol. An average value, ΔHf°(KBF₄, c) = -451.0 ± 1 kcal/mol, of these two results is adopted here.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig (8). S°₂₉₈ is chosen such that a third-law analysis of the equilibrium data for the reaction



reported by de Boer and van Liempt (9) gives the experimentally determined heat of reaction at 25°C (6).

Transition Data

It is from the high temperature studies of Dworkin and Bredig (8). ΔHt° is calculated from their high temperature enthalpy data.

Melting Data

Tm has been reported as 803°K by de Boer and van Liempt (9) and 843°K by Dworkin and Bredig (8). Dworkin and Bredig's value is adopted here. ΔHm° is calculated from their high temperature enthalpy data.

Sublimation Data

ΔHs°₂₉₈ is estimated by comparison with data for LiAlF₄(c) reported by Hildenbrand and Theard (10).

References

1. J. L. Bills and F. A. Cotton, *J. Phys. Chem.*, **64**, 1477 (1960).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Dec. 31, 1964.
3. *Ref.* 2, Dec. 31, 1968 and *Ref.* 4.
4. *Ref.* 2, Dec. 31, 1968 and *Ref.* 4.
5. U. S. Natl. Bur. Std. NBS-NBS2, 1965 and *Ref.* 5.
6. P. Gross, C. Hayman, and H. A. Joël, *Trans. Faraday Soc.*, **64**, 317 (1968).
7. *Ref.* 2, June 30, 1969.
8. A. S. Dworkin and H. A. Bredig, private communication, Oak Ridge Natl. Lab., Sept. 23, 1969.
9. J. H. de Boer and J. A. M. van Liempt, *Rec. Trav. Chim.*, **146**, 124 (1927).
10. D. L. Hildenbrand and L. F. Theard, *Aeronautics*, Division of Ford Motor Company, Publication No. U-2174, June 15, 1961.

Potassium Tetrafluoroborate (KBF₄)

(Liquid) GFW = 125.907

 $\Delta H_f^\circ = \text{Unknown}$ $S_{298.15}^\circ = 35.88 \pm 4.0 \text{ gibbs/mol}$ $\Delta H_f^\circ = -446.8 \pm 1.5 \text{ kcal/mol}$ $\Delta H_m^\circ = 4.22 \pm 0.04 \text{ kcal/mol}$ $T_m = 843^\circ\text{K}$

Heat of Formation

 $\Delta H_f^\circ(l)$ is calculated from $\Delta H_f^\circ(c)$ by adding the heat of melting and the difference in $H_{843}-H_{298}$ between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig (1). S_{298}° is calculated in a manner analogous to the heat of formation.

Melting Data

 T_m has been reported as 803°K by de Boer and van Liempt (2) and 843°K by Dworkin and Bredig (1). Dworkin and Bredig's value is adopted here. ΔH_m° is calculated from their high temperature enthalpy data.

References

1. A. S. Dworkin and M. A. Bredig, private communication, Oak Ridge Natl. Lab., Sept. 23, 1969.
2. J. H. de Boer and J. A. M. van Liempt, Rec. Trav. Chim., 46, 124 (1927).

T, °K	Cp°	— S° —	— -(G°-H° ₂₉₈)/T —	H°-H° ₂₉₈	— ΔH° —	ΔG°	Log Kp
0							
100							
200							
298	39.942	35.882		.000	-446.801	-423.584	310.495
300	39.942	36.129		.074	-446.773	-423.440	309.476
400	39.942	47.520		4.068	-445.955	-415.768	277.165
500	39.942	58.532		8.062	-444.731	-406.369	176.496
600	39.942	63.815	43.720	12.056	-443.602	-401.202	166.136
700	39.942	69.972	47.042	16.051	-442.542	-394.219	123.041
800	39.942	75.305	50.249	20.095	-441.536	-387.369	105.659
843	39.942	78.016	53.300	24.098	-440.584	-380.481	92.751
1000	39.942	84.218	56.105	28.033	-439.654	-374.072	81.753
1100	39.942	88.025	58.909	32.027	-437.685	-366.533	72.623
1200	39.942	91.508	61.482	36.022	-435.601	-358.292	65.254
1300	39.942	94.697	63.916	40.016	-433.543	-350.144	58.684
1400	39.942	97.637	66.222	44.010	-431.507	-342.078	53.400
1500	39.942	100.413	68.410	48.004	-429.493	-334.075	48.675

Dec. 31, 1969

GFW = 125.907

(IDEAL GAS)

POTASSIUM TETRAFLUOROBORATE (KBF₄)Potassium Tetrafluoroborate (KBF₄)

(Ideal Gas)

GFW = 125.907

 $\Delta H_f^\circ = [-369.0 \pm 5] \text{ kcal/mol}$ $\Delta H_f^\circ = [-371.0 \pm 5] \text{ kcal/mol}$ Point Group [C_{3v}]

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies	
ω, cm^{-1}	ω, cm^{-1}
[900] (1) [1000] (1) [300] (2)	
[450] (1) [300] (1) [500] (2)	
[350] (1) [250] (1) [1400] (2)	

Bond Distance: B-F = 1.380 Å K-F = 2.752 Å B-K = [2.863] Å

Bond Angle: F-B-F = 109°28' F_{ax}-B-K = [180°]

Product of Moments of Inertia: $I_{AB} I_C = [4.549 \times 10^{-113}] \text{ g cm}^6$

 $\sigma = [3]$

Heat of Formation

 $\Delta H_f^\circ(\text{g})$ is calculated from $\Delta H_f^\circ(\text{c})$ and the estimated heat of sublimation.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with data for BF₄⁻, BF₃, KF, and K₂F₂. The infrared and Raman spectra of BF₄⁻ in various phases have been reported by Porter and Zeller (5). The B-F and K-F bond lengths and F-B-F bond angle are the same as for LiAlF₄ as discussed by Porter and Zeller (5). The B-F and K-F bond lengths and F-B-F bond angle are average values of the crystallographic data recently reported by Clark and Lynton (6). The B-K bond length is calculated from the above structural data according to the assumed molecular model. The individual moments of inertia are $I_A = I_B = 5.292 \times 10^{-38} \text{ g cm}^2$ and $I_C = 1.617 \times 10^{-38} \text{ g cm}^2$.

References

1. G. L. Coté and H. W. Thompson, Proc. Royal Soc. (London), **210A**, 217 (1951).
2. J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, J. Amer. Chem. Soc., **77**, 268 (1955).
3. J. Leconte, C. Duval, and C. Wadier, Compt. Rend., **243**, 1991 (1959).
4. J. A. Ketelaar and R. L. Fulton, Z. Elektrochem., **64**, 641 (1960).
5. R. F. Porter and E. E. Zeller, J. Chem. Phys., **33**, 858 (1960).
6. M. J. R. Clark and H. Lynton, Can. J. Chem., **47**, 2579 (1969).

T, °K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	10.833	57.949	INFINITE	4.206	-369.001	-369.001	INFINITE
100	17.379	67.628	77.182	3.345	-369.950	-369.950	801.525
200	21.257	75.350	77.182	1.911	-370.616	-363.249	396.940
298	23.115	79.581	75.350	0.39	-371.007	-359.479	261.860
300	23.122	79.581	75.350	0.39	-371.007	-359.479	261.860
400	23.922	81.993	74.220	2.309	-371.913	-355.476	194.223
500	25.768	87.541	77.943	4.799	-372.193	-351.335	153.568
600	27.097	92.363	79.954	7.466	-372.411	-347.151	126.046
700	28.047	96.134	82.036	10.266	-372.555	-342.914	101.045
800	28.780	99.113	84.100	13.050	-372.730	-338.668	80.520
900	29.318	103.436	86.106	15.956	-372.934	-334.402	61.204
1000	29.730	106.947	88.037	18.910	-372.976	-330.123	43.773
1100	30.050	109.796	89.887	21.899	-372.912	-324.808	28.533
1200	30.307	112.052	91.589	24.918	-372.752	-318.452	15.554
1300	30.507	114.052	93.189	27.958	-372.517	-311.061	7.499
1400	30.672	115.823	94.667	31.018	-372.113	-302.646	3.232
1500	30.808	117.294	96.116	34.092	-371.564	-300.435	0.958
1600	30.921	118.516	97.509	37.178	-370.888	-298.360	0.406
1700	31.017	119.516	98.788	40.266	-370.000	-296.430	0.171
1800	31.097	120.389	100.000	43.351	-368.913	-294.629	0.081
1900	31.166	121.172	102.101	46.434	-367.538	-292.955	0.042
2000	31.225	122.000	103.965	49.511	-365.888	-291.411	0.024
2100	31.276	122.887	105.583	52.579	-363.975	-289.989	0.015
2200	31.321	123.823	107.000	55.643	-361.813	-288.686	0.008
2300	31.360	124.806	108.250	58.700	-359.413	-287.499	0.004
2400	31.395	125.831	109.350	61.750	-356.788	-286.426	0.002
2500	31.425	126.900	110.311	64.792	-353.950	-285.466	0.001
2600	31.453	128.017	111.136	67.826	-350.900	-284.613	0.000
2700	31.477	129.186	111.836	70.852	-347.643	-283.866	0.000
2800	31.499	130.412	112.412	73.871	-344.188	-283.223	0.000
2900	31.519	131.695	112.882	76.877	-340.543	-282.686	0.000
3000	31.536	133.036	113.255	79.869	-336.713	-282.253	0.000
3100	31.553	134.438	113.536	82.847	-332.700	-281.923	0.000
3200	31.567	135.898	113.723	85.806	-328.513	-281.686	0.000
3300	31.581	137.423	113.823	88.747	-324.158	-281.536	0.000
3400	31.593	139.012	113.836	91.669	-319.643	-281.466	0.000
3500	31.604	140.665	113.761	94.577	-314.875	-281.466	0.000
3600	31.614	142.386	113.600	97.471	-309.863	-281.536	0.000
3700	31.624	144.171	113.353	100.350	-304.613	-281.686	0.000
3800	31.633	146.012	113.026	103.213	-299.136	-281.923	0.000
3900	31.641	147.906	112.619	106.063	-293.450	-282.253	0.000
4000	31.648	149.853	121.137	108.900	-287.463	-282.686	0.000
4100	31.655	151.855	122.536	111.723	-281.175	-283.223	0.000
4200	31.662	153.912	123.863	114.536	-274.588	-283.866	0.000
4300	31.668	156.023	125.123	117.336	-267.713	-284.613	0.000
4400	31.674	158.186	126.336	120.123	-260.543	-285.466	0.000
4500	31.679	160.406	127.400	122.882	-253.088	-286.426	0.000
4600	31.684	162.681	128.423	125.613	-245.350	-287.499	0.000
4700	31.688	165.012	129.400	128.350	-237.336	-288.686	0.000
4800	31.693	167.396	130.336	131.086	-229.043	-290.000	0.000
4900	31.697	169.831	131.236	133.823	-220.488	-291.411	0.000
5000	31.701	172.316	132.100	136.563	-211.666	-292.955	0.000
5100	31.704	174.851	132.936	139.300	-202.588	-294.629	0.000
5200	31.708	177.436	133.736	142.036	-193.250	-296.430	0.000
5300	31.711	180.066	134.500	144.771	-183.666	-298.360	0.000
5400	31.714	182.741	135.236	147.500	-173.836	-300.435	0.000
5500	31.717	185.466	135.936	150.213	-163.750	-302.646	0.000
5600	31.720	188.236	136.600	152.900	-153.413	-304.989	0.000
5700	31.722	191.061	137.236	155.563	-142.826	-307.466	0.000
5800	31.725	193.936	137.836	158.196	-131.988	-310.088	0.000
5900	31.727	196.861	138.400	160.800	-120.900	-312.866	0.000
6000	31.729	199.836	138.936	163.363	-109.563	-315.800	0.000

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	Log K _p
0	0.000	INFINITE	- 2.065	105.039	INFINITE
100	6.962	33.438	1.360	105.039	225.580
200	6.966	38.265	1.685	105.039	110.329
298	6.975	41.047	2.065	105.039	72.296
300	6.975	41.047	2.065	105.039	71.618
400	7.111	44.576	3.135	105.039	40.083
500	7.252	45.984	4.242	105.039	23.282
600	7.422	47.114	5.354	105.039	16.004
700	7.626	48.037	6.466	105.039	10.378
800	7.856	48.799	7.578	105.039	6.671
900	8.112	49.425	8.690	105.039	3.671
1000	8.394	49.925	9.802	105.039	1.792
1100	8.697	50.311	10.914	105.039	0.618
1200	8.993	51.518	12.026	105.039	- 0.583
1300	9.281	52.569	13.138	105.039	- 1.792
1400	9.561	53.486	14.250	105.039	- 2.992
1500	9.834	54.277	15.362	105.039	- 4.192
1600	10.101	54.951	16.474	105.039	- 5.392
1700	10.362	55.518	17.586	105.039	- 6.592
1800	10.618	55.984	18.698	105.039	- 7.792
1900	10.869	56.351	19.810	105.039	- 8.992
2000	11.116	56.625	20.922	105.039	- 10.192
2100	11.359	56.806	22.034	105.039	- 11.392
2200	11.598	56.894	23.146	105.039	- 12.592
2300	11.834	56.894	24.258	105.039	- 13.792
2400	12.067	56.806	25.370	105.039	- 14.992
2500	12.297	56.625	26.482	105.039	- 16.192
2600	12.524	56.351	27.594	105.039	- 17.392
2700	12.748	55.984	28.706	105.039	- 18.592
2800	12.969	55.518	29.818	105.039	- 19.792
2900	13.187	54.951	30.930	105.039	- 20.992
3000	13.402	54.277	32.042	105.039	- 22.192
3100	13.614	53.501	33.154	105.039	- 23.392
3200	13.823	52.625	34.266	105.039	- 24.592
3300	14.030	51.649	35.378	105.039	- 25.792
3400	14.234	50.573	36.490	105.039	- 26.992
3500	14.436	49.425	37.602	105.039	- 28.192
3600	14.636	48.199	38.714	105.039	- 29.392
3700	14.833	46.894	39.826	105.039	- 30.592
3800	15.027	45.518	40.938	105.039	- 31.792
3900	15.218	44.073	42.050	105.039	- 32.992
4000	15.406	42.569	43.162	105.039	- 34.192
4100	15.591	41.014	44.274	105.039	- 35.392
4200	15.773	39.406	45.386	105.039	- 36.592
4300	15.952	37.749	46.498	105.039	- 37.792
4400	16.129	36.044	47.610	105.039	- 38.992
4500	16.303	34.290	48.722	105.039	- 40.192
4600	16.475	32.486	49.834	105.039	- 41.392
4700	16.645	30.631	50.946	105.039	- 42.592
4800	16.813	28.727	52.058	105.039	- 43.792
4900	16.979	26.773	53.170	105.039	- 44.992
5000	17.143	24.769	54.282	105.039	- 46.192
5100	17.305	22.714	55.394	105.039	- 47.392
5200	17.465	20.606	56.506	105.039	- 48.592
5300	17.623	18.449	57.618	105.039	- 49.792
5400	17.779	16.245	58.730	105.039	- 50.992
5500	17.933	13.992	59.842	105.039	- 52.192
5600	18.085	11.689	60.954	105.039	- 53.392
5700	18.235	9.336	62.066	105.039	- 54.592
5800	18.383	6.933	63.178	105.039	- 55.792
5900	18.529	4.480	64.290	105.039	- 56.992
6000	18.673	1.977	65.402	105.039	- 58.192

Dec. 31, 1960; Mar. 31, 1963; Dec. 31, 1964

Ground State Configuration $1\Sigma^+$

$S_{298.15}^0 = [41.047] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^0 = 105.0 \pm 2.0 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\omega_e = [2566] \text{ cm.}^{-1}$

$B_e = 12.056 \text{ cm.}^{-1}$

$\alpha_e = .415 \text{ cm.}^{-1}$

$\sigma = 1$

$r_e = 1.3325 \text{ \AA}$

Heat of Formation.

ΔH_f^0 298.15 was calculated from D_0 (BH) = 3.39 ± 0.04 e.v. reported by A. C. Hurley, Proc. Royal Soc. (London), A281, 237 (1961). Hurley stated "by combining an analysis of the spectroscopic data with theoretical calculations we obtain a greatly improved estimate of D_0 (BH)". This value and the other D_0 (BH) values which are tabulated below are based on the same spectroscopic data but differ due to different methods of analysis.

D_0 (BH)	Method	Reference
3.0 ± 0.4 e.v.	Birge-Sponer extrapolations	A. G. Gaydon "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1955.
3.5 e.v.	Observed predissociation by rotation in BH, $A''\Pi$ and deduced D_0 (BH).	G. M. Alay and R. B. Horsfall Jr., Phys. Rev., 51, 491 (1957).
< 3.51 e.v.	Pre-dissociation limit. This is only an upper limit due to a maximum in the potential curve of the $A''\Pi$ state.	O. Herzberg and L. G. Mundle, J. Chem. Phys., 8, 265 (1940) and G. Herzberg "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950.
3.38 ± 0.04 e.v.	The potential energy curve of the $A''\Pi$ state was determined and was found to have a maximum and a minimum in agreement with Herzberg and Mundle (loc. cit.)	The selected D_0 (BH) value as reported by Hurley (loc. cit.).

Heat Capacity and Entropy.

The molecular constants from O. Herzberg (loc. cit.) were adjusted for the natural abundance of B^{10} and B^{11} . Because the constants ω_e and $\omega_e x_e$ could not be determined directly from the spectrum, Alay and Horsfall (loc. cit.) obtained estimates for the ground state $X^1\Sigma^+$ from the rotational constants for this state and the relations $D_e = 4 B_e^2 / \omega_e^2$ and $\omega_e x_e / \omega_e = 0.6 \alpha_e / B_e$.

Boron Oxide Hydride (HBO)

(Ideal Gas) Mol. Wt. = 27.828

BORON OXIDE HYDRIDE (HBO)

(IDEAL GAS)

MOL. WT. = 27.828

Point Group C_{2v}

$\Delta H_f^\circ 0 = [-20 \pm 20] \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ 298.15 = [-20 \pm 20] \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = [50.256] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

(cm.^{-1})

[1900](1)

[700](2)

[2300](1)

Bond Distances: H-B = $[1.23] \text{ \AA}$ B-O = $[1.20] \text{ \AA}$

Bond Angle: H-B-O = $[180]^\circ$

Rotational Constants: $B_0 = [1.3011] \text{ cm.}^{-1}$

$\sigma = 1$

Heat of Formation

The heat of formation of the hypothetical species HBO(g) is controversial. Using $\Delta H_f^\circ 298.15 = [255] \text{ kcal. mole}^{-1}$ for the reaction $\text{HBO(g)} = \text{H(g)} + \text{B(g)} + \text{O(g)}$, the value of $\Delta H_f^\circ 298.15$ for HBO(g) is calculated as $[-13] \text{ kcal. mole}^{-1}$. The value of $\Delta H_f^\circ 298.15$ is the sum of the constituent bond energies, i.e. $D(\text{H-B}) = 87$ and $D(\text{B-O}) = 168 \text{ kcal. mole}^{-1}$. The $D(\text{H-B})$ value is derived from the dissociation of $\text{BH}_3(\text{g})$ and D(B-O) value is calculated as the average value of the B-O bond energies, 175 and 161 kcal. mole^{-1} , in BO(g) and $\text{BO}_2(\text{g})$ molecules, respectively.

However, by comparison with the following dissociation reactions:

$(\text{PBO})_3(\text{g}) \rightarrow 3 \text{ PBO(g)} \quad \Delta H_f^\circ 298.15 = 135 \text{ kcal. mole}^{-1} \text{ or } 45 \text{ kcal. mole}^{-1} \text{ per mole of PBO(g)}$

$(\text{HBO})_3(\text{g}) \rightarrow 3 \text{ HBO(g)} \quad \Delta H_f^\circ 298.15 = 141.8 \text{ kcal. mole}^{-1} \text{ or } 47 \text{ kcal. mole}^{-1} \text{ per mole of HBO(g)}$

$(\text{ClBO})_3(\text{g}) \rightarrow 3 \text{ ClBO(g)} \quad \Delta H_f^\circ 298.15 = 170.6 \text{ kcal. mole}^{-1} \text{ or } 57 \text{ kcal. mole}^{-1} \text{ per mole of ClBO(g)}$

It is estimated $\Delta H_f^\circ 298.15 = [70] \text{ kcal. mole}^{-1}$ for the reaction $1/3(\text{HBO})_3(\text{g}) \rightarrow \text{HBO(g)}$, based on the electronegativity difference among the B, Cl and H atoms. Hence the value of $\Delta H_f^\circ 298.15$ for HBO(g) is calculated to be $-27 \text{ kcal. mole}^{-1}$. The adopted value of $\Delta H_f^\circ 298.15$ for HBO(g) is $1/2(-13-27) = -20 \text{ kcal. mole}^{-1}$. The uncertainty is given as $\pm 20 \text{ kcal. mole}^{-1}$. Other methods of estimation have been tried such as the comparison of the difference in $\Delta H_f^\circ 298.15$ between H-CH_3 and HO-CH_3 with the corresponding difference between H-B-O and HO-B-O , etc. They lead to very large negative values for $\Delta H_f^\circ 298.15(\text{HBO, g})$. However, a value of $260 \pm 15 \text{ kcal. mole}^{-1}$ for the atomization of HBO(g) was used by L. V. Gurvichev, et al., "Thermodynamic Properties of Individual Substances," Vol. I, Academy of Science, USSR, Moscow, 1962, which was obtained by comparison with the dissociation energies for BO, BH, CN, CH and HCN molecules.

Heat Capacity and Entropy

The vibrational frequencies and molecular structure were obtained from W. H. Evans, private communication, October 6, 1960. The bond lengths of H-B and B-O in the HBO(g) molecule were assumed to be the same as those in the BH(g) and BO(g) molecules, respectively. The moment of inertia (I) is calculated as $2.1561 \times 10^{-39} \text{ g. cm.}^2$.

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o) ₂₉₈ /T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0							
100					335.000	330.452	-242.228
200				.000			
298	9.067	51.774	51.774				
300	9.095	51.831	51.775	.017	335.008	330.423	-240.713
400	9.591	54.358	52.182	1.999	335.018	327.134	-237.590
500	10.646	56.859	52.692	3.095	335.031	325.134	-235.590
600	11.273	58.857	53.698	4.291	336.222	325.358	-235.511
700	11.615	60.636	54.544	4.291	336.618	323.515	-231.006
800	12.022	62.283	55.453	5.456	337.023	321.616	-227.661
900	12.452	63.713	56.256	7.064	337.458	319.669	-224.477
1000	12.906	65.003	57.019	7.862	337.926	317.689	-221.477
1100	13.326	66.311	57.862	9.294	338.279	315.629	-218.710
1200	13.481	67.471	58.615	10.227	338.699	313.553	-216.106
1300	13.650	68.538	59.338	11.581	339.114	311.439	-213.598
1400	13.770	69.526	60.033	13.294	339.526	309.271	-211.287
1500	13.857	70.524	60.701	15.334	339.926	307.051	-209.167
1600	14.004	71.424	61.344	16.129	340.318	304.821	-207.051
1700	14.056	72.276	61.962	17.534	340.700	302.598	-204.934
1800	14.175	73.084	62.557	18.946	341.072	300.350	-202.818
1900	14.243	73.852	63.132	20.796	341.434	298.089	-200.702
2000	14.302	74.584	63.686	21.796	341.794	295.899	-198.586
2100	14.354	75.284	64.222	23.229	342.144	293.596	-196.470
2200	14.400	75.952	64.740	24.667	342.487	291.276	-194.354
2300	14.441	76.593	65.242	25.109	342.823	288.955	-192.238
2400	14.476	77.200	65.724	25.004	343.085	286.635	-190.122
2500	14.509	77.760	66.199	25.004	343.368	284.315	-188.006
2600	14.538	78.370	66.656	30.456	343.608	282.000	-185.890
2700	14.564	78.919	67.100	31.912	343.728	280.013	-183.774
2800	14.588	79.449	67.532	33.369	343.845	277.830	-181.658
2900	14.610	79.967	67.952	35.291	343.958	275.436	-179.542
3000	14.631	80.467	68.356	35.291	344.068	273.036	-177.426
3100	14.649	80.937	68.756	37.755	344.177	271.222	-175.310
3200	14.667	81.403	69.144	39.221	344.282	269.003	-173.194
3300	14.684	81.854	69.524	40.689	344.384	266.712	-171.078
3400	14.699	82.294	69.894	42.158	344.484	264.422	-168.962
3500	14.715	82.719	70.254	43.629	344.576	262.279	-166.846
3600	14.729	83.134	70.606	45.101	344.672	260.022	-164.730
3700	14.743	83.538	70.950	46.574	344.762	257.753	-162.614
3800	14.756	83.931	71.286	48.049	344.850	255.482	-160.498
3900	14.767	84.314	71.616	49.524	344.936	253.212	-158.382
4000	14.773	84.689	71.936	51.003	345.022	251.052	-156.266
4100	14.785	85.054	72.253	52.482	345.108	248.892	-154.150
4200	14.795	85.410	72.562	53.962	345.194	246.732	-152.034
4300	14.800	85.756	72.865	55.444	345.276	244.572	-149.918
4400	14.803	86.094	73.165	56.924	345.358	242.412	-147.802
4500	14.805	86.433	73.465	58.404	345.436	240.252	-145.686
4600	14.857	86.760	73.739	59.895	345.514	238.092	-143.570
4700	14.869	87.079	74.019	61.382	345.592	235.932	-141.454
4800	14.881	87.383	74.295	62.869	345.666	233.772	-139.338
4900	14.893	87.680	74.567	64.358	345.738	231.612	-137.222
5000	14.905	88.001	74.831	65.848	345.806	229.452	-135.106
5100	14.916	88.266	75.092	67.339	345.874	227.292	-132.990
5200	14.928	88.586	75.349	68.831	345.942	225.132	-130.874
5300	14.940	88.870	75.601	70.324	346.010	222.972	-128.758
5400	14.951	89.144	75.854	71.815	346.078	220.812	-126.642
5500	14.963	89.424	76.094	73.315	346.146	218.652	-124.526
5600	14.974	89.694	76.334	74.811	346.214	216.492	-122.410
5700	14.986	89.959	76.571	76.309	346.282	214.332	-120.294
5800	14.997	90.219	76.804	77.809	346.350	212.172	-118.178
5900	15.008	90.476	77.034	79.309	346.418	210.012	-116.062
6000	15.019	90.726	77.256	80.810	346.486	207.852	-113.946

June 30, 1968

BORON OXIDE HYDRIDE UNIPOSITIVE ION (HBO⁺) (IDEAL GAS)

Point Group [C_{∞v}]
S_{298.15} = [51.8 ± 1.5] gibbs/mol
ΔH_f^o = [335 ± 20] kcal/mol
ΔH_f^o = [335 ± 20] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[20000]	[2]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
[1700] (1)	[600] (2)
[2000] (1)	[2000] (1)

Bond Distance: B-H = [1.25] Å

Bond Angle: H-B-O = [180°]

Rotational Constant: B₀ = [1.208] cm⁻¹

Heat of Formation

Using the correlations developed by A. D. Walsh, J. Chem. Soc. 2288 (1953) for HAB molecules the electron removed by ionization ought to be a bonding electron. This indicates a high ionization potential and also the bond dissociation energy of BO-H⁺ should be significantly less than BO-H. Assuming a decrease of 40 kcal we obtain ΔH_f^o(HBO⁺, g) = 335 ± 20 kcal/mol, which corresponds to an ionization potential of 355 kcal or 15.4 ± 1 eV. This is in accord with the ionization potential of BO, 12.8 eV, from National Bureau of Standards Report 8628, Jan. 1, 1965, which should be less than HBO since the electron in BO is unpaired.

Heat Capacity and Entropy

According to the correlations of Walsh loc.cit., the molecule should be linear and since the unpaired electron is in a pi orbital, the ground state should be ²Π_u. A first excited state is estimated at 20000 cm⁻¹ to be ²Σ_g by analogy with the isoelectronic molecule CO⁺. Since HBO⁺ is lacking a bonding electron compared to HBO, we assume that the bond lengths will be slightly longer than in HBO. The vibrational frequencies are also estimated from those in HBO by assuming all values to be 10 per cent lower due to the weaker bonding.

The enthalpy at 0°K is -2.275 kcal/mol.

σ = 1

BHO⁺

Metaboric Acid (HBO₂)

(Crystal) Mol. Wt. = 43.828

T. °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$\int_0^T C_p dT$ S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH_f°	ΔF_f°	Log K _p
0							
100							
200							
298	13.600	11.700	11.700	0.000	-191.870	-175.677	128.769
300							
400	13.100	11.781	11.700	0.024	-191.870	-175.577	127.902
500	14.700	15.778	12.234	1.417	-191.857	-170.147	92.959
600	15.900	19.187	13.282	2.947	-191.821	-164.723	71.997
700							
800	17.100	22.189	14.529	4.195	-191.773	-159.319	48.051
900	18.400	24.850	16.429	8.435	-191.709	-153.919	34.777
1000	20.200	27.577	17.131	10.446	-191.632	-148.547	30.144
1100	21.425	30.036	18.429	12.630	-190.979	-143.219	26.362
1200	22.200	32.337	19.706	14.865	-190.566	-137.933	23.217
1300	22.480	34.466	20.933	17.131	-189.711	-132.601	20.563
1400	22.850	36.256	23.331	19.403	-188.296	-127.319	18.292
1500	23.000	41.540	25.545	23.993	-186.509	-112.074	16.328

Metaboric Acid (HBO₂)

(CRYSTAL)

MOL. WT. = 43.828

ΔH_f° O = Unknown

ΔH_f° 298.15 = -191.87 ± 0.20 kcal. mole⁻¹

ΔH_m° = Unknown

ΔH_g° 298.15 = 57.9 ± 1.0 kcal. mole⁻¹

T_m = 509 ± 1°K

S_{298.15} = [11.7 ± 1.0] cal. deg.⁻¹ mole⁻¹

Heat of Formation.

The enthalpy change (ΔH_f°) of the reaction HBO₂ (c, I) + H₂O(l) = H₂BO₃(c) has been determined by M. V. Kilday and E. J. Prosen, J. Am. Chem. Soc. 82, 5508 (1960). From the value, ΔH_f° 298.15 = -1.28 kcal. mole⁻¹, the heat of formation (ΔH_f° 298.15) for HBO₂ (c, I) is derived to be -191.87 ± 0.20 kcal. mole⁻¹ which is adopted. The heats of solution of HBO₂ (c, I) in H₂O(l) was measured by N. D. Sokolova, S. M. Skuratov, A. M. Shemonaseva and Y. M. Yuldasheva, Russ. J. Inorg. Chem. 5, 395 (1961). Based on the reported value, ΔH_f° 298.15 = 1.76 ± 0.01 kcal. mole⁻¹ for the reaction HBO₂(c, I) + 501 H₂O(l) = H₂BO₃·500 H₂O(sol.), the heat of formation for HBO₂(c, I) was derived as -189.46 ± 0.20 kcal. mole⁻¹, using ΔH_f° 298.15(H₂O, l) = -68.317 and ΔH_f° 298.15(H₂BO₃·500 H₂O, sol.) = -256.02 ± 0.20 kcal. mole⁻¹.

Heat Capacity and Entropy.

The values of heat capacity for HBO₂(c, I) were estimated by comparison with those of its constituent oxides. S_{298.15} was calculated as the sum of the entropy contributions from H⁺ and BO₂⁻ in HBO₂(c) suggested by K. K. Kelley, private communication, June 1960, and O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958.

Melting Data.

P. C. Kuczek, O. W. Morey and H. E. Merwin, Am. J. Sci. [5] 358, 143 (1938) reported the existence of three crystal forms of HBO₂(c), namely HBO₂(c, I), m.p. 509 ± 1°K, HBO₂(c, II), m.p. 474.1 ± 0.5°K, and HBO₂(c, III), m.p. 449.2 ± 0.2°K. However, there was no solid phase equilibrium found among these three crystals. N. D. Sokolova, S. M. Skuratov, A. M. Shemonaseva and Y. M. Yuldasheva, loc. cit., measured the heats of solution in water of HBO₂(c, I) and HBO₂(c, II) and derived the heat of transition as ΔH_t° 298.15(II → I) = 1.29 kcal. mole⁻¹.

Heat of Sublimation.

The value of ΔH_g° 298.15 was calculated as the difference between the ΔH_f° 298.15 values for HBO₂(g) and HBO₂(c).

T, °K.	C _p	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	<0.00	INFINITE	2.554	-133.175	INFINITE	-133.175	INFINITE	
100	7.407	50.115	1.028	-133.506	144.490	-133.506	144.490	96.310
200	6.814	53.517	0.928	-134.000	144.490	-134.000	144.490	96.310
298	10.094	57.273	0.800	-134.000	144.490	-134.000	144.490	96.310
300	10.118	57.336	0.797	-134.006	144.490	-134.006	144.490	95.705
400	11.366	60.420	1.094	-134.311	144.490	-134.311	144.490	91.275
500	12.466	63.078	1.287	-134.611	144.490	-134.611	144.490	86.564
600	13.402	65.436	1.382	-134.896	144.490	-134.896	144.490	82.401
700	14.189	67.562	1.462	-135.161	144.490	-135.161	144.490	78.742
800	14.831	69.502	1.531	-135.404	144.490	-135.404	144.490	75.463
900	15.434	71.284	1.590	-135.626	144.490	-135.626	144.490	72.489
1000	15.995	72.934	1.640	-135.831	144.490	-135.831	144.490	69.794
1100	16.511	74.469	1.682	-136.026	144.490	-136.026	144.490	67.334
1200	16.971	75.904	1.718	-136.210	144.490	-136.210	144.490	65.063
1300	17.386	77.251	1.749	-136.390	144.490	-136.390	144.490	62.951
1400	17.760	78.520	1.775	-136.566	144.490	-136.566	144.490	60.967
1500	18.101	79.719	1.797	-136.742	144.490	-136.742	144.490	59.107
1600	18.413	80.856	1.815	-136.920	144.490	-136.920	144.490	57.354
1700	18.701	81.935	1.830	-137.100	144.490	-137.100	144.490	55.694
1800	18.966	82.963	1.842	-137.284	144.490	-137.284	144.490	54.122
1900	19.214	83.944	1.851	-137.471	144.490	-137.471	144.490	52.633
2000	19.445	84.882	1.858	-137.659	144.490	-137.659	144.490	51.221
2100	19.662	85.779	1.863	-137.851	144.490	-137.851	144.490	49.883
2200	19.867	86.641	1.866	-138.047	144.490	-138.047	144.490	48.615
2300	20.056	87.468	1.868	-138.246	144.490	-138.246	144.490	47.415
2400	20.234	88.254	1.869	-138.451	144.490	-138.451	144.490	46.281
2500	20.402	89.001	1.869	-138.664	144.490	-138.664	144.490	45.209
2600	20.562	89.713	1.868	-138.886	144.490	-138.886	144.490	44.196
2700	20.715	90.400	1.866	-139.117	144.490	-139.117	144.490	43.239
2800	20.862	91.073	1.863	-139.356	144.490	-139.356	144.490	42.336
2900	21.002	91.735	1.859	-139.602	144.490	-139.602	144.490	41.485
3000	21.136	92.386	1.854	-139.856	144.490	-139.856	144.490	40.683
3100	21.265	93.027	1.848	-140.117	144.490	-140.117	144.490	39.928
3200	21.390	93.658	1.841	-140.386	144.490	-140.386	144.490	39.219
3300	21.511	94.279	1.833	-140.662	144.490	-140.662	144.490	38.554
3400	21.628	94.893	1.825	-140.945	144.490	-140.945	144.490	37.933
3500	21.742	95.502	1.816	-141.236	144.490	-141.236	144.490	37.354
3600	21.853	96.107	1.806	-141.534	144.490	-141.534	144.490	36.816
3700	21.961	96.708	1.795	-141.839	144.490	-141.839	144.490	36.318
3800	22.066	97.305	1.783	-142.151	144.490	-142.151	144.490	35.859
3900	22.168	97.898	1.771	-142.469	144.490	-142.469	144.490	35.439
4000	22.267	98.487	1.758	-142.794	144.490	-142.794	144.490	35.056
4100	22.363	99.072	1.744	-143.126	144.490	-143.126	144.490	34.709
4200	22.456	99.653	1.729	-143.465	144.490	-143.465	144.490	34.396
4300	22.546	100.230	1.713	-143.811	144.490	-143.811	144.490	34.116
4400	22.633	100.803	1.696	-144.164	144.490	-144.164	144.490	33.868
4500	22.717	101.372	1.678	-144.524	144.490	-144.524	144.490	33.651
4600	22.800	101.937	1.659	-144.891	144.490	-144.891	144.490	33.464
4700	22.880	102.500	1.639	-145.265	144.490	-145.265	144.490	33.306
4800	22.958	103.060	1.618	-145.646	144.490	-145.646	144.490	33.176
4900	23.034	103.617	1.596	-146.034	144.490	-146.034	144.490	33.073
5000	23.108	104.172	1.573	-146.429	144.490	-146.429	144.490	32.995
5100	23.180	104.725	1.549	-146.831	144.490	-146.831	144.490	32.941
5200	23.250	105.276	1.524	-147.240	144.490	-147.240	144.490	32.909
5300	23.318	105.825	1.498	-147.656	144.490	-147.656	144.490	32.897
5400	23.384	106.372	1.471	-148.079	144.490	-148.079	144.490	32.904
5500	23.448	106.917	1.443	-148.509	144.490	-148.509	144.490	32.929
5600	23.510	107.460	1.415	-148.946	144.490	-148.946	144.490	32.971
5700	23.570	108.001	1.386	-149.390	144.490	-149.390	144.490	33.029
5800	23.628	108.540	1.356	-149.841	144.490	-149.841	144.490	33.102
5900	23.684	109.077	1.325	-150.299	144.490	-150.299	144.490	33.189
6000	23.738	109.612	1.293	-150.764	144.490	-150.764	144.490	33.290

Dec. 31, 1960; Mar. 31, 1961; June 30, 1963; Dec. 31, 1964

METABORIC ACID (HBO₂)Point Group [C_{2v}]S_{298.15} = [57.273] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W, cm. ⁻¹	W, cm. ⁻¹
3680(1)	[1250](1)
2030(1)	[600](1)
1420(1)	[700](1)

Bond Distances: H-O = [1.0] Å O-B = [1.34] Å B-O = [1.20] Å

Bond Angles: H-O-B = [120]° O-B-O = [180]°

Product of the Moments of Inertia: I_AI_BI_C = 9.6851 X 10⁻¹¹⁷ g.³ cm.⁶

Heat of Formation.

The equilibrium pressures of the reaction 1/2 B₂O₃(l) + 1/2 H₂O(g) = HBO₂(g) have been measured by several investigators. Using the equilibrium data reported, the heats of reaction (ΔH_r⁰) were evaluated by both the second and third law methods. The corresponding heats of formation for HBO₂(g) were derived based on the ΔH_f⁰ 298.15 values obtained by the third law method. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	ΔH _f ⁰ 298.15 kcal. mole ⁻¹
Meschi, et al. ¹	1061 - 1451	45.4 ± 0.6	45.16	-133.38 ± 0.50
White, et al. ²	1323 - 1451	0.25 ± 6.0	45.15	-133.82 ± 0.50
Randall and Margrave ³	1250 - 1450	39.7 ± 2.5	—	-138.87 ± 0.50*
Farber, et al. ⁴	1273	—	44.12	-134.42 ± 1.0
	1070 - 1323	31.0 ± 10.0	44.07	-134.47 ± 3.20
	1143	—	40.9	-137.64 ± 0.70*
	1071 - 1325	44.2 ± 1.8	39.3	-139.3 ± 1.0*
	1146	—	43.2	-135.3 ± 0.4

*The value not used for the calculation of the weighted average of ΔH_f⁰ 298.15 for HBO₂(g).
1. D. J. Meschi, W. A. Chupka and J. Berkowitz, J. Chem. Phys. **33**, 530 (1960). The ΔH_f⁰ 298.15 values, 0.25 ± 6.0 and -5.15 kcal. mole⁻¹, were obtained based on the reaction 1/2 B₂O₃(g) + 1/2 H₂O(g) = HBO₂(g).
2. D. White, D. E. Mann, P. N. Melah and A. Sommer, J. Chem. Phys. **32**, 488 (1960). The ΔH_f⁰ 298.15 value was derived using ΔH_r⁰ 298.15 obtained by the second law method.
3. S. P. Randall and J. L. Margrave, J. Inorg. Nucl. Chem. **16**, 29 (1960). The partial pressure of HBO₂(g), P_{HBO₂} = 3.613 X 10⁻⁴ atm., was calculated from the total pressure by the relation P_{HBO₂} = P_{total} - 3 P_{H₂O} - 3 P_{H₂B₃O₆} where P_{H₂B₃O₆} = 3.030 X 10⁻⁵ and P_{H₂O} = 2.1468 X 10⁻⁵ atm.
4. M. Farber, et al., "Thermodynamics of Reactions Involving Light Metal Oxides and Propellant Gases", QR-1987-5, May 9 - Aug 9, 1961, QR-1987-7, Nov. 9 - Feb. 9, 1962 and Final Report, May 9, 1960 through June 30, 1962, Rocket Power, Inc., California. The first and last sets of data were determined by the Molecular Flow Method and the rest, by Effusion Method.

The value of ΔH_f⁰ 298.15 for HBO₂(g) adopted is the weighted average of the ΔH_f⁰ 298.15 value listed above.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were taken from D. White, D. E. Mann, P. N. Melah and A. Sommer, loc. cit. The three principal moments of inertia are: I_A = 1.155 X 10⁻⁴⁰, I_B = 9.1050 X 10⁻³⁹ and I_C = 9.2205 X 10⁻³⁹ g. cm.²

Boron Dihydride (BH₂)

(Ideal Gas) Mol. Wt. = 12.836

BORON DIHYDRIDE (BH₂) (IDEAL GAS)

MOL. WT. = 12.836

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	8.000	35.000	43.045	2.153	48.163	48.163	48.163	INFINITE
200	7.232	31.674	43.045	1.474	48.088	47.613	47.613	-102.769
300	6.597	29.090	43.045	1.000	48.000	47.138	47.138	-186.883
400	6.133	27.045	43.045	0.650	47.889	46.659	46.659	-272.903
500	5.819	25.406	43.046	0.415	47.797	46.186	46.186	-360.866
600	5.597	24.053	43.375	0.271	47.737	45.713	45.713	-449.798
700	5.422	22.922	44.023	0.179	47.653	45.240	45.240	-539.698
800	5.287	21.967	44.776	0.116	47.546	44.767	44.767	-630.566
900	5.183	21.136	45.556	0.076	47.421	44.294	44.294	-722.413
1000	5.100	20.419	46.333	0.048	47.281	43.821	43.821	-815.240
1100	5.033	19.797	47.091	0.028	47.128	43.348	43.348	-909.047
1200	4.980	19.267	47.827	0.016	46.963	42.875	42.875	-1003.834
1300	4.938	18.821	48.537	0.009	46.788	42.402	42.402	-1100.601
1400	4.904	18.454	49.222	0.005	46.604	41.929	41.929	-1199.348
1500	4.877	18.154	49.882	0.003	46.411	41.456	41.456	-1299.975
1600	4.856	17.918	50.518	0.002	46.210	40.983	40.983	-1402.483
1700	4.839	17.742	51.131	0.001	46.000	40.510	40.510	-1506.871
1800	4.824	17.614	51.722	0.001	45.777	40.037	40.037	-1613.140
1900	4.811	17.524	52.294	0.000	45.549	39.564	39.564	-1721.291
2000	4.800	17.464	52.845	0.000	45.316	39.091	39.091	-1831.324
2100	4.790	17.431	53.376	0.000	45.079	38.618	38.618	-1943.249
2200	4.782	17.421	53.886	0.000	44.838	38.145	38.145	-2057.066
2300	4.775	17.430	54.366	0.000	44.593	37.672	37.672	-2172.775
2400	4.769	17.456	54.811	0.000	44.344	37.199	37.199	-2290.376
2500	4.764	17.500	55.224	0.000	44.091	36.726	36.726	-2409.869
2600	4.760	17.561	55.604	0.000	43.834	36.253	36.253	-2531.254
2700	4.757	17.638	55.956	0.000	43.573	35.780	35.780	-2654.527
2800	4.754	17.731	56.284	0.000	43.308	35.307	35.307	-2779.684
2900	4.752	17.839	56.588	0.000	43.039	34.834	34.834	-2906.724
3000	4.750	17.961	56.864	0.000	42.766	34.361	34.361	-3035.647
3100	4.748	18.097	57.111	0.000	42.489	33.888	33.888	-3166.454
3200	4.746	18.247	57.334	0.000	42.208	33.415	33.415	-3299.145
3300	4.744	18.401	57.531	0.000	41.923	32.942	32.942	-3433.720
3400	4.742	18.560	57.704	0.000	41.634	32.469	32.469	-3569.179
3500	4.740	18.724	57.854	0.000	41.341	31.996	31.996	-3706.522
3600	4.738	18.892	57.984	0.000	41.044	31.523	31.523	-3845.749
3700	4.736	19.064	58.094	0.000	40.743	31.050	31.050	-3986.860
3800	4.734	19.241	58.184	0.000	40.438	30.577	30.577	-4129.854
3900	4.732	19.422	58.254	0.000	40.129	30.104	30.104	-4274.731
4000	4.730	19.607	58.304	0.000	39.816	29.631	29.631	-4421.490
4100	4.728	19.796	58.334	0.000	39.500	29.158	29.158	-4569.131
4200	4.726	19.989	58.344	0.000	39.181	28.685	28.685	-4717.654
4300	4.724	20.186	58.334	0.000	38.859	28.212	28.212	-4867.059
4400	4.722	20.387	58.304	0.000	38.534	27.739	27.739	-5017.346
4500	4.720	20.592	58.254	0.000	38.206	27.266	27.266	-5168.514
4600	4.718	20.801	58.184	0.000	37.875	26.793	26.793	-5320.563
4700	4.716	21.014	58.094	0.000	37.541	26.320	26.320	-5473.494
4800	4.714	21.231	57.984	0.000	37.204	25.847	25.847	-5627.317
4900	4.712	21.452	57.854	0.000	36.864	25.374	25.374	-5782.032
5000	4.710	21.678	57.704	0.000	36.481	24.901	24.901	-5937.649
5100	4.708	21.909	57.534	0.000	36.096	24.428	24.428	-6094.168
5200	4.706	22.145	57.344	0.000	35.709	23.955	23.955	-6251.589
5300	4.704	22.386	57.134	0.000	35.319	23.482	23.482	-6409.912
5400	4.702	22.632	56.904	0.000	34.926	23.009	23.009	-6569.137
5500	4.700	22.883	56.654	0.000	34.531	22.536	22.536	-6729.264
5600	4.698	23.139	56.384	0.000	34.134	22.063	22.063	-6890.292
5700	4.696	23.400	56.094	0.000	33.735	21.590	21.590	-7052.221
5800	4.694	23.666	55.784	0.000	33.334	21.117	21.117	-7215.051
5900	4.692	23.937	55.454	0.000	32.931	20.644	20.644	-7378.781
6000	4.690	24.213	55.104	0.000	32.526	20.171	20.171	-7543.411

Dec. 31, 1960; Dec. 1964

Point Group [D_{∞h}]ΔH_f⁰ = 48 ± 15 kcal. mole⁻¹S_{298.15} = [43.045] cal. deg.⁻¹ mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

[ω₁, cm.⁻¹] [ω₂, cm.⁻¹] [ω₃, cm.⁻¹]

[2430](1) [840](2) [2650](1)

Bond Distance: B-H = [1.20 Å]

Bond Angle: H-B-H = [180°]

Rotational Constant: B₀ = 5.80683 cm.⁻¹

Heat of Formation.

ΔH_f⁰ 298.15 was calculated from appearance potentials reported by T. P. Fehlner and W. S. Koski, J. Am. Chem. Soc. 86, 2733 (1964) and the JANAF (B₂H₆(g)) ΔH_f⁰ 298.15 = +9.8 kcal. mole⁻¹. For exampleB₂H₆(g) → BH₂⁺(ion) + BH₂(g)BH₂(g) → BH₂⁺(ion)ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹B₂H₆(g) → 2BH₂(g) + H₂(g)ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹ΔH_f⁰ 298.15 = 48 ± 15 kcal. mole⁻¹



Boron Dihydroxide (B(OH)₂)

(Ideal Gas) Mol. Wt. = 44.836

BORON DIHYDROXIDE (B(OH)₂) (IDEAL GAS)

MOL. WT. = 44.836

Point Group [C_{2h}]

$\Delta H_f^\circ = [-112 \pm 15] \text{ kcal. mole}^{-1}$

S_{298.15} = [59.116] cal. deg.⁻¹ mole⁻¹

$\Delta H_f^\circ = [-114 \pm 15] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
[2500](1)	[750](1)	[1300](1)
[1150](1)	[460](1)	[1000](1)
[1100](1)	[3000](1)	[450](1)

Bond Distance: B-O = [1.27] Å O-H = [0.97] Å

Bond Angle: H-O-B = [105]° O-B-O = [180]°

Product of the Moments of Inertia: I_AI_BI_C = [2.42627 X 10⁻¹¹⁶] g.³ cm.⁶

σ = 2

Heat of Formation

The value of ΔH_f° 298.15 for B(OH)₂(g) was calculated by using the bond energy, D°(B-OH) = 132.7 kcal. mole⁻¹, and the heats of formation for B(g) and OH(g) as 132.80 and 9.33 kcal. mole⁻¹, respectively.

Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with those for B₂O₃(g), B(OH)₃(g) and other related molecules. The bond distances and angles were estimated by comparison with those for B₂O₃(g) and H₂O₂(g) molecules. The molecular configuration is assumed to be trans which is considered as more stable than the cis-form. The three principal moments of inertia are: I_A = 2.6870 X 10⁻⁴⁰, I_B = 9.3682 X 10⁻³⁹ and I_C = 9.6369 X 10⁻³⁹ g. cm.²

Dec. 31, 1960; Dec. 31, 1964

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	.000	INFINITE	INFINITE	2.814	-112.423	-112.423	INFINITE
100	8.200	47.428	67.576	2.015	-113.102	-113.102	24.5115
200	10.129	53.043	59.178	1.107	-113.557	-109.217	119.342
300	12.432	58.116	.000	.000	-114.000	-106.994	78.425
400	14.625	62.085	58.116	.023	-114.008	-106.951	77.910
500	16.377	65.544	59.675	2.534	-114.377	-104.540	57.115
600	17.769	68.658	60.917	4.644	-114.887	-99.500	36.241
700	18.813	71.469	62.569	6.416	-115.180	-94.326	22.767
800	20.580	74.068	64.852	10.437	-115.231	-91.716	22.271
900	22.126	76.651	66.125	12.528	-115.270	-89.100	16.472
1000	21.771	80.700	67.356	14.679	-115.288	-86.483	17.182
1100	22.630	84.610	68.700	16.813	-115.280	-81.245	13.658
1200	22.970	88.100	70.812	19.123	-115.264	-78.626	12.274
1300	23.262	91.695	73.176	21.404	-115.244	-76.010	11.074
1400	23.514	95.205	75.823	23.600	-115.239	-73.366	10.025
1500	23.725	98.739	78.688	25.721	-115.229	-69.166	8.276
1600	23.902	102.297	81.678	27.782	-115.222	-65.550	7.540
1700	24.044	105.876	84.800	29.790	-115.239	-62.937	6.877
1800	24.161	109.471	88.055	31.754	-115.252	-60.320	6.277
1900	24.254	113.084	91.441	33.682	-115.269	-57.702	5.732
2000	24.326	116.714	94.965	35.582	-115.290	-55.088	5.234
2100	24.378	120.361	98.628	37.454	-115.315	-52.464	4.777
2200	24.411	124.024	102.424	39.300	-115.346	-49.742	4.348
2300	24.426	127.699	106.269	41.121	-115.380	-46.896	3.942
2400	24.424	131.384	110.194	42.924	-115.417	-43.942	3.562
2500	24.406	135.079	114.194	44.700	-115.456	-40.980	3.216
2600	24.373	138.784	118.264	46.450	-115.496	-38.016	2.890
2700	24.326	142.499	122.404	48.174	-115.537	-35.050	2.597
2800	24.266	146.224	126.614	49.882	-115.579	-32.082	2.327
2900	24.194	150.000	130.884	51.574	-115.622	-29.110	2.080
3000	24.111	153.824	135.214	53.250	-115.666	-26.136	1.848
3100	24.018	157.699	139.604	54.910	-115.711	-23.160	1.626
3200	23.915	161.624	144.054	56.554	-115.757	-20.184	1.415
3300	23.802	165.600	148.564	58.184	-115.804	-17.208	1.215
3400	23.679	169.626	153.134	59.800	-115.852	-14.232	1.025
3500	23.546	173.700	157.764	61.400	-115.900	-11.256	0.848
3600	23.403	177.824	162.454	63.000	-115.948	-8.280	0.680
3700	23.250	181.999	167.204	64.590	-115.996	-5.304	0.520
3800	23.087	186.224	172.014	66.174	-116.044	-2.328	0.360
3900	22.914	190.499	176.884	67.754	-116.092	0.644	0.200
4000	22.731	194.824	181.814	69.334	-116.140	3.618	0.040
4100	22.538	199.200	186.804	70.904	-116.188	6.592	0.000
4200	22.335	203.626	191.854	72.474	-116.236	9.566	0.000
4300	22.122	208.100	196.964	74.044	-116.284	12.540	0.000
4400	21.899	212.626	202.134	75.614	-116.332	15.514	0.000
4500	21.666	217.200	207.364	77.184	-116.380	18.488	0.000
4600	21.423	221.824	212.654	78.754	-116.428	21.462	0.000
4700	21.170	226.499	218.004	80.324	-116.476	24.436	0.000
4800	20.907	231.224	223.414	81.894	-116.524	27.410	0.000
4900	20.634	236.000	228.884	83.464	-116.572	30.384	0.000
5000	20.351	240.824	234.414	85.034	-116.620	33.358	0.000
5100	20.058	245.699	240.004	86.604	-116.668	36.332	0.000
5200	19.755	250.624	245.654	88.174	-116.716	39.306	0.000
5300	19.442	255.600	251.364	89.744	-116.764	42.280	0.000
5400	19.119	260.626	257.134	91.314	-116.812	45.254	0.000
5500	18.786	265.700	262.964	92.884	-116.860	48.228	0.000
5600	18.443	270.824	268.854	94.454	-116.908	51.202	0.000
5700	18.090	276.000	274.804	96.024	-116.956	54.176	0.000
5800	17.727	281.224	280.814	97.594	-117.004	57.150	0.000
5900	17.354	286.500	286.884	99.164	-117.052	60.124	0.000
6000	16.971	291.824	293.014	100.734	-117.100	63.098	0.000

Boron Trihydride (BH₃)

(Ideal Gas) Mol. Wt. = 13.844

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	7.922	0.000	INFINITE	2.421	26.407	26.407	INFINITE	
100	7.983	35.983	26.407	2.421	26.407	26.407	26.407	
200	8.159	45.653	26.407	2.421	26.407	26.407	26.407	
298	8.657	48.660	26.407	2.421	26.407	26.407	26.407	
300	8.668	48.934	26.407	2.421	26.407	26.407	26.407	
400	9.304	47.512	26.407	2.421	26.407	26.407	26.407	
500	10.048	49.666	26.407	2.421	26.407	26.407	26.407	
600	10.863	51.507	26.407	2.421	26.407	26.407	26.407	
700	12.509	54.922	26.407	2.421	26.407	26.407	26.407	
800	13.267	56.440	26.407	2.421	26.407	26.407	26.407	
900	13.957	57.874	26.407	2.421	26.407	26.407	26.407	
1000	14.578	59.234	26.407	2.421	26.407	26.407	26.407	
1100	15.132	60.524	26.407	2.421	26.407	26.407	26.407	
1200	15.623	61.756	26.407	2.421	26.407	26.407	26.407	
1300	16.056	62.928	26.407	2.421	26.407	26.407	26.407	
1400	16.436	64.046	26.407	2.421	26.407	26.407	26.407	
1500	16.766	65.115	26.407	2.421	26.407	26.407	26.407	
1600	17.051	66.138	26.407	2.421	26.407	26.407	26.407	
1700	17.297	67.117	26.407	2.421	26.407	26.407	26.407	
1800	17.509	68.056	26.407	2.421	26.407	26.407	26.407	
1900	17.687	68.958	26.407	2.421	26.407	26.407	26.407	
2000	17.832	69.825	26.407	2.421	26.407	26.407	26.407	
2100	17.948	70.659	26.407	2.421	26.407	26.407	26.407	
2200	18.037	71.462	26.407	2.421	26.407	26.407	26.407	
2300	18.107	72.237	26.407	2.421	26.407	26.407	26.407	
2400	18.162	72.986	26.407	2.421	26.407	26.407	26.407	
2500	18.204	73.700	26.407	2.421	26.407	26.407	26.407	
2600	18.236	74.386	26.407	2.421	26.407	26.407	26.407	
2700	18.259	75.048	26.407	2.421	26.407	26.407	26.407	
2800	18.274	75.686	26.407	2.421	26.407	26.407	26.407	
2900	18.282	76.300	26.407	2.421	26.407	26.407	26.407	
3000	18.286	76.895	26.407	2.421	26.407	26.407	26.407	
3100	18.286	77.475	26.407	2.421	26.407	26.407	26.407	
3200	18.282	78.036	26.407	2.421	26.407	26.407	26.407	
3300	18.274	78.579	26.407	2.421	26.407	26.407	26.407	
3400	18.262	79.106	26.407	2.421	26.407	26.407	26.407	
3500	18.246	79.618	26.407	2.421	26.407	26.407	26.407	
3600	18.226	80.116	26.407	2.421	26.407	26.407	26.407	
3700	18.202	80.599	26.407	2.421	26.407	26.407	26.407	
3800	18.175	81.066	26.407	2.421	26.407	26.407	26.407	
3900	18.145	81.517	26.407	2.421	26.407	26.407	26.407	
4000	18.113	81.953	26.407	2.421	26.407	26.407	26.407	
4100	18.079	82.375	26.407	2.421	26.407	26.407	26.407	
4200	18.043	82.783	26.407	2.421	26.407	26.407	26.407	
4300	18.006	83.177	26.407	2.421	26.407	26.407	26.407	
4400	17.968	83.557	26.407	2.421	26.407	26.407	26.407	
4500	17.928	83.923	26.407	2.421	26.407	26.407	26.407	
4600	17.886	84.275	26.407	2.421	26.407	26.407	26.407	
4700	17.843	84.613	26.407	2.421	26.407	26.407	26.407	
4800	17.798	84.937	26.407	2.421	26.407	26.407	26.407	
4900	17.751	85.248	26.407	2.421	26.407	26.407	26.407	
5000	17.702	85.546	26.407	2.421	26.407	26.407	26.407	
5100	17.651	85.831	26.407	2.421	26.407	26.407	26.407	
5200	17.598	86.103	26.407	2.421	26.407	26.407	26.407	
5300	17.543	86.362	26.407	2.421	26.407	26.407	26.407	
5400	17.486	86.608	26.407	2.421	26.407	26.407	26.407	
5500	17.428	86.841	26.407	2.421	26.407	26.407	26.407	
5600	17.368	87.061	26.407	2.421	26.407	26.407	26.407	
5700	17.306	87.268	26.407	2.421	26.407	26.407	26.407	
5800	17.243	87.462	26.407	2.421	26.407	26.407	26.407	
5900	17.178	87.643	26.407	2.421	26.407	26.407	26.407	
6000	17.112	87.811	26.407	2.421	26.407	26.407	26.407	

BH₃

(IDEAL GAS)

BORON TRIHYDRIDE (BH₃)

MOL. WT. = 13.844

Point group [D_{3h}]

ΔH_f⁰ = 25.4 ± 10 kcal. mole⁻¹

S_{298.15}⁰ = [44.880] cal. deg.⁻¹ mole⁻¹

ΔH_f⁰ 298.15 = 25.5 ± 10 kcal. mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

[2384](1)

[1602](1)

[1785](2)

[2976](2)

σ = 6

Bond Distance: B-H = [1.16 Å]

Bond Angle: H-B-H = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [7.71 × 10⁻¹¹g.³ cm.⁶]

Heat of Formation

ΔH_f⁰ 298.15 was calculated from appearance potentials reported by T. P. Fehlner and W. S. Koski, J. Am. Chem. Soc. 86, 2733 (1964). For example

B₂H₆(g) → BH₃⁺(ion) + BH₃(g) 13.1 e.v.

BH₃⁺(ion) → BH₃(g) -11.4 e.v.

B₂H₆(g) → 2BH₃(g) 1.7 e.v.

The heat of formation data is summarized below.

Reaction: B₂H₆(g) → 2BH₃(g)*

*The auxiliary ΔH_f⁰ 298.15(B₂H₆) was from the JANAF Table dated Dec. 31, 1964

Method ΔH_f⁰ ΔH_f⁰ 298.15*

P. C. H. Jordan and H. C. Longuet-Higgins 89.9 kcal. mole⁻¹ 41.7 kcal. mole⁻¹

Mol. Phys. 5, 121 (1962) Bond energy parameters obtained by linear extrapolation from NH and CH bonds

E. J. Snike, G. A. Pressley Jr., A. B. Bayles, and F. E. Stafford, J. Chem. Phys. 41, 2207 (1964) Apparent equilibrium constants 55 ± 8 kcal. mole⁻¹ 33 kcal. mole⁻¹

E. J. Snike, et al. (loc. cit.) A recalculation by JANAF and P = 10⁻¹⁶ atm (ΔH⁰ = degree of dissociation) 49 ± 8 kcal. mole⁻¹ 30 kcal. mole⁻¹

M. C. Price, T. R. Pasmore and D. M. Rosenthal, Discussions Faraday Soc. 35, 201 (1965) Correlations of ionization and dissociation energies of hydrides and fluorides in relation to electronic structure. 41.5 kcal. mole⁻¹ 26.6 kcal. mole⁻¹

T. P. Fehlner and W. S. Koski (loc. cit.) Appearance Potentials 39.2 kcal. mole⁻¹ 25.5 kcal. mole⁻¹

M. E. Gersabedian and S. H. Benson, J. Am. Chem. Soc. 86, 176 (1964). From kinetic data for the decomposition of BH₃CO 22-25 kcal. mole⁻¹

R. E. McCoy and S. H. Bauer J. Am. Chem. Soc. 78, 2061 (1956) From calorimetric measurements of analogous compounds 20.1 kcal. mole⁻¹

L. Pauling, "The Nature of the Chemical Bond" Cornell University Press, Ithaca, N.Y. (1960) 3rd Ed. From electronegativities 23.9 kcal. mole⁻¹ 18 kcal. mole⁻¹

Heat Capacity and Entropy.

The molecular configuration, [planar, H-B-H angle = 120°], was estimated by A. Shepp and S. H. Bauer, J. Am. Chem. Soc. 76, 265 (1954) as well as by P. C. H. Jordan and H. C. Longuet-Higgins, (loc. cit.). In addition Shepp and Bauer estimated the bond distance and the vibrational frequencies. Jordan and Longuet-Higgins estimated the electronic configuration [1_A]. The principal moments of inertia calculated from these molecular constants are, I_A = I_B = 3.578 × 10⁻⁴⁰ and I_C = 6.756 × 10⁻⁴⁰ g. cm.²

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	Log K _p
0	0.000	INFINITE	0.000	INFINITE	3.201	-258.231	INFINITE
100	8.988	14.616	22.615	1.681	-261.529	-258.231	25.632
200	19.440	21.210	21.210	0.000	-261.870	-231.503	169.688
300	29.540	27.376	21.210	-0.316	-261.478	-231.317	168.507
400	37.836	33.302	23.723	2.516	-261.712	-211.088	162.262
500	44.000	38.569	25.764	7.683	-261.476	-200.982	73.204
600	48.260	42.052	26.922	10.854	-261.041	-190.730	59.608
700	51.000	44.000	27.592	12.679	-259.872	-171.046	47.530
800	52.248	44.742	27.923	13.879	-258.785	-161.266	35.243
900	52.928	45.000	28.007	14.413	-257.793	-151.263	30.111
1000	53.105	45.000	28.007	14.413	-256.706	-141.951	25.892
1100	40.187	41.400	28.007	14.413	-255.330	-132.016	22.263
1200	43.397	42.693	28.007	14.413	-253.078	-113.574	16.582
1300	44.000	44.000	28.007	14.413	-253.078	-113.574	16.582
1400	44.000	44.000	28.007	14.413	-253.078	-113.574	16.582
1500	44.000	44.000	28.007	14.413	-253.078	-113.574	16.582

$$\Delta H_f^0 = -258.23 \pm 0.20 \text{ kcal mole}^{-1}$$

$$\Delta H_f^0 = -261.47 \pm 0.20 \text{ kcal mole}^{-1}$$

$$\Delta H_m^0 = \text{Unknown}$$

$$\Delta H_g^0 = 24.3 \pm 0.7 \text{ kcal mole}^{-1}$$

$$T_m = (330)^\circ\text{K}$$

The heat of formation (ΔH_f^0 298.15) of H₃BO₃(c) was taken from W. D. Good, M. Mansson and J. P. McCullough, Quarterly Technical Report No. 9, Nov. 4, 1963, U. S. Bur. Mines, Bartlesville, Oklahoma. The value was derived based on the following measurements

$$\Delta H_f^0 = 298.15 \text{ kcal mole}^{-1}$$

$$-173.4 \pm 0.2$$

$$+14.6 \pm 0.1$$

The heats of solution of H₃BO₃(c) in water have been measured by many investigators. L. G. Fasolino, "Heat of Formation of B₂O₃(c) and B₂O₃(am.)", NONR-3608 (OO), June 2, 1964, National Research Corporation, Massachusetts, obtained the value, ΔH_f^0 298.15 = 5.45 ± 0.01 kcal mole⁻¹ for the reaction H₃BO₃(c) + 504 H₂O(l) = H₃BO₃·504 H₂O(sol.) which leads to ΔH_f^0 298.15 (H₃BO₃·504 H₂O, sol.) = -256.02 kcal mole⁻¹. The ΔH_f^0 298.15 value is in reasonable agreement with the value reported by J. Smieko and L. S. Mason, J. Am. Chem. Soc. 72, 3679 (1950) in which the heats of solution and dilution of H₃BO₃(c) were given. The heats of solution of H₃BO₃(c) in water measured by other previous investigators were reviewed by L. G. Fasolino, loc. cit.

Heat Capacity and Entropy

The low temperature (18-298°K) heat capacities were reported by H. L. Johnston and E. C. Kerr, J. Am. Chem. Soc. 72, 4733 (1950). The heat capacities above 300°K were estimated by comparison with those of its constituent oxides. $S_{298.15}^0$ was obtained from H. L. Johnston and E. C. Kerr, loc. cit., using $S_{17}^0 = 0.18 \text{ cal deg}^{-1} \text{ mole}^{-1}$.

Melting Data

The value of T_m was taken from F. C. Kracok, G. W. Morey and H. E. Merwin, Am. J. Sci. [5] 35A, 143 (1938).

However, H₃BO₃(c) is in a metastable state at T_m . Measurements of the decomposition pressure of H₃BO₃(c) to form HBO₂(c, II or III) and H₂O(g) have been made by H. Menzel, H. Schulz and H. Deckert, Z. anorg. allgem. Chem. 220, 49 (1934); A. Thiel and H. Siebenack, Z. anorg. allgem. Chem. 220, 236 (1934); H. V. Stachelberg, F. Outram and J. Dressel, Z. Elektrochem. 43, 14 (1937); S. Bezzi, Gass. chim. ital. 65, 766 (1935); and H. Tazaki, J. Sci. Hiroshima Univ. Ser. A 10, 37, 55, 63, 109, 113 (1939). The decomposition pressures of the system H₃BO₃(c) = H₂O(g) + HBO₂(c, I), at the temperatures of 312 to 352°K, have been reported by E. D. West, "The properties of Boron Compounds", ARL Technical Report 60-276, May 1960, National Bureau of Standards.

Temperature of Decomposition

The decomposition temperature (T_d) is calculated as the temperature at which the free energy change of the reaction H₃BO₃(c) + HBO₂(c) + H₂O(g) approaches zero.

Heat of Sublimation

The heat of sublimation (ΔH_s^0 298.15) is derived as the difference between the ΔH_f^0 298.15 values for H₃BO₃(g) and H₃BO₃(c).



MOL. WT. = 61.844

(IDEAL GAS)

BORIC ACID (H_3BO_3)

Boric Acid (H_3BO_3) Mol. Wt. = 61.844

T. °K.	C _p	$-\text{cal. mole}^{-1}\text{deg.}^{-1}$ $S^\circ - (H^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$ kcal. mole ⁻¹	ΔH°_f	ΔF°_f	Log K _f
0	11.043	56.791	2.576	-235.509	-231.294	505.469
100	12.073	64.866	1.396	-236.334	-226.770	247.791
298	15.616	70.539	-0.000	-237.160	-162.649	162.649
300	15.669	70.636	-0.029	-237.175	-221.806	161.578
400	18.371	75.522	1.167	-237.900	-118.323	118.323
500	20.640	79.874	3.688	-236.503	-211.166	92.266
600	22.671	83.095	5.867	-239.002	-205.450	74.004
700	24.451	85.411	7.711	-240.483	-200.052	60.457
800	25.215	86.968	77.378	-240.754	-194.411	53.106
900	26.260	93.761	13.208	-240.033	-188.726	45.827
1000	27.159	96.519	60.636	-240.260	-183.011	39.995
1100	27.097	99.156	82.201	-240.451	-177.270	35.250
1200	26.651	101.56	83.717	-240.601	-171.529	30.728
1300	26.300	103.937	85.184	-240.743	-165.786	27.666
1400	26.032	106.159	86.602	-240.860	-159.975	24.975
1500	30.298	108.203	87.974	-240.969	-154.212	22.468
1600	30.708	110.172	89.300	-241.074	-148.427	20.273
1700	31.211	112.000	90.577	-241.177	-142.634	18.163
1800	31.297	113.630	91.826	-241.273	-136.834	16.163
1900	31.669	115.534	93.029	-241.375	-131.026	15.071
2000	31.920	117.165	94.195	-241.477	-125.217	13.662
2100	32.143	118.726	95.327	-241.582	-119.400	12.426
2200	32.522	121.670	97.481	-241.608	-107.756	10.239
2300	32.663	123.056	98.520	-241.631	-95.921	9.291
2400	32.687	124.395	99.536	-241.651	-84.000	8.390
2500	32.928	125.685	100.517	-241.670	-72.000	7.559
2600	32.077	126.136	102.403	-241.686	-60.000	6.711
2700	33.195	126.136	102.403	-241.698	-48.000	6.071
2800	33.263	129.302	103.311	-241.706	-36.000	5.403
2900	33.373	130.432	104.196	-241.708	-24.000	4.760
3000	33.455	131.528	105.040	-241.710	-12.000	4.197
3100	33.520	132.580	105.904	-241.710	0.000	3.613
3200	33.559	133.624	106.728	-241.710	12.000	3.013
3300	33.663	134.658	107.534	-241.710	24.000	2.413
3400	33.721	135.604	108.322	-241.710	36.000	1.813
3500	33.776	136.555	109.093	-241.710	48.000	1.213
3600	33.776	136.555	109.093	-241.710	60.000	0.613
3700	33.776	136.555	109.093	-241.710	72.000	0.013
3800	33.613	136.394	110.597	-241.710	84.000	-0.587
3900	33.613	136.394	110.597	-241.710	96.000	-1.187
4000	33.613	136.394	110.597	-241.710	108.000	-1.787
4100	33.613	136.394	110.597	-241.710	120.000	-2.387
4200	33.613	136.394	110.597	-241.710	132.000	-2.987
4300	33.613	136.394	110.597	-241.710	144.000	-3.587
4400	33.613	136.394	110.597	-241.710	156.000	-4.187
4500	33.613	136.394	110.597	-241.710	168.000	-4.787
4600	33.613	136.394	110.597	-241.710	180.000	-5.387
4700	33.613	136.394	110.597	-241.710	192.000	-5.987
4800	33.613	136.394	110.597	-241.710	204.000	-6.587
4900	33.613	136.394	110.597	-241.710	216.000	-7.187
5000	33.613	136.394	110.597	-241.710	228.000	-7.787
5100	33.613	136.394	110.597	-241.710	240.000	-8.387
5200	33.613	136.394	110.597	-241.710	252.000	-8.987
5300	33.613	136.394	110.597	-241.710	264.000	-9.587
5400	33.613	136.394	110.597	-241.710	276.000	-10.187
5500	33.613	136.394	110.597	-241.710	288.000	-10.787
5600	33.613	136.394	110.597	-241.710	300.000	-11.387
5700	33.613	136.394	110.597	-241.710	312.000	-11.987
5800	33.613	136.394	110.597	-241.710	324.000	-12.587
5900	33.613	136.394	110.597	-241.710	336.000	-13.187
6000	33.613	136.394	110.597	-241.710	348.000	-13.787

Point Group C_{3h}

$S^\circ_{298.15} = [70.539] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

$\Delta H^\circ_f 0 = \text{Unknown}$

$\Delta H^\circ_f 298.15 = -237.16 \pm 0.80 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
3250(1)	Rotation	1185(2)
1080(1)	3150(2)	Rotation
881(1)	1440(2)	Rotation
652(1)	544(2)	

Bond Distances: B-O = $[1.36] \text{ \AA}$ O-H = $[0.96] \text{ \AA}$

Bond Angle: H-O-B = $[114]^\circ$ O-B-O = $[120]^\circ$

Product of the Moments of Inertia: $I_{AB}I_C = [1.15684 \times 10^{-114}] \text{ g.}^3 \text{ cm.}^6$

$\sigma^- = 3$

Heat of Formation.

The vapor pressures of $\text{H}_3\text{BO}_3(\text{c})$, 109 - 140°C, were measured by M. V. Stackelberg, P. Quatram and J. Dressel, Z. Elektrochem. **53**, 14 (1957). Using the vapor pressures reported, the heats of sublimation of $\text{H}_3\text{BO}_3(\text{c})$ were evaluated to be 24.4 ± 0.6 and $24.22 \text{ kcal. mole}^{-1}$ by the second and third law methods, respectively. The heat of formation ($\Delta H^\circ_f 298.15$) for $\text{H}_3\text{BO}_3(\text{c})$ was calculated from the $\Delta H^\circ_f 298.15$ and $\Delta H^\circ_s 298.15$ for $\text{H}_3\text{BO}_3(\text{c})$. The $\Delta H^\circ_s 298.15$ value adopted is the average of the second and third law values mentioned previously.

Heat Capacity and Entropy.

The molecular structure and constants were taken from C. W. F. T. Pistorius, J. Chem. Phys. **31**, 1454 (1959) based on an X-ray diffraction study on $\text{H}_3\text{BO}_3(\text{c})$ by W. H. Zachariasen, Acta Cryst. **7**, 305 (1954). The O-H bond distance was reestimated as 0.96 \AA instead of 0.88 \AA reported. From the existing infrared and Raman spectra data on $\text{H}_3\text{BO}_3(\text{c})$ and its aqueous solution C. W. F. T. Pistorius, loc. cit., carried out a normal coordinate treatment by means of Wilson's F-O matrix method and calculated the fifteen fundamental frequencies for $\text{H}_3\text{BO}_3(\text{c})$. For $\text{H}_3\text{BO}_3(\text{g})$ twelve reported frequencies were used and corrected to the average isotopic species. The three torsional frequencies, 824(1) and 209(2) cm.⁻¹, were not used based on an assumption that there are three internal rotations, i.e. three OH groups, each rotates about its own B-O bond. Employing the model of having three free rotating OH tops, the value of S_{400} was evaluated statistically as $75.522 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The corresponding value obtained by using the second law value of ΔS°_{400} , $48.39 \pm 1.42 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, for the reaction $\text{H}_3\text{BO}_3(\text{c}) = \text{H}_3\text{BO}_3(\text{g})$, is $75.97 \pm 1.42 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ which is in good agreement with the S°_{400} value based on a model having three free rotating groups. Thus the assumed model is adopted to evaluate the thermodynamic functions. The three principal moments of inertia are $I_A = I_C = 8.3320 \times 10^{-40} \text{ g. cm.}^2$ and $I_B = 1.6664 \times 10^{-36} \text{ g. cm.}^2$. The reduced moment of inertia for OH top is $I_r = 1.15321 \times 10^{-40} \text{ g. cm.}^2$. The infrared absorption spectrum of $\text{H}_3\text{BO}_3(\text{g})$ was observed under conditions where one atmosphere of water vapor with a path length of approximately one meter as background, by F. T. Greene, O. E. Leroy, S. P. Randall, J. R. Soulen, L. H. Spilner and J. L. Margrave, "Spectra and Thermodynamic Properties of Light-Element Oxides and Hydroxides", Proceedings of the Conference on Propellant Thermodynamics and Handling, Columbus, Ohio, July, 1969. The following fundamentals were obtained: 3220 cm.⁻¹ S., 1490 cm.⁻¹ S., 1199 cm.⁻¹ S., 681 cm.⁻¹ W., and 669 cm.⁻¹ W.



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	10.370	7.782	3.949	52.146	52.146	INFINITE
200	17.566	27.440	3.441	53.576	48.618	106.249
298	25.081	29.480	0.000	54.062	43.446	47.474
300	25.120	29.423	0.043	54.231	38.002	27.748
400	24.120	32.456	2.420	54.678	32.594	17.608
500	24.410	37.066	28.175	55.007	27.010	11.806
600	25.343	42.383	30.176	55.120	21.308	7.304
700	26.500	48.160	32.223	55.150	15.772	4.924
800	27.830	54.534	34.100	55.006	10.159	3.275
900	29.240	56.594	36.079	54.850	4.562	1.408
1000	30.720	58.392	38.092	54.688	1.016	0.222
1100	32.270	60.000	40.000	54.444	7.603	1.511
1200	33.890	61.452	41.811	54.111	14.997	2.724
1300	35.570	62.762	43.523	53.708	22.274	3.744
1400	37.300	63.932	45.139	53.232	29.570	4.616
1500	39.070	64.964	46.664	52.692	36.861	5.367
1600	40.880	65.864	48.107	52.109	44.080	6.022
1700	42.720	66.632	49.467	51.485	51.233	6.596
1800	44.580	67.272	50.740	50.772	58.339	7.107
1900	46.460	67.792	51.931	50.000	65.342	7.562
2000	48.360	68.192	53.041	49.172	72.294	7.969

Mar. 31, 1963; Dec. 31, 1964

POTASSIUM TETRAHYDROBORATE (KBH_4) (CRYSTAL)

MOL. WT. = 53.952

$$\Delta H_f^0 = -52.15 \pm .55 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -54.25 \pm .55 \text{ kcal. mole}^{-1}$$

$$S_{298.15} = 25.48 \text{ cal. deg.}^{-1} \text{ mole}$$

$$T_d = [770]^\circ \text{K}$$

Heat of Formation.

The heat of reaction of $\text{KBH}_4(\text{c})$ with hydrochloric acid has been measured by solution calorimetry and reported by W. H. Johnson, R. H. Schumm, I. H. Wilson, and E. J. Prosen, *J. Res. Nat'l. Bur. Std.* 85A, 97 (1961)

$\text{KBH}_4(\text{c}) + \text{HCl}(\text{g}) + 3\text{H}_2\text{O}(\text{liq}) \rightarrow \text{KCl}(\text{c}) + \text{H}_3\text{BO}_3(\text{c}) + 4\text{H}_2(\text{g}) \quad \Delta H_r = -84.62 \pm .44 \text{ kcal. mole}$
The $\Delta H_f^{298.15}$ values for $\text{HCl}(\text{g})$ and $\text{H}_3\text{BO}_3(\text{c})$ were obtained from the JANAP Tables. The $\Delta H_f^{298.15}$ value for $\text{KCl}(\text{c})$ was calculated from $\Delta H_f^{298.15} \text{ K}^+ = -60.52 \text{ kcal. mole}^{-1}$, $\Delta H_f^{298.15} \text{ Cl}^- = -59.952 \text{ kcal. mole}^{-1}$ and $\Delta H \text{ dilution} = 4.12 \text{ kcal. mole}^{-1}$ obtained from NES. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans. $\Delta H_f^{298.15}$ for $\text{H}_2\text{O}(\text{liq})$ was obtained from W. H. Evans, loc. cit. Unpublished data of The Dow Chemical Company Thermal Laboratory give a value of $\Delta H_f^{298.15} = -55.0 \pm 1.0 \text{ kcal. mole}^{-1}$ by solution calorimetry.

Heat Capacity and Entropy.

C_p and S° at temperatures below 298.15°K were reported by G. T. Furukawa, M. L. Reilly, and J. H. Piciorelli, *J. Res. Nat'l. Bur. Std.* 69A, 651 (1964). The values of C_p in the range from 298.15 to 700°K were obtained from T. B. Douglas and A. W. Harman, *J. Res. Nat'l. Bur. Std.* 60, 117 (1956). These two sets of C_p data were plotted and joined smoothly at 298.15°K. The values of C_p above 700°K were estimated by graphical extrapolation.

Temperature of Decomposition.

The temperature of decomposition (into constituent elements) was estimated according to a report by T. B. Douglas and A. W. Harman, loc. cit.



Lithium Tetrahydroborate (LiBH_4)
(Crystal) Mol. Wt. = 21.792

LITHIUM TETRAHYDROBORATE (LiBH_4) (CRYSTAL)

MOL. WT. = 21.792

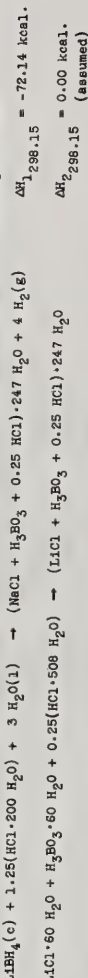
T, °K.	C _p	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+0.00	INFINITE	-	3.028	- 43.105	-	INFINITE
100	7.175	4.084	31.660	- 2.798	- 44.476	- 39.625	87.033
200	14.239	11.470	19.727	- 1.651	- 45.097	- 34.917	38.154
298	19.727	18.120	-	+0.000	- 45.522	- 29.624	21.860
300	19.835	18.243	-	+0.037	- 45.527	- 29.727	21.455
400	21.750	22.231	18.924	2.123	- 45.772	- 24.422	13.943
500	23.440	29.273	20.502	4.385	- 46.739	- 18.983	8.297
600	25.130	33.708	22.341	6.821	- 46.891	- 13.415	4.866
700	26.270	37.672	24.253	9.304	- 46.938	- 7.630	2.444
800	27.071	41.437	26.055	11.827	- 46.979	- 3.453	1.010
900	27.635	45.035	27.635	14.780	- 46.983	- 0.810	0.481
1000	27.870	47.327	29.802	17.525	- 46.848	8.915	1.948
1100	27.818	49.967	31.517	20.295	- 46.822	14.490	2.879
1200	28.040	52.397	33.157	23.086	- 46.804	20.064	3.654
1300	28.070	54.468	34.780	25.800	- 46.800	25.630	4.304
1400	28.256	56.294	36.223	28.729	- 46.811	31.208	4.872
1500	28.517	58.706	37.657	31.573	- 46.843	36.782	5.359
1600	28.660	60.591	39.031	34.432	- 46.894	42.357	5.785
1700	28.795	62.293	40.368	37.305	- 47.007	47.927	6.333
1800	28.914	63.841	41.681	40.184	- 47.181	53.496	6.842
1900	29.040	65.509	42.830	43.089	- 47.421	59.067	7.310
2000	29.150	67.001	44.002	45.949	- 47.748	64.701	7.742
						72.412	7.912

$\Delta H_f^0 = -43.105 \pm 0.05 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 298.15 = -45.522 \pm 0.05 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = \text{Unknown}$

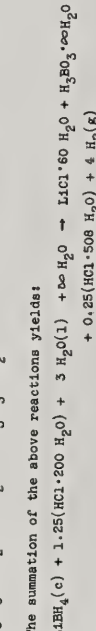
$S_{298.15}^0 = 18.120 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = [750^\circ \text{K.}]$

Heat of Formation.

The heat of formation of $\text{LiBH}_4(\text{c})$ was calculated from the solution calorimetry of W. D. Davis, L. S. Mason, and G. Stegeman J. Am. Chem. Soc. **71**, 2775 (1949). The heats of reaction were measured for the following reactions:



The summation of the above reactions yields:



The heat of formation of Lithium Borohydride crystal was calculated to be $-45.522 \text{ kcal. mole}^{-1}$ with the following auxiliary data:

Compound	Heat of Formation at 298.15	Reference
HCl (508 H ₂ O)	-39.815	HCl(g) JANAF; Dilution data from NES. Rept. 8504, 1 July 1964 Appendix III by W. H. Evans
HCl (200 H ₂ O)	-39.696	HCl(g) JANAF; Dilution data from W. H. Evans, loc. cit.
LiCl (60 H ₂ O)	-106.023	Li ⁺ see NaBH_4 tables; Cl ⁻ and dilution data W. H. Evans, loc. cit.
H ₂ BO ₃ (∞ H ₂ O)	-256.05	JANAF H ₂ BO ₃ (c) and dilution data from J. Smisko and L. S. Mason J. of Am. Chem. Soc. 72 , 3879 (1950)

*This $\Delta H_f^0 298.15$ value was obtained from J. Smisko and L. S. Mason loc. cit.

Heat Capacity and Entropy.

The low temperature heat capacities, 15.72 - 302.88 °K were obtained from the measurements by N.C. Hallett and H. L. Johnston, J. Am. Chem. Soc., **75**, 1496 (1953). The C_p values above 298.15°K were estimated by comparison with the C_p 's for NaBH_4 .

The entropy was based on S_{15}^0 (extrap) = 0.0874 reported by N. C. Hallett and H. L. Johnston loc. cit.

Melting Data.

T_m was estimated by comparison with the T_m for NaBH_4 .



Sodium Tetrahydroborate (NaBH₄)

(Crystal) Mol. Wt. = 37.84

SODIUM TETRAHYDROBORATE (NaBH₄)

(CRYSTAL)

MOL. WT. = 37.84

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	0.000	0.000	INFINITE	3.893	-43.862	-43.862	INFINITE
100	11.123	11.123	24.232	3.893	-43.862	-43.862	88.446
200	17.076	19.658	24.232	3.893	-43.862	-43.862	85.471
298	20.670	24.232	24.232	4.000	-45.855	-30.380	22.208
300	20.708	24.360		4.038	-45.855	-30.284	22.061
400	22.600	30.583		2.206	-46.741	-35.007	13.862
500	24.230	35.814		4.253	-46.946	-39.548	8.544
600	25.960	40.395		7.068	-47.027	-44.038	5.120
700	27.550	44.517		0.744	-46.977	-48.565	2.674
800	28.760	48.276		12.561	-46.812	-53.089	0.844
900	29.700	51.720		15.486	-46.567	-57.363	0.574
1000	30.460	54.889		18.494	-46.270	-61.484	1.701
1100	31.080	57.821		21.571	-45.945	-65.417	2.617
1200	31.490	60.544		24.700	-45.584	-69.160	3.458
1300	31.710	63.074		27.862	-45.190	-72.727	4.236
1400	31.820	65.429		31.039	-44.775	-76.133	4.966
1500	31.860	67.626		34.210	-44.340	-79.389	5.649
1600	31.890	69.683		37.411	-43.880	-82.512	6.289
1700	31.910	71.617		40.601	-43.394	-85.512	6.889
1800	31.920	73.441		43.782	-42.884	-88.394	7.457
1900	31.950	75.167		46.986	-42.357	-91.167	7.998
2000	32.000	76.807		50.183	-41.813	-93.833	8.514

Dec. 31, 1960; Dec. 31, 1964

$$S_{298}^{0} = 24.232 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 189.9^{\circ}\text{K}$$

$$T_m = 770^{\circ}\text{K}$$

$$\Delta H_f^0 = -43.86 \pm .07 \text{ kcal. mole}^{-1}$$

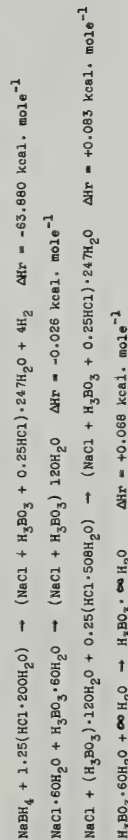
$$\Delta H_f^0 = -45.85 \pm .07 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 0.2388 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = \text{Unknown}$$

Heat of Formation.

The heat of formation was calculated from the solution calorimetry of W. D. Davis, L. S. Mason and G. Stegeman, J. Am. Chem. Soc. 71, 2775 (1949). The heats of reaction and mixing were measured for the following reactions:



The summation of the above equations yields:



$$\Delta H_r = -63.869 \text{ kcal. mole}^{-1}$$

The ΔH_f^0 298.15 values for HCl were obtained from JANAF value for HCl(g) and heat of dilution data of NBS. Rept. 8504, 1 July 1964 - Appendix III by W. H. Evans. The ΔH_f^0 298.15 $\text{H}_2\text{O}(l)$ value was obtained from W. H. Evans loc. cit. The ΔH_f^0 298.15 value for NaCl was obtained from JANAF value of NaCl(c) together with dilution data from W. H. Evans, loc. cit. The ΔH_f^0 298.15 value for H_3BO_3 was obtained from JANAF value for $\text{H}_3\text{BO}_3(c)$ together with dilution data of J. Sziklo and L. S. Mason, J. of Am. Chem. Soc. 72, 3679 (1950).

Heat Capacity and Entropy.

The low temperature heat capacity (15.76 - 301.26) was obtained from H. L. Johnston and N. C. Hallett, J. Am. Chem. Soc. 75, 1467 (1953). In the area of transition (189-193.5°K) the average $\Delta H = 635.3$ cal./mole and the average $\Delta S = 3.35$ cal./mole °K were adopted from H. L. Johnston and N. C. Hallett, loc. cit. Using the present base line these ΔH and ΔS values yield a heat of transition of 0.2388 kcal. mole⁻¹. The low temperature heat capacity was fitted with the smoothed heat capacity data (298.15 - 700°K) of T. B. Douglas and A. W. Harman, J. Research Natl. Bur. Standards 60, 117 (1956). The heat capacity above 700°K was extrapolated from the plot of both sets of data.

Transition Data.

The temperature and heat of transition were obtained from H. L. Johnston and N. C. Hallett loc. cit.

Melting Data.

The melting data was obtained from T. B. Douglas and A. W. Harman loc. cit.

Boron Iodide (BI)

(Ideal Gas) Mol. Wt. = 137.73

BORON MONOIODIDE (BI)

(IDEAL GAS)

MOL. WT. = 137.73

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	-	2.178	72.691	72.691	INFINITE
100	6.986	47.539	62.363	-1.482	68.999	-150.791	
200	7.485	52.508	56.322	-763	64.952	-70.973	
298	7.821	55.804	53.004	.000	60.978	-44.696	
300	8.029	55.653	55.604	.015	60.903	-44.366	
400	8.366	58.013	55.923	.836	56.962	-31.121	
500	8.568	59.804	56.537	1.684	53.980	-23.593	
600	8.696	61.478	57.333	2.567	51.664	-18.818	
700	8.782	62.825	57.938	3.421	49.381	-15.111	
800	8.844	64.002	58.624	4.303	47.073	-12.859	
900	8.891	65.047	59.280	5.190	44.799	-10.876	
1000	8.927	65.985	59.905	6.081	42.543	-9.297	
1100	8.958	66.838	60.497	6.974	40.299	-8.006	
1200	8.983	67.618	61.058	7.872	38.073	-6.939	
1300	9.006	68.338	61.591	8.771	35.862	-6.029	
1400	9.026	69.006	62.097	9.673	33.666	-5.255	
1500	9.044	69.630	62.579	10.577	31.482	-4.587	
1600	9.061	70.214	63.038	11.482	29.317	-4.004	
1700	9.076	70.764	63.476	12.389	27.163	-3.492	
1800	9.091	71.283	63.896	13.297	25.025	-3.038	
1900	9.105	71.775	64.298	14.207	22.900	-2.634	
2000	9.119	72.242	64.683	15.118	20.780	-2.272	
2100	9.132	72.687	65.054	16.031	18.693	-1.945	
2200	9.145	73.113	65.411	16.945	16.605	-1.650	
2300	9.158	73.519	65.754	17.860	14.534	-1.381	
2400	9.170	73.909	66.086	18.776	12.474	-1.136	
2500	9.182	74.284	66.407	19.694	10.431	-.921	
2600	9.194	74.644	66.716	20.612	8.413	-.732	
2700	9.205	74.992	67.017	21.532	6.414	-.559	
2800	9.217	75.326	67.307	22.453	4.438	-.399	
2900	9.228	75.650	67.590	23.376	2.481	-.250	
3000	9.239	75.963	67.863	24.299	54.763	-.112	
3100	9.251	76.266	68.130	25.224	54.490	-.016	
3200	9.262	76.560	68.389	26.149	54.218	.136	
3300	9.273	76.845	68.641	27.076	53.945	.248	
3400	9.284	77.122	68.886	28.004	53.674	.353	
3500	9.295	77.392	69.125	28.933	53.403	.451	
3600	9.306	77.654	69.358	29.863	53.132	.543	
3700	9.317	77.909	69.586	30.794	52.861	.630	
3800	9.327	78.157	69.808	31.726	52.592	.712	
3900	9.338	78.400	70.026	32.659	52.322	.790	
4000	9.349	78.636	70.238	33.594	52.052	.866	
4100	9.360	78.867	70.446	34.529	51.782	.943	
4200	9.370	79.093	70.649	35.466	51.512	1.020	
4300	9.381	79.314	70.848	36.403	51.242	1.097	
4400	9.392	79.529	71.043	37.342	50.972	1.174	
4500	9.402	79.741	71.234	38.281	50.702	1.251	
4600	9.413	79.947	71.421	39.222	50.432	1.328	
4700	9.423	80.150	71.604	40.164	50.162	1.405	
4800	9.434	80.348	71.784	41.107	49.892	1.482	
4900	9.445	80.543	71.961	42.051	49.622	1.559	
5000	9.455	80.734	72.135	42.996	49.352	1.636	
5100	9.466	80.921	72.305	43.942	49.082	1.713	
5200	9.476	81.105	72.473	44.889	48.812	1.790	
5300	9.487	81.286	72.637	45.837	48.542	1.867	
5400	9.497	81.463	72.799	46.786	48.272	1.944	
5500	9.508	81.638	72.958	47.737	48.002	2.021	
5600	9.518	81.809	73.115	48.688	47.732	2.098	
5700	9.529	81.977	73.269	49.640	47.462	2.175	
5800	9.539	82.143	73.420	50.594	47.192	2.252	
5900	9.550	82.306	73.570	51.548	46.922	2.329	
6000	9.560	82.467	73.716	52.503	46.652	2.406	

June 30, 1963; Dec. 31, 1963; Dec. 31, 1964

Ground State Configuration [¹Σ⁺]

S_{298.15} = [55.604] cal. deg.⁻¹ mole⁻¹

ΔH_f⁰ = [72.7 ± 10] kcal. mole⁻¹

ΔH_f⁰ 298.15 = [73.0 ± 10] kcal. mole⁻¹

Electronic Levels and Quantum Weight

$\frac{E_i, \text{cm}^{-1}}{E_1, \text{cm}^{-1}}$ $\frac{g_i}{[1]}$

ω_e = [600] cm.⁻¹

σ' = 1

α_e = [0.3912] cm.⁻¹

r_e = [2.08] Å

Heat of Formation.

The ratio D(BI) / (ΔH_f(BF₃)/3) = 1.177, where ΔH_f signifies the heat of atomization, was applied to BI₃ giving D(BI) = 84.4 kcal. mole⁻¹ and ΔH_f 298 = 75 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond length was first estimated by comparison with the ratio of the bond lengths in the other boron trihalides and monohalides. The vibrational frequency was then calculated using Guggenheimer's Relation [Proc. Phys. Soc. (London) 58, 456 (1946)] which was checked using BBr and shown to give an excellent fit. The quantity $\chi_e \mu^{1/2}$, where μ is the reduced mass, has been shown to be constant for similar molecules and its value was transferred from BBr to give χ_e and ω_e for BI. α_e was then calculated using the Morse potential function and B_e was determined from the bond length. The ground state configuration was assumed to be the same as that in BBr.

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	0.000	INFINITE	-2.993	58.453	58.453	INFINITE
100	9.318	62.311	2.116	2.116	-2.116	58.453	58.453	-
200	10.696	66.490	7.806	-1.103	-1.103	58.453	58.453	-
298	11.731	73.964	73.964	0.000	0.000	58.000	44.642	-32.722
300	11.748	74.037	73.964	0.022	0.022	57.993	44.560	-32.460
400	12.447	77.520	78.434	1.234	1.234	53.711	40.280	-22.007
500	12.880	80.346	79.343	2.502	2.502	43.043	37.937	-16.561
600	13.155	82.722	79.480	3.805	3.805	36.921	36.921	-13.448
700	13.336	84.765	77.435	5.130	42.884	35.920	-11.214	-
800	13.461	86.554	78.466	6.470	42.778	34.932	-9.542	-
900	13.549	88.145	78.454	7.821	42.659	33.957	-8.245	-
1000	13.615	89.576	80.356	9.178	42.527	32.999	-7.211	-
1100	13.664	90.876	81.290	10.543	42.380	32.052	-6.368	-
1200	13.702	92.067	82.140	11.912	42.221	31.120	-5.657	-
1300	13.732	93.165	82.946	13.284	42.050	30.208	-5.077	-
1400	13.756	94.183	83.713	14.658	41.865	29.298	-4.573	-
1500	13.776	95.133	84.443	16.035	41.668	28.405	-4.136	-
1600	13.792	96.022	85.139	17.413	41.459	27.530	-3.760	-
1700	13.805	96.859	85.804	18.793	41.238	26.666	-3.428	-
1800	13.816	97.648	86.440	20.174	41.007	25.814	-3.134	-
1900	13.826	98.386	87.046	21.556	40.767	24.973	-2.873	-
2000	13.834	99.073	87.633	22.939	40.521	24.150	-2.639	-
2100	13.841	99.760	88.197	24.323	40.269	23.339	-2.429	-
2200	13.847	100.424	88.739	25.707	40.010	22.538	-2.239	-
2300	13.853	101.040	89.260	27.092	39.746	21.752	-2.067	-
2400	13.857	101.607	89.768	28.478	39.477	20.976	-1.910	-
2500	13.861	102.135	90.249	29.864	39.203	20.218	-1.776	-
2600	13.865	102.739	90.719	31.250	38.943	19.472	-1.663	-
2700	13.868	103.262	91.174	32.637	38.700	18.740	-1.559	-
2800	13.871	103.767	91.615	34.024	38.474	18.024	-1.463	-
2900	13.874	104.244	92.042	35.411	38.271	17.321	-1.375	-
3000	13.876	104.724	92.457	36.798	38.084	16.630	-1.293	-
3100	13.879	105.179	92.860	38.186	37.917	15.950	-1.217	-
3200	13.881	105.620	93.252	39.574	37.774	15.289	-1.146	-
3300	13.882	106.047	93.633	40.962	37.650	14.646	-1.081	-
3400	13.884	106.461	94.005	42.350	37.543	14.021	-1.019	-
3500	13.886	106.864	94.368	43.739	37.450	13.414	-0.962	-
3600	13.887	107.255	94.719	45.128	37.364	12.824	-0.909	-
3700	13.888	107.635	95.053	46.517	37.290	12.250	-0.858	-
3800	13.890	108.006	95.379	47.905	37.224	11.691	-0.811	-
3900	13.891	108.367	95.697	49.294	37.167	11.146	-0.767	-
4000	13.891	108.718	96.047	50.684	37.119	10.613	-0.722	-
4100	13.892	109.061	96.360	52.073	37.073	10.091	-0.684	-
4200	13.893	109.396	96.667	53.462	37.031	9.579	-0.648	-
4300	13.894	109.723	96.966	54.851	37.000	9.074	-0.611	-
4400	13.895	110.045	97.248	56.241	36.969	8.579	-0.576	-
4500	13.895	110.355	97.540	57.630	36.938	8.093	-0.542	-
4600	13.896	110.660	97.829	59.020	36.908	7.618	-0.508	-
4700	13.897	110.959	98.105	60.410	36.879	7.153	-0.474	-
4800	13.897	111.252	98.376	61.799	36.851	6.697	-0.440	-
4900	13.898	111.538	98.642	63.189	36.824	6.250	-0.406	-
5000	13.898	111.818	98.903	64.579	36.799	5.811	-0.372	-
5100	13.899	112.094	99.159	65.969	36.769	5.379	-0.338	-
5200	13.899	112.364	99.410	67.359	36.739	4.953	-0.304	-
5300	13.900	112.629	99.657	68.749	36.709	4.534	-0.270	-
5400	13.900	112.889	99.900	70.139	36.679	4.121	-0.236	-
5500	13.901	113.144	100.138	71.529	36.649	3.714	-0.202	-
5600	13.901	113.394	100.372	72.919	36.619	3.313	-0.168	-
5700	13.901	113.640	100.603	74.309	36.589	2.917	-0.134	-
5800	13.902	113.882	100.830	75.699	36.559	2.526	-0.100	-
5900	13.902	114.120	101.053	77.089	36.529	2.140	-0.066	-
6000	13.902	114.355	101.273	78.479	36.499	1.759	-0.032	-

Mar. 31, 1962; Dec. 31, 1962; Dec. 31, 1964

Point Group [C_{2v}]
S₂98.15 = [73.964] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight [2]

ΔH_f^o = [58.5 ± 15] kcal. mole⁻¹
ΔH_f^o 298.15 = [58.0 ± 15] kcal. mole⁻¹

Vibrational Levels and Degeneracies

ω, cm.⁻¹
[550](1)
[110](1)
[770](1)

Bond Distance: B-I = [2.06] Å
Bond Angle: I-B-I = [120°]
Product of the Moments of Inertia: I_AI_BI_C = 3.33503 X 10⁻¹¹³ g.³ cm.⁶
σ = 2

Heat of Formation.

The heat of formation was estimated by analogy with BP₃, specifically the ratio

$$\Delta H_f(BP_3) \rightarrow BP_3 + X / \Delta H_f(BP_3) \rightarrow B + 3X$$

was taken as 0.347.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from force constants transferred from the trihalide given by G. Herzberg "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand, Inc., (1945). The bond length was taken between those of the mono and trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The individual moments of inertia were I_B = 1.6278 X 10⁻³⁹ g. cm.², I_A = 134.1670 X 10⁻³⁹ g. cm.² and I_C = 135.9848 X 10⁻³⁹ g. cm.²

Boron Triiodide (BI_3)

(Ideal Gas)	Mol. wt.	=	391.55
-------------	----------	---	--------

[illegible]

Dec. 31, 1961; Sept. 30, 1962; Dec. 31, 1964

BORON TRIIODIDE (BI₃)

(IDEAL GAS)

MOL. WT. = 391,55

Point Group D_{3h}
$$\Delta H_{f,0}^{\circ} = 18.0 + 12 \text{ kcal. mole}^{-1}$$
$$S_{298}^{\circ} = 83.322 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$\Delta H^{\circ}_{\text{f}} \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies

-1 cm.

$$\frac{1.90(1)}{1.90(1)}$$

339(1)

710(2)

100(2)

Bond Angle: I-B-I = $[120^\circ]$

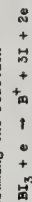
6-5

Product of the Moments of Inertia = $[4.418202] \times 10^{-111} \text{ g. cm.}^6$

THE UNIVERSITY OF CHICAGO PRESS

Heat of Formation.

W. S. Koski, J. J. Kaufman and C. F. Pachucki, J. Am. Chem. Soc. **81**, 1326 (1959) measured the appearance potential of the P^+ ion from BI_2 . Assuming the reaction



one can calculate the heat of atomization of Br_2 as 8.31 ± 0.5 e.v. The analogous reaction for Br_2 can be checked independently and shows the process to be valid. This value leads to a $\Delta H_f^\circ 298 = 17.0 \pm 12$ kcal. mole $^{-1}$, if the process is assumed to occur at 298°K.

Heat Capacity and Entropy.

Vibrational frequencies were taken from T. Wentink and V. H. Tiensau, *J. Chem. Phys.* **28**, 826 (1958) modified according to the natural abundance of boron. The B-I distance was estimated by Koski et al., loc. cit., and the angle was estimated by analogy with the other boron trihalides. The three principal moments of inertia are: $I_A = I_B = 3.30238 \times 10^{-37}$ and $I_C = 2.60476 \times 10^{-37}$ gm.²

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	∞.000	INFINITE	-2.142	-241.960	-241.960	INFINITE
100	4.501	22.204	-1.977	-238.540	-238.540	521.304
200	10.511	7.429	-1.223	-235.252	-235.252	255.067
298	14.291	12.551	∞.000	-228.870	-228.870	168.491
300	14.394	12.581	∞.026	-228.788	-228.788	167.392
400	16.992	12.950	1.604	-228.271	-228.271	123.077
500	18.854	20.960	3.400	-220.658	-220.658	96.449
600	20.411	24.538	5.365	-214.113	-214.113	78.668
700	21.759	27.759	7.463	-208.290	-208.290	64.848
800	23.157	30.796	9.727	-203.637	-203.637	54.048
900	24.448	33.596	12.108	-202.011	-202.011	49.053
1000	25.711	36.237	14.616	-197.423	-197.423	43.145
1100	26.984	38.764	17.240	-192.864	-192.864	38.321
1200	28.197	41.162	20.000	-188.332	-188.332	34.572
1300	29.410	43.444	22.886	-183.827	-183.827	30.824
1400	30.627	45.672	25.886	-179.349	-179.349	28.032
1500	31.840	47.826	28.011	-174.903	-174.903	25.534
1600	33.049	49.920	30.246	-170.488	-170.488	23.387
1700	34.254	51.960	32.621	-166.104	-166.104	21.275
1800	35.458	53.952	35.107	-161.753	-161.753	19.334
1900	36.661	55.901	37.421	-157.442	-157.442	17.606
2000	37.862	57.812	39.593	-153.169	-153.169	16.061
2100	39.062	59.688	41.524	-148.936	-148.936	14.671
2200	40.261	61.533	43.261	-144.745	-144.745	13.416
2300	41.461	63.349	44.907	-140.595	-140.595	12.278
2400	42.656	65.139	46.479	-136.487	-136.487	11.243
2500	43.852	66.905	48.157	-132.422	-132.422	10.289

June 30, 1961; Dec. 31, 1964

$\Delta H_f^0 = -241.96 \pm .20$ kcal. mole⁻¹
 ΔH_f^0 298.15 = -243.29 \pm .20 kcal. mole⁻¹
 $\Delta H_m^0 = 8.033 \pm .10$ kcal. mole⁻¹

Heat of Formation.

G. O. Sinks, Thermal Research Laboratory, The Dow Chemical Co., private communication, July 1960 has measured ΔH_f^0 298.15 for the following reaction:



From this heat of reaction the ΔH_f^0 298.15 for $\text{LiBO}_2(c)$ is calculated to be -243.29 kcal. mole⁻¹ with the following auxiliary heats of formation:

	ΔH_f^0 298.15 (kcal. mole ⁻¹)	Source
$\text{H}_3\text{BO}_3 \cdot 11\text{H}_2\text{O}$	-256.23	Dilution data from J. Smisko and L. S. Mason, J. of Am. Chem. Soc. 72, 3678 (1950)
$\text{HNO}_3 \cdot 11\text{H}_2\text{O}$	-49.44	NBS. Rept. 6504, 1 July 1964 - Appendix III by W. H. Evans
$\text{H}_2\text{O}(l)$	-68.315	W. H. Evans, loc. cit.
$\text{LiNO}_3 \cdot 11\text{H}_2\text{O}$	-115.747	*S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958); J. R. Gunn, R. Gunn Lawrence Radiation Lab. UCRL-7992, 5, July, (1964).

**Dilution and other auxiliary data from W. H. Evans, loc. cit.

L. Shartniss and W. Cappa, J. Am. Ceram. Soc. 37, 27 (1954), measured the heats of solution in nitric acid of various $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses and crystalline mixtures containing 0 to 48 mole % Li_2O . These results were extrapolated to 50 mole % and yielded ΔH_f^0 298.15 = -45.20 kcal. for the following reaction:



With JANAF values for $\text{Li}_2\text{O}(c)$ and $\text{B}_2\text{O}_3(c)$ the ΔH_f^0 298.15 for $\text{LiBO}_2(c)$ was calculated to be -245.97 \pm .80 kcal. mole⁻¹. This value is in fair agreement with the value adopted for the table.

* $\text{Li}(c) + \text{H}_2\text{O}(l) \rightarrow \text{LiOH} \cdot 1000 \text{H}_2\text{O}(sol.) + 1/2 \text{H}_2$	ΔH_f^0 298.15 = -53.115 \pm 0.019 kcal. mole ⁻¹
** $\text{LiOH} \cdot 1000 \text{H}_2\text{O}(sol.) \rightarrow \text{LiOH} \infty \text{H}_2\text{O}$	$\Delta H_{\text{dilution}}^0$ 298.15 = +1.02 kcal. mole ⁻¹
$\text{LiOH}(\infty \text{H}_2\text{O}) \rightarrow \text{Li}^+(\infty \text{H}_2\text{O}) + \text{OH}^-(\infty \text{H}_2\text{O})$	ΔH_f^0 298.15 = 0.00
$\text{LiNO}_3(\infty \text{H}_2\text{O}) \rightarrow \text{Li}^+(\infty \text{H}_2\text{O}) + \text{NO}_3^-(\infty \text{H}_2\text{O})$	ΔH_f^0 298.15 = 0.00
$\text{LiNO}_3(\infty \text{H}_2\text{O}) \rightarrow \text{LiNO}_3 \cdot 11\text{H}_2\text{O}$	ΔH_f^0 dilution = .171 kcal. mole ⁻¹

Heat Capacity and Entropy.

P. L. Oetting and W. E. Hutton, The Dow Chemical Company, private communication, April, 1961, have measured C_p from 13° to 328°K. R. A. McDonald, Thermal Research Laboratory The Dow Chemical Company, private communication, April, 1961 has measured H_f^0 -298.15 from 289° to 1115°K. The above data were adopted for the table. The C_p values above T_m were obtained by graphical extrapolation.

The entropy was based on $S^0 = .013$ cal. mole⁻¹ deg.⁻¹ at 15°K. calculated from the low temperature C_p values of P. L. Oetting and W. E. Hutton loc. cit.

Melting Data.

The T_m and ΔH_m adopted for this table were obtained from R. A. McDonald loc. cit. The following cryoscopic data have been published: C. Petit and M. Jaeger, Compt. rend. 244, 1734 (1957), $T_m = 1108^\circ\text{K}$, $\Delta H_m = 7.4$ kcal. mole⁻¹; O. Zarych, colloques intern, centre, nat'l. recherche sci. (Paris) 39, Electrolyse 634-637 (1962), $\Delta H_m = 6.3 \pm 0.6$ kcal. mole⁻¹; O. Sutra, Compt. rend. 234, 1883 (1952), $T_m = 1113^\circ\text{K}$. and $\Delta H_m = 8.3$ kcal. mole⁻¹.

Lithium Metaborate (LiBO₂)

(Liquid) Mol. Wt. = 49.76

LITHIUM METABORATE (LiBO₂)

(LIQUID)

MOL. WT. = 49.76

T, °K.	C _p	S°	$-(F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔH°_f	ΔF°_f	Log K _p
0							
100	14.291	15.591	15.591	.000	-236.810	-226.365	165.022
200	14.354	15.680	15.591	.026	-236.822	-226.289	164.863
300	14.400	15.740	15.604	.060	-236.898	-222.096	121.342
400	14.434	15.780	15.620	.100	-236.964	-217.817	95.203
500	14.459	15.806	15.636	.140	-236.943	-213.447	77.744
600	14.477	15.823	15.652	.180	-236.923	-209.090	65.274
700	14.490	15.836	15.665	.220	-236.904	-204.781	55.661
800	14.500	15.846	15.676	.260	-236.886	-200.529	48.717
900	14.508	15.854	15.684	.300	-236.869	-196.328	42.671
1000	14.514	15.860	15.690	.340	-236.853	-192.174	38.207
1100	14.518	15.864	15.694	.380	-236.838	-188.061	34.223
1200	14.521	15.867	15.697	.420	-236.823	-184.000	30.695
1300	14.523	15.869	15.699	.460	-236.809	-180.000	27.590
1400	14.525	15.871	15.701	.500	-236.795	-176.051	24.865
1500	14.527	15.873	15.703	.540	-236.781	-172.156	22.480
1600	14.528	15.874	15.704	.580	-236.768	-168.316	20.395
1700	14.529	15.875	15.705	.620	-236.755	-164.531	18.568
1800	14.530	15.876	15.706	.660	-236.742	-160.800	16.950
1900	14.531	15.877	15.707	.700	-236.730	-157.120	15.515
2000	14.532	15.878	15.708	.740	-236.718	-153.495	14.240
2100	14.533	15.879	15.709	.780	-236.706	-149.915	13.110
2200	14.534	15.880	15.710	.820	-236.695	-146.377	12.110
2300	14.535	15.881	15.711	.860	-236.684	-142.880	11.230
2400	14.536	15.882	15.712	.900	-236.673	-139.423	10.460
2500	14.537	15.883	15.713	.940	-236.662	-136.005	9.790
2600	14.538	15.884	15.714	.980	-236.651	-132.626	9.210
2700	14.539	15.885	15.715	1.020	-236.640	-129.286	8.710
2800	14.540	15.886	15.716	1.060	-236.630	-126.000	8.280
2900	14.541	15.887	15.717	1.100	-236.620	-122.750	7.910
3000	14.542	15.888	15.718	1.140	-236.610	-119.530	7.600
3100	14.543	15.889	15.719	1.180	-236.600	-116.350	7.340
3200	14.544	15.890	15.720	1.220	-236.590	-113.200	7.120
3300	14.545	15.891	15.721	1.260	-236.580	-110.080	6.940
3400	14.546	15.892	15.722	1.300	-236.570	-107.000	6.790
3500	14.547	15.893	15.723	1.340	-236.560	-104.000	6.670
3600	14.548	15.894	15.724	1.380	-236.550	-101.000	6.570
3700	14.549	15.895	15.725	1.420	-236.540	-98.000	6.480
3800	14.550	15.896	15.726	1.460	-236.530	-95.000	6.400
3900	14.551	15.897	15.727	1.500	-236.520	-92.000	6.330
4000	14.552	15.898	15.728	1.540	-236.510	-89.000	6.270

 $S^\circ_{298.15} = [15.591] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H^\circ_f 298.15 = [-236.819] \text{ kcal. mole}^{-1}$ $\Delta H^\circ_m = 8.09 \pm .10 \text{ kcal. mole}^{-1}$ $T_m = 1117 \pm 1^\circ \text{K.}$ $\Delta H^\circ_v = [50.79] \text{ kcal. mole}^{-1}$ $T_b = [2284]^\circ \text{K.}$

Heat of Formation.

 $\Delta H^\circ_f(l)$ was obtained from $\Delta H^\circ_f(c)$ by addition of ΔH°_m and difference between ($H^\circ_{1117} - H^\circ_{298.15}$) for the crystal and liquid.

Heat Capacity and Entropy.

R. A. McDonald, Thermal Research Laboratory, The Dow Chemical Company, private communication, April 1961, has measured $H_p - H_{298.15}$ from 1118° to 1707°K. The constant value of C_p measured between 1118° and 1707°K. has been extrapolated above and below this range. Lithium metaborate is assumed to have a glass transformation temperature at 745°K. below which C_p of the glass is assumed equal to that of the crystal.

The entropy of the liquid was calculated from the entropy of the crystal in a manner analogous to the heat of formation.

Melting Data.

The ΔH°_m and T_m values were obtained from R. A. McDonald loc. cit.

Vaporization Data.

The boiling point was found from graphing the ΔH°_f 's of the liquid and gas. The heat of vaporization was found from the difference in ΔH°_f 's of the liquid and gas at T_b .

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _f
0	∞	∞	∞	∞	∞	∞
100	8.053	51.878	70.249	-1.837	-159.543	INFINITE
200	9.260	51.779	62.672	-1.837	-159.585	350.618
298	10.666	61.742	∞	-1.837	-160.382	176.110
300	10.666	61.742	∞	-1.837	-160.382	118.515
350	10.691	61.808	61.742	-1.837	-160.382	117.700
400	11.002	61.966	61.742	-1.837	-160.382	117.700
450	11.318	62.124	61.742	-1.837	-160.382	117.700
500	11.634	62.282	61.742	-1.837	-160.382	117.700
600	12.218	62.711	61.742	-1.837	-160.382	117.700
700	12.694	63.011	61.742	-1.837	-160.382	117.700
800	13.094	63.282	61.742	-1.837	-160.382	117.700
900	13.410	63.524	61.742	-1.837	-160.382	117.700
1000	13.630	63.735	61.742	-1.837	-160.382	117.700
1100	13.761	63.911	61.742	-1.837	-160.382	117.700
1200	13.892	64.061	61.742	-1.837	-160.382	117.700
1300	14.023	64.192	61.742	-1.837	-160.382	117.700
1400	14.154	64.313	61.742	-1.837	-160.382	117.700
1500	14.285	64.424	61.742	-1.837	-160.382	117.700
1600	14.416	64.525	61.742	-1.837	-160.382	117.700
1700	14.547	64.616	61.742	-1.837	-160.382	117.700
1800	14.678	64.697	61.742	-1.837	-160.382	117.700
1900	14.809	64.768	61.742	-1.837	-160.382	117.700
2000	14.940	64.829	61.742	-1.837	-160.382	117.700
2100	15.071	64.880	61.742	-1.837	-160.382	117.700
2200	15.202	64.921	61.742	-1.837	-160.382	117.700
2300	15.333	64.952	61.742	-1.837	-160.382	117.700
2400	15.464	64.973	61.742	-1.837	-160.382	117.700
2500	15.595	64.994	61.742	-1.837	-160.382	117.700
2600	15.726	65.005	61.742	-1.837	-160.382	117.700
2700	15.857	65.016	61.742	-1.837	-160.382	117.700
2800	15.988	65.027	61.742	-1.837	-160.382	117.700
2900	16.119	65.038	61.742	-1.837	-160.382	117.700
3000	16.250	65.049	61.742	-1.837	-160.382	117.700
3100	16.381	65.060	61.742	-1.837	-160.382	117.700
3200	16.512	65.071	61.742	-1.837	-160.382	117.700
3300	16.643	65.082	61.742	-1.837	-160.382	117.700
3400	16.774	65.093	61.742	-1.837	-160.382	117.700
3500	16.905	65.104	61.742	-1.837	-160.382	117.700
3600	17.036	65.115	61.742	-1.837	-160.382	117.700
3700	17.167	65.126	61.742	-1.837	-160.382	117.700
3800	17.298	65.137	61.742	-1.837	-160.382	117.700
3900	17.429	65.148	61.742	-1.837	-160.382	117.700
4000	17.560	65.159	61.742	-1.837	-160.382	117.700
4100	17.691	65.170	61.742	-1.837	-160.382	117.700
4200	17.822	65.181	61.742	-1.837	-160.382	117.700
4300	17.953	65.192	61.742	-1.837	-160.382	117.700
4400	18.084	65.203	61.742	-1.837	-160.382	117.700
4500	18.215	65.214	61.742	-1.837	-160.382	117.700
4600	18.346	65.225	61.742	-1.837	-160.382	117.700
4700	18.477	65.236	61.742	-1.837	-160.382	117.700
4800	18.608	65.247	61.742	-1.837	-160.382	117.700
4900	18.739	65.258	61.742	-1.837	-160.382	117.700
5000	18.870	65.269	61.742	-1.837	-160.382	117.700
5100	19.001	65.280	61.742	-1.837	-160.382	117.700
5200	19.132	65.291	61.742	-1.837	-160.382	117.700
5300	19.263	65.302	61.742	-1.837	-160.382	117.700
5400	19.394	65.313	61.742	-1.837	-160.382	117.700
5500	19.525	65.324	61.742	-1.837	-160.382	117.700
5600	19.656	65.335	61.742	-1.837	-160.382	117.700
5700	19.787	65.346	61.742	-1.837	-160.382	117.700
5800	19.918	65.357	61.742	-1.837	-160.382	117.700
5900	20.049	65.368	61.742	-1.837	-160.382	117.700
6000	20.180	65.379	61.742	-1.837	-160.382	117.700

June 30, 1962; Dec. 31, 1964; Mar. 31, 1965

Point Group C_{2v}

$$S_{298.15}^{\circ} = [61.742] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_{298.15}^{\circ} = -159.54 \pm 1.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_{298.15}^{\circ} = -160.38 \pm 1.1 \text{ kcal. mole}^{-1}$$

$$\Delta G_{298.15}^{\circ} = -160.38 \pm 1.1 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ν , cm. ⁻¹	ν , cm. ⁻¹
[2040](1)	[1100](1)
[1935](1)	[500](1)
[1340](1)	800 (1)

$$\text{Bond Distances: Li-O} = 1.82 \text{ \AA}, \text{ O-B} = 1.36 \text{ \AA}, \text{ B-O} = 1.20 \text{ \AA}$$

$$\text{Bond Angles: LiOB} = 100^{\circ}, \text{ O-B-O} = 180^{\circ}$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = 4.01933 \times 10^{-115} \text{ g. cm.}^2$$

Heat of Formation.

The adopted heat of formation at 298.15 was evaluated by the third-law method using vapor pressure data reported by D. L. Hildenbrand, M. P. Hall and N. D. Potter, J. Chem. Phys. **39**, No. 2, 298 (1963). The heat of reaction at 298.15 was found to be 82.908 kcal. mole⁻¹ thus giving the value $\Delta H_{298.15}^{\circ} = -160.382$ kcal. mole⁻¹. A second-law method was also used on the data of D. L. Hildenbrand et. al., loc. cit. and yielded a $\Delta H_{298.15}^{\circ} = 81.375$ kcal. mole⁻¹ thus giving $\Delta H_{298.15}^{\circ} = -161.915$ kcal. mole⁻¹. A. Bichler and J. B. Berkowitz-Matuck, J. Chem. Phys. **39**, No. 2, 286 (1963), have measured the vaporization of lithium metaborate mass spectrometrically in an effusion cell. The second law value reported by A. Bichler and J. B. Berkowitz-Matuck, loc. cit. for ΔH_{1000}° was 79 ± 3 kcal. mole⁻¹ which yields $\Delta H_{298.15}^{\circ} = 84.078$ kcal. mole⁻¹ thus giving $\Delta H_{298.15}^{\circ} = -159.212$ kcal. mole⁻¹ with JANAF auxiliary values.

Heat Capacity and Entropy.

A. Bichler and E. P. Marram, J. Chem Phys. **39**, No. 2, 292, (1963), observed and assigned two vibrational frequencies to lithium metaborate which were adopted for this table. The other vibrational frequencies were estimated by comparison with similar molecules. D. White, Ohio State University, in a private communication quoted in D. L. Hildenbrand et. al. loc. cit. assigned vibrational frequencies from matrix-isolation experiments. When these frequencies were used in a third and second law analysis of Hildenbrand's data, the drift in the third law was much larger and the agreement between the second and third law was also much poorer than that using the frequencies employed in this table. The molecular constants were obtained from P. A. Aldrich and V. P. Spiridonov, Zhur. Strukt. Khim. **2**, 63 (1963). The individual moments of inertia are: $I_A = 1.22164 \times 10^{-38}$ g. cm.², $I_B = 2.2710 \times 10^{-39}$ g. cm.², and $I_C = 1.44675 \times 10^{-38}$ g. cm.².

T, °K	C_p°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	-	-	-	INFINITE
100	1.183	0.667	6.497	-	-59.270	-	126.164
200	2.967	2.025	3.910	-	-59.578	-	60.962
300	4.713	3.536	3.536	0.000	-59.970	-	39.424
400	6.474	5.148	3.436	0.009	-59.973	-	39.153
500	8.280	6.866	3.471	0.563	-60.089	-	28.220
600	10.120	8.638	3.504	1.254	-60.162	-	21.650
700	11.970	10.470	3.537	2.052	-60.195	-	17.265
800	13.840	12.360	3.570	2.858	-60.199	-	13.133
900	15.720	14.310	3.603	3.681	-60.128	-	9.058
1000	17.600	16.320	3.636	4.521	-60.061	-	8.490
1100	19.500	18.390	3.669	5.379	-59.980	-	7.306
1200	21.420	20.520	3.702	6.258	-59.891	-	6.374
1300	23.360	22.710	3.735	7.158	-59.795	-	5.676
1400	25.320	24.960	3.768	8.079	-59.711	-	4.758
1500	27.300	27.280	3.801	9.021	-59.627	-	4.137
1600	29.300	29.670	3.834	10.000	-59.551	-	3.594
1700	31.320	32.120	3.867	11.000	-59.488	-	3.116
1800	33.360	34.640	3.900	12.030	-59.438	-	2.700
1900	35.420	37.230	3.933	13.090	-59.398	-	2.311
2000	37.500	39.890	3.966	14.180	-59.366	-	1.970
2100	39.600	42.620	4.000	15.300	-59.342	-	1.661
2200	41.720	45.420	4.033	16.450	-59.324	-	1.370
2300	43.860	48.290	4.067	17.630	-59.310	-	1.100
2400	46.020	51.230	4.100	18.840	-59.300	-	0.860
2500	48.200	54.240	4.133	20.090	-59.292	-	0.664
2600	50.400	57.320	4.166	21.380	-59.286	-	0.496
2700	52.620	60.470	4.200	22.710	-59.282	-	0.345
2800	54.860	63.690	4.233	24.080	-59.279	-	0.205
2900	57.120	66.980	4.267	25.490	-59.276	-	0.076
3000	59.400	70.340	4.300	26.940	-59.274	-	0.000
3100	61.700	73.770	4.333	28.430	-59.272	-	0.000
3200	64.020	77.280	4.367	29.960	-59.270	-	0.000
3300	66.360	80.860	4.400	31.530	-59.268	-	0.000
3400	68.720	84.510	4.433	33.140	-59.266	-	0.000
3500	71.100	88.240	4.467	34.790	-59.264	-	0.000

BORON NITRIDE (BN)
(CRYSTAL)

OPW = 24.8177

$$\Delta H_f^\circ = -59.27 \pm 0.37 \text{ kcal/mol}$$

$$\Delta H_f^{298} = -59.97 \pm 0.37 \text{ kcal/mol}$$

$$\Delta H_f^{298} = 3.536 \text{ gibbs/mol}$$

$$T_d = 2600 \pm 100^\circ\text{K}$$

Heat of Formation.

The adopted heat of formation was determined by Wise et al. using combustion in fluorine. Other recent calorimetric values are in good agreement as summarized below. Torsion-effusion studies of the decomposition $\text{BN(c)} \rightarrow \text{B(am)} + 0.5 \text{ N}_2(\text{g})$ by D. L. Hildenbrand and W. P. Hall, *J. Phys. Chem.* **67**, 888 (1963), yield essentially the same ΔH_f° and indicate that the condensation coefficient, α , is $< 6 \times 10^{-3}$ for $\text{N}_2(\text{g})$ on the surface of the sample. Use of $\alpha = 6 \times 10^{-3}$ brings the following decomposition studies into reasonable agreement: Langmuir studies by L. H. Dreger, V. V. Dadape and J. L. Margrave, *J. Phys. Chem.* **66**, 1556 (1962); mass spectrometric studies by P. O. Schissel and W. S. Williams, *Bull. Am. Phys. Soc.*, **II**, 4, 139 (1959); and Knudsen effusion studies by M. Hoch and D. White, Technical Research Report MCC-1023-TM-214, Ohio State University Research Foundation, Columbus, Ohio, October, 1956.

Source	Reaction	ΔH_f^{298} kcal/mol	ΔH_f^{298} kcal/mol
1. Dworikin et al. (1954)	$\text{BN(c)} + 3/4 \text{ O}_2(\text{g}) \rightarrow 0.5 \text{ B}_2\text{O}_3(\text{am}) + 0.5 \text{ N}_2$	-90.1 ± 0.5	-59.7 ± 0.7
2. Gal'chenko et al. (1959)	$\text{B(am)} + 0.5 \text{ N}_2(\text{g}) \rightarrow \text{BN(c)}$	-80.8 ± 0.3	-59.6 ± 0.8
3. Gross (1961)	$\text{BN(c)} + 1.5 \text{ F}_2(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2$	-211.2 ± 0.1	
	$\text{B(c)} + 1.5 \text{ F}_2(\text{g}) \rightarrow \text{BF}_3(\text{g})$	-271.4	-60.2
4. Thompson et al. (1961)	$\text{BN(c)} + \text{NF}_3(\text{g}) \rightarrow \text{BF}_3(\text{g}) + \text{N}_2$	-177.63 ± 0.3	-60.1 ± 2
	$\text{B(c)} + \text{NF}_3(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2$	-237.77 ± 0.5	-59.9 ± 1.5
5. Keavney (1962)	Combustion in O_2 - H_2O		-59.97 ± 0.37
6. Wise et al. (1966)	$\text{BN(c)} + 1.5 \text{ F}_2(\text{g}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2$	-211.68 ± 0.3	

References

1. A. S. Dworikin, D. J. Samor and E. R. Van Arsdale, *J. Chem. Phys.* **22**, 837 (1954).
2. G. L. Gal'chenko, A. N. Kornilov, and S. M. Skuratov, *Russ. J. Inorg. Chem.* **5**, 1292 (1960).
3. F. Gross, Fulmer Research Institute, Report R. 163/6/15 December 1961, Stoke Poges, England.
4. C. J. Thompson and G. C. Sinke, Dow Chemical Co., Report ARPA 1-164, Jan. 1961.
5. J. J. Keavney, Stamford Research Laboratories, American Cyanamid Co., Stamford, Conn., private communication to Wise et al., loc. cit.
6. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.* **70**, 7 (1966).

Heat Capacity and Entropy.

The low temperature heat capacity was taken from E. F. Westrum, Jr., private communication, May 19, 1960. The intermediate heat capacity (300-1650°C) was obtained from R. A. McDonald and D. R. Stull, *J. Phys. Chem.* **65**, 1918 (1961). The high temperature Cp was taken from H. Prophet and D. R. Stull, *J. Chem. Eng. Data* **9**, No. 1, 78, January 1963. The heat capacities in the three temperature ranges were plotted and then graphically smoothed. A. S. Dworikin, D. J. Samor, and A. R. Van Arsdale, loc. cit., also reported heat capacity (50-500°K) not employed in this table.

The entropy was obtained by integration of the heat capacity data from E. F. Westrum, Jr., loc. cit., based upon $S_{10}^\circ = 0.0028 \text{ eu}$.

Temperature of Decomposition.

Observations by The Dow Chemical Company under Contract No. AF 33(616)-6149 show decomposition to elements at 1 atm total pressure at $2600 \pm 100^\circ\text{K}$. The decomposition temperature calculated from these tables is 2632°K ; presumably this discrepancy is associated with uncertainties in the high temperature enthalpies of BN(c) , B(c) and N(c) and the enthalpy of melting of B(c) .

T, °K	Cp ^b	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	+0.000	INFINITE	- 2.076	113+252	113+252	INFINITE
100	6.957	43+114	56+935	113+593	- 243+024	- 243+024
200	6.963	47+937	51+368	113+691	- 118+772	- 118+772
298	7.039	50+728	+0.000	114+000	106+117	- 77+786
300	7.061	50+771	50+728	114+002	106+068	- 77+270
400	7.237	52+822	51+006	114+044	103+415	- 56+503
500	7.489	54+463	51+559	114+016	100+759	- 44+042
600	7.735	55+891	52+145	113+946	98+114	- 35+738
700	7.959	57+059	52+762	113+851	95+483	- 29+411
800	8.162	58+183	53+348	113+745	92+849	- 24+161
1000	8.390	59+059	53+952	113+613	90+266	- 21+019
1100	8.488	60+781	55+045	113+474	87+679	- 19+162
1200	8.570	61+523	63+100	113+320	85+105	- 16+909
1300	8.635	62+284	68+153	113+154	82+048	- 13+084
1400	8.701	62+854	76+504	112+978	77+476	- 12+095
1500	8.755	63+457	86+948	112+782	74+959	- 10+921
1600	8.805	64+023	97+373	112+569	72+460	- 9+698
1800	8.858	64+708	117+000	112+345	67+492	- 8+195
2000	8.937	65+568	134+303	111+675	65+036	- 7+481
2100	9.018	66+446	149+089	111+433	62+589	- 6+439
2200	9.095	67+270	169+918	111+187	60+152	- 6+260
2300	9.169	68+043	190+582	110+686	55+314	- 5+256
2400	9.233	67+658	206+232	110+431	52+913	- 4+818
2500	9.289	68+032	224+437	104+788	50+629	- 4+426
2600	9.338	68+392	240+537	104+538	48+468	- 4+076
2700	9.376	69+077	257+771	104+291	44+172	- 3+449
2800	9.424	69+477	274+917	103+804	42+172	- 3+448
2900	9.467	70+895	291+124	103+627	31+490	- 2+024
3000	9.484	71+169	314+169	103+564	39+915	- 2+908
3100	9.500	70+035	324+197	103+397	37+797	- 2+645
3200	9.516	71+598	342+586	103+230	35+688	- 2+437
3300	9.429	70+613	362+680	102+858	31+586	- 2+224
3400	9.457	70+895	382+917	102+627	31+490	- 2+024
3500	9.484	71+169	404+169	102+398	29+400	- 1+836
3600	9.510	71+437	424+376	102+171	27+318	- 1+658
3700	9.536	71+698	444+607	101+644	24+241	- 1+651
3800	9.559	71+952	464+814	101+423	23+175	- 1+333
3900	9.582	72+201	484+025	101+502	21+107	- 1+183
4000	9.604	72+444	504+233	101+897	21+193	- 1+158
4100	9.626	72+681	524+436	101+884	22+221	- 1+184
4200	9.648	72+901	544+636	101+869	23+240	- 1+210
4300	9.666	73+141	564+830	101+852	24+275	- 1+234
4400	9.685	73+363	584+022	101+836	25+302	- 1+257
4500	9.704	73+581	604+211	101+818	26+325	- 1+279
4600	9.723	73+794	624+394	101+798	27+350	- 1+299
4700	9.740	74+004	644+575	101+778	28+376	- 1+319
4800	9.757	74+209	664+753	101+758	29+404	- 1+339
4900	9.774	74+410	684+927	101+737	30+426	- 1+357
5000	9.790	74+608	704+099	101+716	31+449	- 1+375
5100	9.806	74+802	724+266	101+695	32+471	- 1+391
5200	9.822	74+993	744+430	101+672	33+493	- 1+408
5300	9.838	75+180	764+597	101+650	34+513	- 1+423
5400	9.853	75+364	784+757	101+629	35+535	- 1+438
5500	9.864	75+545	804+916	101+607	36+562	- 1+453
5600	9.884	75+723	824+071	101+585	37+577	- 1+467
5700	9.898	75+898	844+225	101+564	38+601	- 1+480
5800	9.913	76+070	864+376	101+544	39+622	- 1+491
5900	9.928	76+240	884+524	101+523	40+639	- 1+505
6000	9.942	76+407	904+671	101+504	41+660	- 1+517

Dec. 31, 1960; Sept. 30, 1963; June 30, 1966

Ground State Configuration 3π
 $S_{298.15}^{\circ} = 50.73$ gibbs/mol
 $\Delta H_{298.15}^{\circ} = 114 \pm 30$ kcal/mol
 $\Delta H_{298.15}^{\circ} = 113$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	6
[8500]	1
[8900]	2
27877	6

$\omega_0 = 1514.6$ cm⁻¹ $\omega_0 x_0 = 12.3$ cm⁻¹ $\sigma = 1$
 $B_0 = 1.666$ cm⁻¹ $\alpha_0 = 0.025$ cm⁻¹ $r_0 = 1.281$ Å

Heat of Formation.

The heat of formation is based on $D_0 = 5.7$ eV which was calculated from ω_0 and $\omega_0 x_0$ observed by A. E. Douglas and G. Herzberg, Can. J. Research **18A**, 179 (1940). An uncertainty of ± 1.5 eV was assigned from consideration of other information which places the dissociation energy between 4 and 7 eV. The value $D_0 = 4.0 \pm 0.5$ eV was selected by A. G. Gaydon, "Dissociation Energies," second edition, Chapman and Hall Ltd, London, 1953, from his own extrapolation of the spectroscopic data. An upper limit of $D_0 \leq 7.0$ eV results from the upper limit for the pressure of BN(c) \rightarrow BN(g) obtained from the B^+ ion intensity at 1600°C observed by P.A. Akhshin and Yu. S. Klotsev, Zh. Neorgan. Khim. **7**, 941 (1962). It is likely that the BN(g) pressure is even smaller since it is known that BN(c) \rightarrow B(s) + 0.5 N₂(g) and Akhshin's pressure limit are the same magnitude as that of B(s) \rightarrow B(g). V. V. Pesenko, Forshkovaya Met., Akad. Nauk Ukr. S. S. R. **3**, No. 4, 80-5 (1961) [cf. Chem. Abs. **55**, 10997 (1962)], reports a standard heat of sublimation of 160 kcal/mol for BN(c) \rightarrow BN(g) and also gives pressures for BN(g) at 2500 and 3000°K which are stated to be two orders less than the equilibrium pressure of nitrogen. Pesenko's original article is not yet available to us and it is not clear from the abstract whether the values are based on new data or are mere calculations. The reported pressures yield $D_0 = 6.2$ eV, but here again the BN(g) pressures are of the same magnitude as the JANAF values for B(s) \rightarrow B(g).

Some estimated values for D_0 (ranging from 5.4 to 6.4 eV) are summarized below along with the experimental evidence.

Source	D_0 (eV)	ΔH_{298}° (kcal/mol)	ΔH_{298}° (kcal/mol)
Gaydon's extrapolation of spectroscopic data	4.0 ± 0.5	213	153
Linear Birge-Sponer extrapolation	5.7	174	114
Pesenko's "BN(g) pressures"	6.2	161	101
Akhshin's upper limit for BN(g) pressure	7.0	146	85
Estimate from geometric mean of D_0 for B ₂ and N ₂	5.4	180	120
Estimate from D_0 for series N ₂ , CH, BN, Ben	5.6	177	117
Estimate M ₂ + N ₂ = 2 MN for M=B from M=C	6.0	166	106
Estimate from arithmetic mean of D_0 for B ₂ and N ₂	6.4	158	98

Heat Capacity and Entropy.

The molecular constants are based on emission spectra of the $3\pi - 3\pi$ transition obtained by Douglas and Herzberg, loc. cit. Observation of the same triplet in absorption by B. A. Thrush, Nature **160**, 1044 (1960), strongly suggests that the ground state of BN is 3π in contrast to 1Σ as observed for the isoelectronic molecules BeO and C₂. Electronic levels for the 3π states are taken from Douglas and Herzberg while values for $1\Sigma^+$ and 1π have been estimated from the SCF calculations of J. L. Mease and M. Barriocher, Helv. Chim. Acta **47**, 314 (1964).

Sodium Metaborate (NaBO₂)

(Crystal) Mol. Wt. = 65.811

SODIUM METABORATE (NaBO₂)

(CRYSTAL)

MOL. WT. = 65.811

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ⁰	ΔF ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.751	4.780	2.782	-232.874	-232.874	INFINITE
200	12.740	11.890	1.407	-233.592	-233.592	501.401
298	15.760	17.573	0.000	-234.000	-234.000	245.606
300	15.780	17.573	0.029	-234.001	-234.001	161.655
400	17.370	22.434	1.669	-234.718	-234.718	160.407
500	18.700	26.458	3.485	-234.797	-234.797	117.949
600	19.880	29.972	5.424	-234.819	-234.819	92.206
700	20.930	33.017	7.458	-234.819	-234.819	75.191
800	21.900	35.617	9.638	-234.819	-234.819	62.814
900	22.800	37.818	11.933	-234.818	-234.818	53.695
1000	23.600	41.272	14.357	-234.096	-187.637	41.006
1100	24.300	43.705	16.912	-233.660	-183.012	36.350
1200	24.900	45.990	19.570	-233.660	-177.879	32.511
1300	25.400	48.090	22.320	-233.660	-172.879	29.361
1400	25.800	50.073	25.154	-234.641	-168.032	26.761
1500	26.100	51.841	28.068	-234.641	-163.332	24.561
1600	26.300	53.462	31.063	-234.641	-158.668	22.711
1700	26.500	54.962	34.141	-234.641	-154.032	21.111
1800	26.600	56.362	37.299	-234.641	-149.432	19.611
1900	26.700	57.662	40.534	-234.641	-144.868	18.211
2000	26.800	58.862	43.848	-234.641	-140.332	16.911
2100	26.900	60.062	47.234	-234.641	-135.832	15.711
2200	27.000	61.262	50.698	-234.641	-131.368	14.611
2300	27.100	62.462	54.234	-234.641	-126.932	13.611
2400	27.200	63.662	57.834	-234.641	-122.532	12.711
2500	27.300	64.862	61.498	-234.641	-118.168	11.911
2600	27.400	66.062	65.234	-234.641	-113.832	11.211
2700	27.500	67.262	69.034	-234.641	-109.532	10.611
2800	27.600	68.462	72.898	-234.641	-105.268	10.111
2900	27.700	69.662	76.814	-234.641	-101.032	9.711
3000	27.800	70.862	80.784	-234.641	-96.832	9.411

$$\Delta H_f^0 = -232.9 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = -234 \pm 2 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 8.66 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 298.15 = 77.00 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 17.573 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1239^\circ \text{K.}$$

Heat of Formation.

W. H. Evans, D. D. Wegman and E. J. Froese in NBS Report No. 4943, "Thermodynamic Properties of Some Boron Compounds", August, 1955, extrapolated from the graph of L. Shartais and W. Capps, J. Am. Ceram. Soc. 37, 27 (1954) the heat of solution to be $-25.4 \text{ kcal. mole}^{-1}$ for the first reaction in 2N nitric acid. G. Grenier and D. White, J. Chem. Phys. 61, 1681 (1957) measured the heat of solution at 273.15°K. in 2N nitric acid for the first reaction and found a value of $-20.43 \text{ kcal. mole}^{-1}$. The heats of solution for the second and third reactions were obtained from L. Shartais and W. Capps, loc. cit.

1. $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3(\text{c}) + \text{Solvent I} = \text{end Solution I}$
2. $\text{B}_2\text{O}_3(\text{c}) + \text{Solvent II} = \text{end Solution I}$
3. $\text{Na}_2\text{O}(\text{c}) + \text{Solvent II} = \text{end Solution II}$

The combination of the above reactions yields:

$$\text{Na}_2\text{O}(\text{c}) + \text{B}_2\text{O}_3(\text{c}) = \text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3(\text{c})$$

$$1/2 \text{ Na}_2\text{O}(\text{c}) + 1/2 \text{ B}_2\text{O}_3(\text{c}) = \text{NaBO}_2(\text{c})$$

The $\Delta H_f^0 298.15$'s for Na_2O and B_2O_3 are JANAP values. The $\Delta H_f^0 298.15$ value of $-234.000 \text{ kcal. mole}^{-1}$ employed in this table was obtained by taking the average of the values given above for reaction 1. Since there were uncertainties in the extrapolation and in assuming no correction for the measurements at 273.15°K. , an average value was considered preferable.

Heat Capacity and Entropy.

The low temperature heat capacities ($5-298.15^\circ \text{K.}$) and $S_{298.15}^0$ were obtained from G. Grenier and E. P. Westrum, J. Am. Chem. Soc. 78, 6226 (1956). The heat capacities at the higher temperatures were altered slightly from the estimate of K. K. Kelley, U. S. Bureau of Mines Bulletin 395 (1935).

Melting Data.

The T_m was obtained from H. S. Van Klooster, Z. Anorg. Chem. 59, 122 (1911). The adopted ΔH_m^0 was calculated by K. K. Kelley loc. cit. from H. S. Van Klooster's work. K. K. Kelley also calculated a ΔH_m^0 of $9.3 \text{ kcal. mole}^{-1}$ from M. H. LeChâtelier, Compt. rend. 118, 800 (1894).

Sublimation Data.

The ΔH_g^0 was obtained from the mass spectrometric investigations of A. Büchler and J. B. Berkowitz-Mattuck, J. Chem. Phys. 39, 286 (1963).

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100								
200								
298	15.760	20.560	20.560	0.000	-229.439	-216.773	159.692	
300	15.780	20.658	20.560	0.020	-229.440	-216.695	157.855	
400	17.370	26.421	21.899	1.499	-229.437	-216.695	157.855	
500	18.700	29.443	22.456	3.494	-230.137	-207.999	90.012	
600	19.880	32.957	23.919	5.423	-230.159	-203.568	74.140	
700	21.050	36.106	25.439	7.469	-230.113	-199.139	62.171	
800	22.200	38.885	26.985	9.585	-229.876	-194.723	53.193	
900	23.330	41.271	28.548	11.810	-228.876	-189.315	46.255	
1000	24.440	43.261	30.100	14.311	-227.481	-186.161	40.683	
1100	25.530	44.747	31.737	16.911	-226.120	-182.008	36.178	
1200	26.600	45.772	33.366	19.611	-224.897	-177.699	32.361	
1300	27.650	46.342	35.000	22.411	-223.710	-173.213	29.046	
1400	28.680	46.537	36.537	25.311	-222.552	-168.535	26.104	
1500	29.690	46.602	38.061	28.311	-221.422	-163.636	23.404	
1600	30.680	46.542	39.542	31.411	-220.319	-158.515	21.192	
1700	31.650	46.363	40.976	34.611	-219.242	-153.175	19.293	
1800	32.600	46.076	42.363	37.911	-218.190	-147.622	17.536	
1900	33.530	45.683	43.712	41.311	-217.163	-141.852	15.912	
2000	34.440	45.191	45.015	44.811	-216.165	-135.872	14.424	
2100	35.330	44.602	46.278	48.411	-215.195	-129.695	13.063	
2200	36.200	43.927	47.502	52.111	-214.252	-123.315	11.823	
2300	37.050	43.168	48.691	55.911	-213.335	-116.832	10.699	
2400	37.880	42.327	49.839	59.811	-212.442	-110.252	9.689	
2500	38.690	41.407	50.957	63.811	-211.573	-103.573	8.785	
2600	39.480	40.412	52.042	67.911	-210.727	-96.803	7.980	
2700	40.250	39.349	53.096	72.111	-209.902	-90.007	7.270	
2800	41.000	38.222	54.120	76.411	-209.095	-83.185	6.650	
2900	41.730	37.035	55.120	80.811	-208.307	-76.335	6.124	
3000	42.440	35.792	56.092	85.311	-207.535	-69.463	5.689	

$S_{298.15}^o = 20.560$ cal. deg.⁻¹ mole⁻¹
 $T_m = 1239^\circ K.$
 $\Delta H_f^o = 8.66$ kcal. mole⁻¹
 $\Delta F_f^o = 8.66$ kcal. mole⁻¹
 $\Delta H_f^o = 8.66$ kcal. mole⁻¹

Heat of Formation.

ΔH_f^o 298.15(l) was obtained from $\Delta H_f^o(c)$ by addition of ΔH_m^o and difference between ($H_{298.15}^o$) for the crystal and liquid.

Heat Capacity and Entropy.

Sodium metaborate is assumed to have a glass transformation at 826°K. below which C_p of the glass is assumed equal to that of the crystal. Above 826°K. the heat capacity was estimated as a constant value by assuming 8.75 calories contribution from each atom. The $S_{298.15}$ was obtained in a manner analogous with ΔH_f^o 298.15°.

Melting Data.

See crystal table.



Sodium Metaborate (NaBO₂)

(Ideal Gas) Mol. Wt. = 65.811

MOL. WT. = 65.811

(IDEAL GAS)

SODIUM METABORATE (NaBO₂)

Point Group C_s

$\Delta H_f^\circ = [-156 \pm 3] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-157 \pm 3] \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ = [64.937] \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\sigma = 1$

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	-	2.738	-155.830	-155.830	INFINITE
100	8.188	54.584	73.071	1.939	-156.070	-156.070	342.607
200	9.784	60.701	65.036	1.047	-156.525	-157.356	171.982
298	11.504	64.937	64.937	0.000	-157.000	-157.356	115.566
300	11.534	65.008	64.937	0.021	-157.009	-157.669	114.856
400	12.939	68.527	65.408	1.248	-158.159	-157.764	86.194
500	14.062	71.539	66.340	2.600	-158.692	-157.602	68.884
600	14.984	74.187	67.481	4.053	-159.100	-157.336	57.307
700	15.745	76.554	68.703	5.593	-159.492	-156.972	48.012
800	16.371	78.701	69.703	7.108	-160.083	-156.582	42.774
900	16.884	80.660	70.813	8.862	-160.489	-156.120	37.909
1000	17.305	82.461	71.889	10.572	-160.881	-155.611	34.007
1100	17.651	84.127	72.927	12.320	-161.272	-155.048	30.806
1200	17.937	85.676	73.926	14.100	-161.692	-154.439	28.151
1300	18.174	87.121	74.886	15.906	-162.081	-153.789	25.440
1400	18.373	88.475	75.808	17.734	-162.441	-153.100	23.236
1500	18.541	89.749	76.696	19.579	-162.765	-152.386	21.308
1600	18.683	90.950	77.550	21.441	-163.050	-151.650	19.618
1700	18.804	92.086	78.372	23.311	-163.292	-150.892	18.153
1800	18.909	93.164	79.122	25.201	-163.494	-150.114	16.768
1900	18.999	94.189	79.828	27.097	-163.654	-149.315	15.450
2000	19.077	95.166	80.665	29.001	-163.780	-148.494	14.193
2100	19.146	96.098	81.378	30.912	-163.872	-147.650	13.000
2200	19.206	96.980	82.048	32.832	-163.932	-146.786	11.868
2300	19.260	97.815	82.735	34.763	-163.960	-145.900	10.796
2400	19.307	98.606	83.382	36.681	-163.957	-144.994	9.784
2500	19.349	99.455	84.009	38.614	-163.922	-144.065	8.834
2600	19.387	100.215	84.618	40.551	-163.856	-143.114	7.944
2700	19.420	100.947	85.207	42.499	-163.758	-142.142	7.108
2800	19.451	101.654	85.784	44.435	-163.628	-141.146	6.326
2900	19.478	102.337	86.343	46.361	-163.466	-140.126	5.599
3000	19.503	102.997	86.887	48.330	-163.272	-139.086	4.926
3100	19.526	103.637	87.417	50.282	-163.056	-138.026	4.306
3200	19.546	104.258	87.934	52.235	-162.810	-136.946	3.736
3300	19.565	104.859	88.438	54.191	-162.544	-135.846	3.216
3400	19.583	105.444	88.929	56.148	-162.258	-134.726	2.746
3500	19.598	106.012	89.409	58.108	-161.952	-133.586	2.316
3600	19.613	106.564	90.878	60.068	-161.626	-132.426	1.926
3700	19.627	107.101	92.337	62.037	-161.272	-131.246	1.576
3800	19.639	107.625	93.787	64.019	-160.892	-130.046	1.266
3900	19.651	108.135	95.223	66.019	-160.486	-128.826	0.996
4000	19.661	108.633	96.642	67.924	-160.056	-127.586	0.766
4100	19.671	109.119	98.207	69.860	-159.600	-126.326	0.566
4200	19.681	109.593	99.787	71.826	-159.119	-125.046	0.396
4300	19.689	110.056	101.376	73.826	-158.614	-123.746	0.256
4400	19.697	110.508	102.982	75.766	-158.086	-122.426	0.146
4500	19.705	110.951	104.617	77.666	-157.536	-121.086	0.076
4600	19.712	111.385	106.119	79.577	-156.966	-119.726	0.046
4700	19.719	111.809	107.625	81.501	-156.376	-118.346	0.016
4800	19.725	112.224	109.101	83.430	-155.766	-116.946	0.006
4900	19.731	112.631	110.544	85.363	-155.136	-115.526	0.000
5000	19.736	113.029	111.951	87.304	-154.486	-114.086	0.000
5100	19.742	113.420	113.385	89.254	-153.816	-112.626	0.000
5200	19.747	113.800	114.809	91.219	-153.126	-111.146	0.000
5300	19.751	114.180	116.224	93.199	-152.416	-109.646	0.000
5400	19.756	114.546	117.625	95.199	-151.686	-108.126	0.000
5500	19.760	114.911	119.019	97.184	-150.936	-106.586	0.000
5600	19.764	115.268	120.409	99.177	-150.166	-105.026	0.000
5700	19.767	115.617	121.797	101.184	-149.376	-103.446	0.000
5800	19.771	115.961	123.176	103.199	-148.566	-101.846	0.000
5900	19.774	116.290	124.544	105.219	-147.736	-100.226	0.000
6000	19.778	116.632	125.904	107.239	-146.886	-98.586	0.000



(Ideal Gas) GFW = 26.8104

BORON MONOXIDE (BO) (IDEAL GAS)

GFW = 26.8104

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.000	-0.000	INFINITE	-2.073	-7.84	-7.84	INFINITE
100	6.956	41.001	54.764	-1.379	-4.03	-2.425	5.300
200	6.958	45.824	49.241	-0.684	-1.35	-4.560	4.983
298	6.978	48.604	48.604	-0.000	-0.00	-6.768	4.961
300	6.979	48.647	48.604	-0.13	-0.01	-6.810	4.961
400	7.068	50.665	48.879	-0.15	-0.02	-9.087	4.965
500	7.230	52.259	49.401	-0.26	-0.03	-11.359	4.965
600	7.427	53.524	49.991	-0.42	-0.05	-13.642	4.958
700	7.640	54.590	50.594	-0.61	-0.08	-15.942	4.966
800	7.870	55.716	51.176	-0.82	-0.10	-18.251	4.931
900	8.117	56.714	51.741	-1.07	-0.13	-20.573	4.914
1000	8.380	57.561	52.281	-1.36	-0.16	-22.919	4.895
1100	8.655	58.267	52.787	-1.69	-0.20	-25.284	4.876
1200	8.940	58.836	53.260	-2.04	-0.24	-27.668	4.857
1300	9.235	59.279	53.703	-2.41	-0.28	-30.074	4.837
1400	9.540	60.600	54.114	-2.80	-0.32	-32.502	4.816
1500	9.854	61.812	54.500	-3.20	-0.36	-34.952	4.799
1600	10.176	62.916	54.864	-3.61	-0.40	-37.424	4.779
1700	10.506	63.914	55.207	-4.04	-0.44	-39.918	4.761
1800	10.843	64.808	55.528	-4.48	-0.48	-42.434	4.744
1900	11.187	65.600	55.831	-4.94	-0.52	-44.972	4.723
2000	11.537	66.293	56.118	-5.41	-0.56	-47.532	4.704
2100	11.892	66.888	56.391	-5.89	-0.60	-50.114	4.684
2200	12.252	67.388	56.650	-6.38	-0.64	-52.718	4.668
2300	12.617	67.799	56.896	-6.88	-0.68	-55.344	4.653
2400	12.987	68.124	57.129	-7.39	-0.72	-57.992	4.637
2500	13.362	68.368	57.349	-7.91	-0.76	-60.662	4.621
2600	13.742	68.533	57.556	-8.44	-0.80	-63.354	4.607
2700	14.126	68.619	57.750	-8.98	-0.84	-66.068	4.594
2800	14.514	68.628	57.931	-9.53	-0.88	-68.804	4.582
2900	14.906	68.562	58.099	-10.09	-0.92	-71.562	4.570
3000	15.301	68.424	58.255	-10.66	-0.96	-74.342	4.559
3100	15.699	68.216	58.399	-11.24	-1.00	-77.144	4.549
3200	16.100	67.940	58.532	-11.83	-1.04	-79.968	4.540
3300	16.503	67.599	58.655	-12.43	-1.08	-82.814	4.532
3400	16.908	67.187	58.768	-13.04	-1.12	-85.682	4.525
3500	17.314	66.708	58.872	-13.66	-1.16	-88.572	4.519
3600	17.721	66.165	58.963	-14.29	-1.20	-91.484	4.514
3700	18.129	65.562	59.041	-14.93	-1.24	-94.418	4.510
3800	18.537	64.903	59.107	-15.58	-1.28	-97.374	4.507
3900	18.945	64.184	59.162	-16.24	-1.32	-100.352	4.505
4000	19.352	63.412	59.207	-16.91	-1.36	-103.352	4.504
4100	19.759	62.593	59.243	-17.59	-1.40	-106.374	4.504
4200	20.165	61.732	59.270	-18.28	-1.44	-109.418	4.505
4300	20.570	60.834	59.288	-18.98	-1.48	-112.484	4.507
4400	20.974	60.000	59.297	-19.69	-1.52	-115.572	4.510
4500	21.377	59.134	59.298	-20.41	-1.56	-118.682	4.514
4600	21.779	58.238	59.291	-21.14	-1.60	-121.814	4.519
4700	22.180	57.314	59.276	-21.88	-1.64	-124.968	4.525
4800	22.580	56.364	59.253	-22.63	-1.68	-128.144	4.532
4900	22.978	55.389	59.222	-23.39	-1.72	-131.342	4.540
5000	23.374	54.390	59.183	-24.16	-1.76	-134.562	4.549
5100	23.768	53.368	59.136	-24.94	-1.80	-137.804	4.559
5200	24.160	52.324	59.081	-25.73	-1.84	-141.068	4.570
5300	24.550	51.258	59.018	-26.53	-1.88	-144.344	4.582
5400	24.938	50.079	58.948	-27.34	-1.92	-147.632	4.594
5500	25.324	48.878	58.872	-28.16	-1.96	-150.942	4.607
5600	25.708	47.618	58.791	-28.99	-2.00	-154.274	4.621
5700	26.090	46.300	58.706	-29.83	-2.04	-157.628	4.637
5800	26.470	44.934	58.617	-30.68	-2.08	-161.002	4.653
5900	26.848	43.532	58.524	-31.54	-2.12	-164.396	4.668
6000	27.224	42.096	58.427	-32.41	-2.16	-167.810	4.684

Dec. 31, 1960; Jan. 30, 1962; Mar. 31, 1965; June 30, 1968

Ground State Configuration $2s^2 2p^2$
 $S_{298.15}^\circ = 48.60 \pm 0.01$ gibbs/mol
 $\Delta H_f^\circ = -0.7 \pm 2$ kcal/mol
 $\Delta H_f^\circ(298.15) = 0 \pm 2$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	2
23836	2
23959	2
39357	2
43175	2
$\omega_e X_e = 11.90$ cm ⁻¹	$\sigma = 1$
$\omega_e = 1895.66$ cm ⁻¹	$r_e = 1.2049$ Å
$B_e = 1.400$ cm ⁻¹	$r_e = 0.01676$ cm ⁻¹

Heat of Formation

The heat of formation has recently been determined by several workers whose values are in close agreement. P. E. Blackburn, A. Buchler, and J. L. Stauffer, *J. Phys. Chem.* **70**, 2469 (1966), measured the ion currents corresponding to BO^+ and B_2O^+ as a function of temperature in a mass spectrometer. From a least squares fit of the data they report $\Delta H = 86.6 \pm 1.8$ kcal for the reaction $1/2B_2O_2(g) + BO(g)$; this yields $\Delta H_f^\circ(BO, g) = 2.1 \pm 2.8$ kcal/mol using $\Delta H_f^\circ(B_2O_2, g) = -109 \pm 2$ kcal/mol.

L. De Galan, *Physica*, **31**, 1286 (1965), from flame photometric measurements reports $D_0^\circ(BO) = 8.3e(191.4$ kcal), which corresponds to $\Delta H_f^\circ(BO, g) = -0.1$ kcal/mol.

P. Coppens, S. Smoes and J. Drouart, *Trans. Faraday Soc.* **64**, 630 (1968), from a mass spectrometric study of several isomolecular exchange reactions, conclude that $D_0^\circ(BO) = 8.29 \pm 0.2e(191.2 \pm 2.3$ kcal) or $\Delta H_f^\circ(BO, g) = 0.1 \pm 2.3$ kcal/mol. H. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Rocket Power, Inc., Report No. AFRL-TP-67-244, Final Report under Contract F04611-67-C-0010, Nov. 1967 (available as AD80327), investigated the same reaction as Blackburn et al. and report $\Delta H_{1800}^\circ = 53.8 \pm 1.9$ kcal/mol, which yields $\Delta H_f^\circ(BO, g) = 0.9 \pm 2.9$ kcal/mol.

We adopt a median value of 0 ± 2 kcal/mol which includes all the determinations.

Heat Capacity and Entropy

The molecular and vibrational constants for the ground state are from G. Herzberg "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950. The electronic levels are also given by Herzberg with the exception of the level at 39957, a 2 level designated B' by A. A. Mal'tsev and D. I. Kataev, *Vestn. Mosk. Univ. Ser. II* **22**, 2 (1967). The molecular constants were all adjusted to reflect normal isotopic abundances.

BORON DIOXIDE UNINEGATIVE ION (BO₂⁻) (IDEAL GAS) GFW = 42.81035

Point Group [D_{∞h}]

ΔHf° = -166 ± 6 kcal/mol

S_{298.15} = [51.6 ± 2] gibbs/mol

ΔHf_{298.15} = -166 ± 6 kcal/mol

Boron Dioxide Uninegative Ion (BO₂⁻) (Ideal Gas) GFW = 42.81035

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
100							
200							
298	9.349	51.579		.000	= 166.000	= 164.862	120.687
300	9.371	51.580		.017	= 166.010	= 164.855	120.007
400	9.511	51.581		1.000	= 167.116	= 163.751	115.816
500	11.121	56.873	52.709	2.002	= 167.116	= 163.754	71.590
600	11.725	58.956	53.580	3.225	= 167.000	= 163.063	59.396
700	12.214	60.801	54.482	4.423	= 166.242	= 162.242	50.654
800	12.614	62.459	55.377	5.665	= 164.890	= 161.339	44.076
900	12.942	63.942	56.268	6.865	= 163.000	= 160.000	38.618
1000	13.212	65.382	57.091	8.252	= 170.089	= 159.312	34.618
1100	13.435	66.612	57.699	9.564	= 176.497	= 158.206	31.423
1200	13.620	67.700	58.095	10.838	= 171.307	= 157.044	28.602
1300	13.775	68.686	59.419	12.307	= 171.925	= 155.829	26.197
1400	13.912	69.582	60.612	13.912	= 172.181	= 154.563	24.130
1500	14.015	70.475	60.816	15.008	= 173.181	= 153.263	22.330
1600	14.108	71.783	61.474	16.494	= 173.822	= 151.812	20.750
1700	14.188	72.640	62.106	17.909	= 174.871	= 150.524	19.351
1800	14.257	73.453	62.714	19.331	= 175.129	= 149.096	18.103
1900	14.316	74.224	63.298	20.765	= 175.466	= 147.466	16.982
2000	14.369	74.962	63.864	22.195	= 176.466	= 146.133	15.940
2100	14.415	75.664	64.410	23.634	= 177.144	= 144.598	15.048
2200	14.455	76.335	64.936	25.077	= 177.430	= 143.033	14.209
2300	14.491	76.974	65.446	26.525	= 178.519	= 141.436	13.439
2400	14.521	77.584	65.940	27.978	= 179.319	= 140.436	12.737
2500	14.551	78.190	66.418	29.429	= 180.310	= 138.044	12.068
2600	14.576	78.781	66.882	30.885	= 180.013	= 136.138	11.443
2700	14.598	79.311	67.332	32.344	= 180.719	= 134.207	10.863
2800	14.617	79.799	67.769	33.805	= 181.426	= 132.250	10.332
2900	14.634	80.254	68.194	35.266	= 182.133	= 130.287	9.842
3000	14.654	80.682	68.608	36.732	= 182.855	= 128.253	9.393
3100	14.669	81.333	69.011	38.199	= 183.572	= 126.224	8.899
3200	14.683	81.799	69.403	39.666	= 190.294	= 124.172	8.481
3300	14.696	82.251	69.786	41.135	= 191.016	= 122.094	7.906
3400	14.708	82.683	70.158	42.604	= 191.743	= 120.000	7.361
3500	14.719	83.116	70.523	44.077	= 192.474	= 117.877	6.751
3600	14.728	83.531	70.879	45.549	= 193.207	= 115.732	6.026
3700	14.736	83.935	71.226	47.022	= 193.943	= 113.567	6.708
3800	14.744	84.328	71.566	48.495	= 194.674	= 111.388	6.119
3900	14.754	84.711	71.898	49.972	= 195.420	= 109.188	6.119
4000	14.762	85.095	72.223	51.448	= 317.361	= 104.491	5.727
4100	14.769	85.449	72.541	52.924	= 317.856	= 99.500	5.304
4200	14.776	85.805	72.853	54.401	= 318.371	= 94.166	4.900
4300	14.783	86.156	73.158	55.878	= 318.886	= 88.481	4.511
4400	14.786	86.493	73.457	57.358	= 319.410	= 83.469	4.146
4500	14.794	86.825	73.751	58.837	= 319.932	= 78.100	3.793
4600	14.799	87.151	74.036	60.316	= 320.457	= 72.717	3.455
4700	14.803	87.471	74.318	61.797	= 320.984	= 67.325	3.131
4800	14.807	87.781	74.594	63.278	= 321.511	= 61.933	2.819
4900	14.815	88.086	74.870	64.759	= 322.045	= 56.515	2.521
5000	14.820	88.386	75.137	66.240	= 322.576	= 51.090	2.233
5100	14.825	88.679	75.400	67.722	= 323.115	= 45.649	1.956
5200	14.830	88.965	75.659	69.205	= 323.652	= 40.210	1.690
5300	14.835	89.250	75.916	70.686	= 324.191	= 34.771	1.431
5400	14.840	89.527	76.162	72.172	= 324.733	= 29.287	1.185
5500	14.845	89.799	76.407	73.656	= 325.275	= 23.804	.946
5600	14.850	90.067	76.649	75.141	= 325.820	= 18.322	.715
5700	14.855	90.330	76.886	76.626	= 326.368	= 12.831	.492
5800	14.860	90.588	77.121	78.111	= 326.916	= 7.340	.272
5900	14.866	90.842	77.351	79.598	= 327.464	= 1.805	.067
6000	14.871	91.092	77.576	81.085	= 328.021	= 3.720	.135

June 30, 1968; Dec. 31, 1968

Electronic Levels and Quantum Weights

State	ϵ_i , cm ⁻¹	g_i
1 ₂ ⁺	0	1
1 _g		
1 _{B₂}	[35000]	1

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	
[1150] (1)	
[580] (2)	
[2200] (1)	

Bond Distance: B-O = [1.25] Å

Bond Angle: O-B-O = [180]°

Rotational Constant: B₀ = [0.3372] cm⁻¹

Heat of Formation

D. E. Jensen, AeroChem TP-187A, Dec. 1968, AeroChem Research Laboratories, Inc., Princeton, N. J., has obtained equilibrium constants for the reaction $\text{HBO}_2 + e^- \rightarrow \text{H} + \text{BO}_2^-$. This involves several assumptions the most basic of which is that boron added to H_2/O_2 flames is converted completely to HBO_2 . The free electrons are produced by addition of potassium to the flame, and their concentration is measured directly by a microwave cavity resonance method. The hydrogen atom concentration is taken from previous studies on such flames. The BO_2^- concentration is obtained from the difference between the K^+ concentration and the free electron measurement. The K^+ concentration is measured by an electrostatic probe.

By 2nd and 3rd law analysis of the data, 11 points read back from a plot, we obtain $\Delta H_{298}^\circ(\text{II}) = 27.5 \pm 4$ kcal and $\Delta H_{298}^\circ(\text{III}) = 20 \pm 2$ kcal with a drift of -3.7 ± 1.5 eu. The third law value yields $\Delta H_{298}^\circ(\text{BO}_2^-) = -166 \pm 6$ kcal/mol where the uncertainty includes possible errors in the functions. This corresponds to an electron affinity of BO_2 equal to 98 ± 6 kcal/mol (4.25 eV).

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh (1) prediction for 16 valence electron XY_2 molecules. The electronic states are taken from those for $\text{CO}_2(\text{g})$ (2), which is isoelectronic with $\text{BO}_2^-(\text{g})$. The electronic level 35000 cm⁻¹ and vibrational frequencies are estimated by comparison with the corresponding values for CO_2 , CO_2^+ , and BO_2 , and, the data of Vasco and Srb (3) on the BO_2^- ion in alkali halide lattices. The B-O bond distance in $\text{BO}_2^-(\text{g})$ is assumed to be smaller than the B-O bond in $\text{BO}_2(\text{g})$, because the $\text{BO}_2^-(\text{g})$ molecule has one more bonding electron than the $\text{BO}_2(\text{g})$ molecule. The moment of inertia is 8.302×10^{-39} g cm². The enthalpy at 0°K is -2.30 kcal/mol.

References

1. A. D. Walsh, J. Chem. Soc. 1953, 2286 (1953).
2. G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.
3. A. Vasco and I. Srb, Czech. J. Phys. 17, 1110 (1967).

Boron Monosulfide (BS)

(Ideal Gas) Mol. Wt. = 42.89

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f	ΔF _f	Log K _p
0	0.000	INFINITE	2.085	79.260	79.260	INFINITE
100	6.957	43.098	57.802	79.785	75.689	-165.411
200	6.988	48.825	52.295	80.008	71.485	-78.111
298	7.182	51.645	0.000	80.000	67.296	-49.327
300	7.188	51.690	0.013	79.998	67.216	-48.945
400	7.499	53.799	51.931	79.311	62.997	-38.618
500	7.799	55.506	52.480	78.726	58.985	-25.781
600	8.044	56.950	53.108	78.186	55.089	-20.065
700	8.239	58.114	53.776	77.686	51.300	-15.016
800	8.379	59.134	54.376	77.216	47.618	-10.478
900	8.491	60.108	54.981	76.776	44.078	-7.053
1000	8.579	61.207	55.599	76.368	41.877	-4.877
1100	8.649	62.029	56.111	75.998	39.689	-3.462
1200	8.703	62.682	56.519	75.658	37.514	-2.462
1300	8.753	63.186	56.836	75.346	35.374	-1.809
1400	8.792	63.633	57.072	75.060	33.270	-1.354
1500	8.825	64.040	57.236	74.800	31.198	-1.054
1600	8.854	64.411	57.336	74.564	29.157	-0.854
1700	8.879	64.756	57.376	74.352	27.146	-0.704
1800	8.901	65.076	57.356	74.164	25.164	-0.604
1900	8.920	65.376	57.276	74.000	23.212	-0.534
2000	8.938	65.656	57.136	73.860	21.290	-0.484
2100	8.954	65.916	56.936	73.744	19.400	-0.444
2200	8.968	66.156	56.676	73.652	17.540	-0.414
2300	8.982	66.376	56.356	73.584	15.712	-0.384
2400	8.995	66.576	55.976	73.540	13.916	-0.354
2500	9.007	66.756	55.536	73.520	12.152	-0.324
2600	9.018	66.920	55.036	73.524	10.420	-0.294
2700	9.029	67.068	54.476	73.544	8.720	-0.264
2800	9.039	67.196	53.856	73.580	7.056	-0.234
2900	9.048	67.304	53.176	73.632	5.432	-0.204
3000	9.057	67.396	52.436	73.696	3.848	-0.174
3100	9.066	67.472	51.636	73.780	2.304	-0.144
3200	9.073	67.532	50.776	73.884	0.800	-0.114
3300	9.080	67.576	49.856	73.996	-0.764	-0.084
3400	9.087	67.604	48.876	74.124	-2.280	-0.054
3500	9.093	67.616	47.836	74.268	-3.848	-0.024
3600	9.100	67.612	46.736	74.428	-5.468	0.006
3700	9.107	67.592	45.576	74.604	-7.140	0.036
3800	9.112	67.556	44.356	74.796	-8.864	0.066
3900	9.116	67.504	43.076	75.004	-10.640	0.096
4000	9.120	67.436	41.736	75.228	-12.468	0.126
4100	9.123	67.352	40.336	75.468	-14.348	0.156
4200	9.126	67.252	38.876	75.724	-16.280	0.186
4300	9.129	67.136	37.356	76.000	-18.264	0.216
4400	9.131	67.004	35.776	76.296	-20.304	0.246
4500	9.133	66.856	34.136	76.612	-22.400	0.276
4600	9.135	66.696	32.436	76.948	-24.552	0.306
4700	9.137	66.524	30.676	77.304	-26.760	0.336
4800	9.139	66.340	28.856	77.680	-29.024	0.366
4900	9.141	66.144	26.976	78.076	-31.344	0.396
5000	9.143	65.936	25.036	78.492	-33.720	0.426
5100	9.145	65.716	23.036	78.928	-36.152	0.456
5200	9.147	65.484	20.976	79.384	-38.640	0.486
5300	9.149	65.240	18.856	79.860	-41.184	0.516
5400	9.151	64.984	16.676	80.356	-43.784	0.546
5500	9.153	64.716	14.436	80.872	-46.440	0.576
5600	9.155	64.436	12.136	81.408	-49.152	0.606
5700	9.157	64.144	9.776	81.964	-51.920	0.636
5800	9.159	63.840	7.356	82.540	-54.744	0.666
5900	9.161	63.524	4.876	83.136	-57.624	0.696
6000	9.163	63.200	2.336	83.752	-60.560	0.726

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Mar. 31, 1965

BORON MONOSULFIDE (BS)

(IDEAL GAS)

MOL. WT. = 42.89

Ground State Configuration 2Σ $\Delta H_f^0 = 79 \pm 18$ kcal. mole⁻¹ $S_{298.15}^0 = 51.645$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^0 = 80 \pm 18$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

$$\frac{E_1}{0} \text{ cm.}^{-1}$$

 $\omega_e x_e = 1186.23$ cm.⁻¹ $\sigma = 1$ $\omega_e = 6.596$ cm.⁻¹ $r_e = 1.609$ Å $\alpha_e = 0.80596$ cm.⁻¹

Heat of Formation.

The value of ΔH_f^0 298.15 for BS(g) was calculated based on $D_0^0 = 5.1 \pm 0.8$ e.v. for BS(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy.

The ground state configuration, ω_e , $\omega_e x_e$, B_e , α_e and r_e were reported by P. B. Zeeman, Can. J. Phys. 29, 336 (1951). The molecular constants used for calculation were corrected to the average isotopic species. The moment of inertia is 3.47762×10^{-39} g. cm.²

TITANIUM MONOBORIDE (TiB) (CRYSTAL) MOL. WT. = 58.711

Mar. 31, 1963; June 30, 1965

BTi

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈ °)/T eu	H° - H ₂₉₈ kcal. mole ⁻¹	ΔF _f kcal. mole ⁻¹	Log K _p
0					
100					
200					
298	7.092	8.300	0.000	- 38.300	27.979
300					
350	7.150	8.344	-0.13	- 38.303	27.806
400	7.640	10.771	8.63	- 38.395	20.821
500	10.926	13.071	1.866	- 38.424	16.624
600	11.608	15.128	3.075	- 38.443	13.824
700	12.160	16.568	4.266	- 38.472	11.823
800	12.580	17.933	5.414	- 38.519	10.321
900	12.906	20.002	6.638	- 38.586	9.151
1000	12.408	21.304	7.874	- 38.675	8.213
1100	12.474	22.490	9.118	- 38.789	7.444
1200	12.506	23.577	10.437	- 38.920	6.824
1300	12.509	24.569	11.724	- 39.064	6.234
1400	12.570	25.509	13.013	- 39.216	5.752
1500	12.602	26.378	14.134	- 39.418	5.333
1600	12.634	27.192	15.195	- 39.641	4.963
1700	12.658	27.957	16.199	- 39.880	4.643
1800	12.698	28.684	17.174	- 40.139	4.343
1900	12.730	29.371	18.126	- 40.412	4.079
2000	12.762	30.025	19.266	- 40.701	3.830
2100	12.794	30.649	20.290	- 41.009	3.594
2200	12.826	31.242	21.222	- 41.331	3.377
2300	12.858	31.815	22.072	- 41.668	3.179
2400	12.890	32.363	22.844	- 42.031	2.996
2500	12.922	32.890	23.532	- 42.424	2.817
2600	12.954	33.397	24.149	- 42.848	2.642
2700	12.986	33.884	24.694	- 43.304	2.472
2800	13.018	34.360	25.165	- 43.794	2.327
2900	13.050	34.817	25.572	- 44.319	2.185
3000	13.082	35.260	25.918	- 44.880	2.052
3100	13.114	35.690	26.204	- 45.478	1.927
3200	13.146	36.100	26.430	- 46.114	1.809
3300	13.178	36.512	26.598	- 46.788	1.698
3400	13.210	36.905	26.736	- 47.501	1.593
3500	13.242	37.289	26.867	- 48.254	1.494
3600	13.274	37.662	26.889	- 49.048	1.312
3700	13.306	38.024	26.804	- 49.884	1.154
3800	13.338	38.382	26.612	- 50.764	1.010
3900	13.370	38.729	26.313	- 51.689	0.878
4000	13.402	39.067	25.908	- 52.661	0.740

ΔH_f° 0 = UnknownΔH_f° 298.15 = -38.3 ± 9 kcal. mole⁻¹S_{298.15}° = [8.3 ± 1.5] cal. deg.⁻¹ mole⁻¹T_d = [2500]°K.

Heat of Formation.

P. O. Schissel and O. C. Trulsen, *J. Phys. Chem.*, **66**, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system and obtained $\Delta F_{2340}^{\circ} = -118.54$ kcal. mole⁻¹ for the reaction $\text{TiB}(c) = \text{Ti}(g) + \text{B}(g)$. This corresponds to $\Delta F_{2340}^{\circ}(\text{TiB}(c)) = -33.266 \pm 9$ kcal. mole⁻¹, where 4 kcal. mole⁻¹ of the uncertainty is due to the heat of sublimation of boron. When this is reduced to 298°K, one obtains $\Delta H_{298}^{\circ}(\text{TiB}(c)) = -38.3 \pm 9$ kcal. mole⁻¹. This value implies a high stability for TiB. This is also indicated by the phase studies of H. Nowotny, F. Benesovsky, C. Bruckl and O. Schob, Monatshefte für Chemie **92**, 403 (1961).

Heat Capacity and Entropy.

The heat capacities from 298 to 1200°K. were estimated from that of TiB₂ by assuming the difference to be the same as that between CrB and CrB₂ as determined by R. Meszki, E. W. Tilleux, D. W. Barnes and J. L. Margrave (Paper presented at the International Symposium on Nuclear Materials, Vienna, May 1962). A linear extrapolation was assumed above 1200°K.

The heat capacities above 298°K. were also estimated from the relationship $C_p(\text{Ti}) + C_p(\text{B}) - C_p(\text{TiB}_2) = 2/3 [C_p(\text{Ti}) + C_p(\text{B}) - C_p(\text{TiB})]$. This estimation agreed with the above to 4% over the temperature range 400 to 1000°K.

$S_{298}^{\circ}(\text{TiB}, c) = 8.3$ cal. mole⁻¹ deg.⁻¹ was calculated by the method of W. M. Latimer, *J. Am. Chem. Soc.*, **73**, 1480 (1951). Using JANAF $S_{298}^{\circ}(\text{TiB}_2, c) = 6.8$ cal. mole⁻¹ deg.⁻¹ and Latimer's value of 9.8 e.u. for the entropy contribution of Ti, an entropy contribution of -1.5 e.u. per Boron atom was calculated.

Decomposition Data.

The phase diagram given in, "The Metallurgy of the Rarer Metals - No. 4 Titanium", by A. D. McQuillan and M. K. McQuillan, Academic Press, New York (1956) was used to estimate the decomposition temperature. This diagram shows the decomposition products are TiB₂ and Ti₃B₂. However, Nowotny et al. (loc. cit.) have shown Ti₃B₂ to be non-existent and so the decomposition products are not defined, probably a eutectic of TiB and TiB₂ is involved.

Boron, Diatomic (B₂)
(Ideal Gas) Mol. Wt. = 21.64

BORON, DIATOMIC (B₂) (IDEAL GAS)

MOL. WT. = 21.64

Ground State Configuration \sum_g^-
 $\Delta H_f^0 = 193.5 \pm 6.4 \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 48.228 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 298.15 = 195.0 \pm 6.4 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\frac{C_1}{C_1 + C_2} \frac{g_1}{g_2}$

$\frac{C_1}{C_1 + C_2} \frac{g_1}{g_2}$	$\omega_e x_e = 9.58 \text{ cm.}^{-1}$	$\omega_e = 1061.0 \text{ cm.}^{-1}$	$B_e = 1.235 \text{ cm.}^{-1}$	$\alpha_e = 0.0144 \text{ cm.}^{-1}$	$r_e = 1.589 \text{ \AA}$
0	3				

$\sigma = 2$

Heat of Formation.

The equilibrium vapor pressure of the reaction $B_2(g) \rightarrow B(g) + B(g)$ was determined by G. Verhaegen and J. Drowart, J. Chem. Phys. 32, 1367 (1962). Using the value, $P_{B_2}(g)/P_{B(g)} = 9 \times 10^{-5}$ at 2350°K. where P is partial pressure, the heat of reaction ($\Delta H_f^0 298.15$) was evaluated to be $-62.2 \pm 5.0 \text{ kcal mole}^{-1}$. This leads to $\Delta H_f^0 298.15 = 195.0 \pm 6.4 \text{ kcal. mole}^{-1}$ for B₂(g) or $D_0 = 3.0 \text{ e.v.}$ which is in excellent agreement with the value, $D_0^0 = 3.0 \pm 0.5 \text{ e.v.}$ reported by A. G. Daydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The value, $D_0 = 3.6 \text{ e.v.}$, estimated by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950, yields $\Delta H_f^0 298.15 = 181.6 \text{ kcal. mole}^{-1}$ for B₂(g) which is not used.

Heat Capacity and Entropy.

Molecular and spectroscopic constants were obtained from G. Herzberg, loc. cit. and corrected to the average isotopic species. The principal moment of inertia (I) is $2.26779 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	6.000	INFINITE	-2.094	193.490	193.490	INFINITE
100	6.958	40.545	54.536	194.173	190.135	-415.510
200	7.023	45.378	48.885	194.710	185.870	-203.100
298	7.301	48.228	48.228	195.000	181.457	-193.005
300	7.307	48.273	48.258	195.004	181.473	-192.124
400	7.667	50.425	48.519	195.108	172.810	-96.600
500	7.976	52.170	49.080	195.065	172.237	-75.281
600	8.232	53.646	49.721	194.925	167.664	-61.076
800	8.521	54.926	50.375	194.724	163.159	-50.938
1000	8.763	57.065	51.033	194.476	158.566	-43.343
1200	8.963	59.000	51.698	194.190	153.920	-37.342
1400	9.125	60.682	52.373	193.874	149.177	-32.732
1600	9.256	62.135	53.057	193.527	144.379	-28.683
1800	9.364	63.482	53.746	193.150	140.016	-25.681
2000	9.456	64.682	54.438	192.749	135.699	-22.977
2200	9.535	65.757	55.135	192.319	131.425	-20.511
2400	9.603	66.716	55.839	191.866	127.197	-18.251
2600	9.661	67.567	56.549	191.398	123.016	-16.181
2800	9.710	68.314	57.264	190.916	118.884	-14.287
3000	9.750	68.969	57.984	190.424	114.801	-12.541
3200	9.782	69.537	58.609	189.924	110.763	-10.925
3400	9.807	70.020	59.141	189.418	106.771	-9.422
3600	9.825	70.428	59.584	188.908	102.824	-8.016
3800	9.838	70.766	60.041	188.394	98.925	-6.695
4000	9.846	71.037	60.511	187.876	95.085	-5.453
4200	9.850	71.246	60.994	187.354	91.305	-4.285
4400	9.851	71.397	61.490	186.828	87.584	-3.186
4600	9.850	71.497	61.998	186.300	83.921	-2.147
4800	9.847	71.552	62.517	185.769	80.315	-1.166
5000	9.842	71.572	62.945	185.236	76.763	-0.242
5200	9.836	71.558	63.384	184.700	73.265	0.714
5400	9.828	71.501	63.834	184.161	69.821	1.644
5600	9.818	71.404	64.295	183.619	66.433	2.547
5800	9.806	71.270	64.767	183.074	63.106	3.424
6000	9.792	71.101	65.250	182.526	59.841	4.277
6200	9.776	70.898	65.744	181.974	56.637	5.114
6400	9.758	70.663	66.250	181.418	53.493	5.934
6600	9.738	70.398	66.767	180.858	50.410	6.737
6800	9.716	70.104	67.295	180.293	47.387	7.524
7000	9.692	69.782	67.834	179.724	44.424	8.297
7200	9.666	69.433	68.384	179.151	41.521	9.056
7400	9.638	69.058	68.945	178.574	38.678	9.799
7600	9.608	68.658	69.517	177.992	35.894	10.526
7800	9.576	68.234	70.099	177.405	33.169	11.238
8000	9.542	67.787	70.692	176.814	30.503	11.935
8200	9.506	67.318	71.295	176.218	27.895	12.617
8400	9.468	66.828	71.917	175.618	25.345	13.284
8600	9.428	66.318	72.557	175.013	22.854	13.936
8800	9.386	65.788	73.214	174.404	20.422	14.573
9000	9.342	65.238	73.887	173.790	18.048	15.195
9200	9.296	64.669	74.576	173.172	15.731	15.802
9400	9.248	64.082	75.280	172.549	13.471	16.394
9600	9.198	63.478	75.999	171.922	11.267	16.971
9800	9.146	62.857	76.732	171.291	9.118	17.534
10000	9.092	62.219	77.480	170.656	7.023	18.082

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	ΔH _f ^o	Log K _f
0	0.000	INFINITE	-	- 322.253	INFINITE
100	12.591	58.199	94.638	- 322.253	700.148
200	21.932	78.079	94.638	- 322.253	231.287
298	21.932	78.079	94.638	- 322.253	231.287
300	22.001	78.080	94.638	- 322.253	229.828
400	25.297	85.016	78.985	- 322.253	170.993
500	27.839	90.946	80.767	- 322.253	135.677
600	29.762	96.202	82.935	- 322.253	112.124
700	31.266	100.909	85.172	- 322.253	95.295
800	32.407	105.162	87.409	- 322.253	82.670
900	33.294	109.032	89.600	- 322.253	72.846
1000	33.969	112.577	91.723	- 322.253	64.985
1100	34.543	115.844	93.769	- 294.718	58.552
1200	34.988	118.869	95.736	- 292.058	53.188
1300	35.350	121.685	97.625	- 289.387	48.648
1400	35.647	124.315	99.439	- 286.699	44.754
1500	35.895	126.784	101.180	- 284.000	41.377
1600	36.102	129.107	102.854	- 281.198	38.408
1700	36.278	131.301	104.463	- 278.285	35.774
1800	36.427	133.379	106.013	- 275.361	33.432
1900	36.555	135.352	107.509	- 272.421	31.334
2000	36.666	137.230	108.945	- 269.470	29.445
2100	36.763	139.021	110.335	- 266.500	27.734
2200	36.847	140.734	111.678	- 263.522	26.177
2300	36.922	142.373	112.977	- 260.527	24.755
2400	36.987	143.946	114.235	- 257.514	23.449
2500	37.046	145.457	115.454	- 254.479	22.228
2600	37.098	146.911	116.636	- 251.400	21.081
2700	37.144	148.312	117.783	- 248.277	20.017
2800	37.186	149.664	118.898	- 245.109	18.942
2900	37.224	150.969	119.981	- 241.898	17.830
3000	37.258	152.232	121.036	- 238.645	16.792
3100	37.289	153.454	122.062	- 235.352	15.820
3200	37.317	154.638	123.061	- 232.020	14.909
3300	37.343	155.787	124.036	- 228.650	14.052
3400	37.366	156.902	124.986	- 225.250	13.246
3500	37.388	157.986	125.913	- 221.820	12.486
3600	37.408	159.039	126.819	- 218.360	11.767
3700	37.426	160.064	127.704	- 214.870	11.087
3800	37.443	161.063	128.569	- 211.350	10.442
3900	37.459	162.035	129.414	- 207.800	9.830
4000	37.474	162.984	130.242	- 204.220	9.244
4100	37.487	163.909	131.052	- 200.620	8.688
4200	37.500	164.813	131.845	- 197.000	8.158
4300	37.511	165.695	132.622	- 193.360	7.650
4400	37.522	166.558	133.383	- 189.700	7.160
4500	37.533	167.401	134.130	- 186.020	6.694
4600	37.542	168.226	134.862	- 182.330	6.250
4700	37.551	169.034	135.581	- 178.620	5.826
4800	37.560	169.825	136.286	- 174.890	5.422
4900	37.568	170.599	136.978	- 171.140	5.036
5000	37.575	171.358	137.658	- 167.380	4.666
5100	37.582	172.102	138.328	- 163.610	4.311
5200	37.589	172.832	138.983	- 159.830	3.968
5300	37.595	173.548	139.628	- 156.040	3.636
5400	37.601	174.251	140.263	- 152.240	3.314
5500	37.607	174.941	140.887	- 148.430	3.002
5600	37.612	175.619	141.501	- 144.610	2.700
5700	37.617	176.284	142.106	- 140.780	2.408
5800	37.622	176.939	142.701	- 136.940	2.126
5900	37.626	177.584	143.287	- 133.090	1.854
6000	37.631	178.214	143.863	- 129.240	1.592

Dec. 31, 1962; June 30, 1965

Point Group [C_{2h}]
S_{298.15} = [78.079] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight [1]

Vibrational Frequencies and Degeneracies
 ω_e , cm.⁻¹ ω_e , cm.⁻¹ ω_e , cm.⁻¹

[2000] (1) [1050] (1) [400] (1)
[1600] (1) [650] (1) [350] (1)
[1200] (1) [600] (1) [200] (1)
[1200] (1) [600] (1) [150] (1)
[1050] (1) [500] (1) [120] (1)

Bond Distance: Be-O = [1.63] Å O-B = [1.34] Å B-O = [1.20] Å
Bond Angle: O-B-O = [180°] O-Be-O = [180°] B-O-Be = [95°]
Product of Moments of Inertia: I_AI_BI_C = 5.3801 X 10⁻¹¹³ g.³ cm.⁶

Heat of Formation.
The heat of formation was obtained from mass spectrometric studies; the following reactions at 1500°K. were reported by P. E. Blackburn and A. Eichler, Interim Technical Report No. 1, March 1965:

1. B₂O₃(1) → B₂O₃(g) ΔH₁ = 92.226 kcal/mole
2. 1/5 Be₃P₂O₆(c) + 2/5 B₂O₃(1) → Be(B₂O₃)₂(g) ΔH₂ = 118 ± 2 kcal/mole
3. Be₃P₂O₆(c) → 3BeO(c) + B₂O₃(g) ΔH₃ = 112 ± 1 kcal/mole
4. Be₃P₂O₆(c) → 2BeO(c) + Be(B₂O₃)₂(g) ΔH₄ = 137 ± 3 kcal/mole
5. 3BeO(c) + B₂O₃(1) → Be₃P₂O₆(c) ΔH₅ = -23 kcal/mole
6. BeO(c) + B₂O₃(g) → Be(B₂O₃)₂(g) ΔH₆ = 22 kcal/mole

The values for ΔH₂, ΔH₃ and ΔH₄ were obtained from P. E. Blackburn and A. Eichler loc. cit. The value for ΔH₅ was obtained by taking the average of ΔH₂-ΔH₁ + 1/5 ΔH₃ = -19.774 kcal/mole, and ΔH₅ = 5/2 (ΔH₂-ΔH₄) = -28.5 kcal/mole. The ΔH₆ value was obtained by taking the average of ΔH₆ = ΔH₄-ΔH₃ = 25 kcal/mole and ΔH₆ = ΔH₂-ΔH₁ + 1/5 ΔH₃ = 18.107 kcal/mole. The ΔH_f 298.15 of BeB₂O₄ was calculated from reaction 6 with auxiliary JANAF values.

Heat Capacity and Entropy.
The vibrational frequencies estimated by comparison with B₂O₃, were adjusted to obtain an S_{298.15} = 127 obtained in a manner analogous with ΔH_f from the report of P. E. Blackburn and A. Eichler loc. cit. The frequencies listed are not in point group order. All other molecular constants were estimated by comparison with related boron oxide molecules. The individual moments of inertia are I_A = 8.5561 X 10⁻³⁹ g. cm.², I_B = 75.1345 X 10⁻³⁹ g. cm.² and I_C = 83.6903 X 10⁻³⁹ g. cm.²

Triberyllium Dicoxide ($\text{Be}_3\text{Be}_2\text{O}_6$)
(Crystal) $\Delta H_f^\circ = 144.655$

T, K	C_p	S°	$-G^\circ - H^\circ_{298}/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
298	33.400	24.000	24.000	0.000	-741.960	-702.463	554.679
300	33.560	24.207	24.001	0.042	-741.968	-702.463	551.523
400	41.820	35.033	25.421	3.845	-742.279	-698.239	575.264
500	48.480	45.100	28.362	8.360	-742.786	-692.470	595.429
600	54.160	54.451	31.061	13.206	-741.990	-682.320	611.181
700	59.170	63.167	35.787	19.180	-741.398	-668.462	622.584
800	63.290	71.369	39.759	25.312	-740.536	-653.403	633.656
900	66.320	79.059	43.064	31.602	-739.470	-637.459	643.282
1000	68.420	86.212	47.567	38.245	-738.298	-620.739	651.629
1100	69.890	92.703	51.376	45.463	-737.038	-604.243	658.432
1200	70.840	98.825	55.077	52.608	-735.611	-587.294	664.427
1300	71.450	104.526	58.664	59.621	-734.063	-570.263	669.755
1400	72.220	109.856	62.132	66.415	-732.405	-553.560	674.289
1500	72.780	114.858	65.482	73.064	-730.620	-537.354	678.059
1600	73.310	119.573	68.717	81.340	-728.718	-521.136	681.090
1700	73.820	124.022	71.855	89.724	-726.704	-505.211	683.419
1800	74.310	128.232	74.885	98.133	-724.586	-489.587	685.000
1900	74.800	132.324	77.777	106.601	-722.362	-474.277	685.852
2000	75.280	136.319	80.550	115.126	-720.038	-459.277	686.000
2100	75.920	139.850	83.334	118.682	-717.577	-444.526	686.000
2200	76.400	143.353	85.984	126.298	-715.091	-430.041	685.522
2300	76.820	146.755	88.555	133.861	-712.586	-415.811	684.362
2400	77.200	150.079	91.051	141.460	-710.069	-401.831	682.469
2500	77.720	153.429	93.483	149.220	-707.544	-388.174	680.766
2600	78.180	156.301	95.833	157.215	-705.009	-374.849	678.312
2700	78.610	158.729	98.126	165.256	-702.468	-361.840	675.017
2800	79.070	161.226	100.363	172.739	-700.000	-349.120	671.000
2900	79.520	163.599	102.541	180.668	-697.600	-336.634	666.334
3000	80.000	165.651	104.665	188.045	-695.268	-324.368	661.000

Triberyllium Dicoxide ($\text{Be}_3\text{Be}_2\text{O}_6$) (CRISTAL)

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

$\Delta G_f^\circ = 144.655$

$\Delta S_f^\circ = 144.655$

$\Delta H_f^\circ = 144.655$

Boron Dichloride, Dimeric (B₂Cl₄)
(Ideal Gas) Mol Wt. = 163.468

BORON DICHLORIDE, DIMERIC (B₂Cl₄) (IDEAL GAS)

MOL. WT. = 163.468

Point Group D_{2d}
S_{298.15} = 85.767 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1
ΔF₀⁰ = Unknown
ΔF₀⁰ 298.15 = -116.9 ± 1.2 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω _v , cm. ⁻¹	ω _v , cm. ⁻¹	ω _v , cm. ⁻¹
113(1)	Rotation	917(2)
401(1)	730(1)	617(2)
225(1)	291(1)	180(2)

Bond Distances: B-Cl = 1.73 ± 0.02 Å B-B = 1.75 ± 0.01 Å

Bond Angle: Cl-B-Cl = 120 ± 2°

Dihedral angle between two BCl₂ planes = 90°Product of the Moments of Inertia: I_AI_BI_C = 5.33449 X 10⁻¹¹² g.² cm.⁶

Heat of Formation.

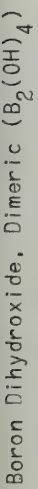
S. R. Gunn, L. O. Green and A. I. Von Rgidy, J. Phys. Chem. 63, 1787 (1959) determined the enthalpy change (ΔH_f⁰) of the reaction B₂Cl₄(l) + Cl₂(g) = 2BCl₃(g). From the value, ΔH_f⁰ 298.15 = -67.3 ± 0.6 kcal. mole⁻¹, the heat of formation for B₂Cl₄(l) was calculated as -125.32 ± 1.20 kcal. mole⁻¹. Based on ΔH_f⁰ 338.7 = 8.029 kcal. mole⁻¹ reported by G. Urry, I. Warkik, R. E. Moore and H. I. Schaeffer, J. Am. Chem. Soc. 76, 5283 (1954), the heat of formation for B₂Cl₄(g) was derived to be -116.9 ± 1.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational frequencies, molecular structure and constants were taken from D. E. Mann and L. Pano, J. Chem. Phys. 25, 1665 (1957). The barrier restricting internal rotation about the B-B single bond is fixed at 1.53 ± 0.60 kcal. mole⁻¹ obtained from E. A. Mason and M. M. Kreevy, J. Am. Chem. Soc. 77, 5808 (1955). The three principal moments of inertia are: I_A = 1.00465 X 10⁻³⁷, I_B = 5.28520 X 10⁻³⁸ and I_C = 1.00465 X 10⁻³⁷ g.² cm.². The reduced moment of inertia for BCl₂ top is I_r = 1.3215 X 10⁻³⁸ g.² cm.².

T, °K.	C _p	S ⁰	-(F ⁰ -H ₂₉₈ ^{0)/T}	H ⁰ -H ₂₉₈ ⁰	ΔH _f ⁰	ΔF ₀ ⁰	Log K _p
0	14.151	65.880	103.472	-3.758	-117.100	-116.635	250.523
100	19.277	77.397	87.759	-2.069	-117.013	-116.194	122.594
200	22.667	85.767	75.787	-0.000	-116.900	-109.859	60.525
300	22.719	85.907	65.787	0.042	-116.808	-109.815	70.907
400	25.048	82.780	56.682	2.437	-116.807	-107.469	56.715
500	26.603	88.564	48.459	5.024	-116.752	-105.140	45.945
600	27.649	93.493	40.586	7.740	-116.725	-102.820	37.451
700	28.270	97.598	33.213	10.513	-116.713	-100.513	30.823
800	28.670	101.028	26.478	13.400	-116.721	-98.274	25.874
900	28.921	103.949	20.217	16.305	-116.721	-96.074	21.280
1000	29.051	106.413	14.401	19.242	-116.742	-93.957	20.446
1100	29.084	108.464	9.000	22.202	-116.784	-91.238	18.126
1200	29.078	110.108	4.800	25.189	-116.847	-88.582	15.755
1300	29.078	111.498	1.600	28.149	-116.927	-86.062	13.317
1400	29.093	112.674	-1.600	31.173	-117.025	-83.743	10.865
1500	29.125	113.684	-5.067	34.188	-117.144	-81.600	8.430
1600	29.163	114.569	-8.046	37.212	-117.282	-79.543	6.002
1700	29.205	115.351	-10.946	40.246	-117.439	-77.573	3.582
1800	29.251	116.051	-13.774	43.275	-117.610	-75.686	1.161
1900	29.300	116.684	-16.542	46.315	-117.800	-73.878	-1.250
2000	29.351	117.264	-19.264	49.359	-118.013	-72.148	-3.681
2100	29.405	117.800	-21.934	52.406	-118.246	-70.493	-6.077
2200	29.463	118.294	-24.556	55.456	-118.500	-68.916	-8.437
2300	29.525	118.751	-27.134	58.507	-118.770	-67.416	-10.757
2400	29.591	119.174	-29.674	61.561	-119.057	-65.993	-13.037
2500	29.661	119.569	-32.224	64.618	-119.370	-64.643	-15.277
2600	29.735	119.940	-34.774	67.676	-119.700	-63.363	-17.477
2700	29.813	120.284	-37.324	70.735	-120.050	-62.143	-19.637
2800	29.895	120.604	-39.874	73.797	-120.420	-61.000	-21.757
2900	29.981	120.904	-42.424	76.860	-120.810	-59.923	-23.837
3000	30.071	121.184	-44.974	79.924	-121.220	-58.913	-25.877
3100	30.165	121.444	-47.524	82.986	-121.640	-57.963	-27.877
3200	30.263	121.684	-50.074	86.046	-122.080	-57.073	-29.837
3300	30.365	121.904	-52.624	89.106	-122.540	-56.243	-31.757
3400	30.471	122.104	-55.174	92.166	-123.020	-55.473	-33.637
3500	30.581	122.284	-57.724	95.226	-123.520	-54.763	-35.477
3600	30.695	122.444	-60.274	98.286	-124.040	-54.113	-37.277
3700	30.813	122.584	-62.824	101.346	-124.580	-53.523	-39.037
3800	30.935	122.704	-65.374	104.406	-125.140	-52.993	-40.757
3900	31.061	122.804	-67.924	107.466	-125.720	-52.523	-42.437
4000	31.191	122.884	-70.474	110.526	-126.320	-52.113	-44.077
4100	31.325	122.944	-73.024	113.586	-126.940	-51.763	-45.677
4200	31.463	122.984	-75.574	116.646	-127.580	-51.473	-47.237
4300	31.605	123.004	-78.124	119.706	-128.240	-51.243	-48.757
4400	31.751	123.004	-80.674	122.766	-128.920	-51.073	-50.237
4500	31.901	123.004	-83.224	125.826	-129.620	-50.963	-51.677
4600	32.055	123.004	-85.774	128.886	-130.340	-50.903	-53.077
4700	32.213	123.004	-88.324	131.946	-131.080	-50.893	-54.437
4800	32.375	123.004	-90.874	135.006	-131.840	-50.933	-55.757
4900	32.541	123.004	-93.424	138.066	-132.620	-51.023	-57.037
5000	32.711	123.004	-95.974	141.126	-133.420	-51.163	-58.277
5100	32.885	123.004	-98.524	144.186	-134.240	-51.353	-59.477
5200	33.063	123.004	-101.074	147.246	-135.080	-51.593	-60.637
5300	33.245	123.004	-103.624	150.306	-135.940	-51.883	-61.757
5400	33.431	123.004	-106.174	153.366	-136.820	-52.223	-62.837
5500	33.621	123.004	-108.724	156.426	-137.720	-52.613	-63.877
5600	33.815	123.004	-111.274	159.486	-138.640	-53.053	-64.877
5700	34.013	123.004	-113.824	162.546	-139.580	-53.543	-65.837
5800	34.215	123.004	-116.374	165.606	-140.540	-54.083	-66.757
5900	34.421	123.004	-118.924	168.666	-141.520	-54.673	-67.637
6000	34.631	123.004	-121.474	171.726	-142.520	-55.313	-68.477

Dec. 31, 1960; Dec. 31, 1964



Mol. Wt. = 89.65148

(Crystal)

T, °K.	C _p	S°	-(F°-H _{298°)/T}	H°-H _{298°}	ΔH _f °	ΔF _f °	Log K _p
0							
100	27.776	30.000	30.000	0.000	-337.100	-297.377	217.983
200							
298							
300	27.910	30.172	30.001	0.052	-337.110	-297.332	216.460
400	34.210	39.097	31.175	3.169	-337.447	-283.744	155.031
500	39.140	47.272	33.589	6.842	-337.460	-270.311	118.153
600	43.430	54.797	36.505	10.976	-337.186	-256.902	93.577
700	47.090	61.273	39.622	15.505	-336.679	-243.519	76.074
800	50.230	67.273	42.738	20.542	-336.175	-230.175	60.719
900	52.930	74.354	45.974	25.242	-335.694	-217.175	52.737
1000	55.290	80.056	49.100	30.956	-335.740	-204.154	44.618
1100	57.360	85.425	52.100	36.591	-332.443	-191.259	38.000
1200	59.140	90.289	55.126	42.418	-321.038	-178.434	27.590
1300	60.750	94.781	58.181	48.481	-307.881	-165.681	19.831
1400	61.900	99.832	60.874	54.341	-327.895	-153.304	23.932
1500	62.860	104.137	63.616	60.781	-326.251	-140.892	20.528

BORON DIHYDROXIDE, DIMERIC (B₂(OH)₄)₂

(CRYSTAL)

MOL. WT. = 89.65148

$\Delta H_f^\circ 0$ = Unknown
 $\Delta H_f^\circ 298.15$ = -337.1 ± 2.0 kcal. mole⁻¹
 ΔH_m° = Unknown
 $\Delta H_g^\circ 298.15$ = [30.1] kcal. mole⁻¹

$S_{298.15}^\circ$ = [30 ± 1] cal. deg.⁻¹ mole⁻¹

T_m = Unknown

Heat of Formation.

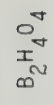
The enthalpy change, $\Delta H_f^\circ 298.15$ = -91.3 ± 1.0 kcal. mole⁻¹, for the reaction B₂(OH)₄(c) + (m + 2)·AgNO₃(aq.) + (n + 2)·H₂O(l) = 2Ag(c) + [2H₃BO₃ + 2HNO₃ + mAgNO₃]·nH₂O(aq.) was determined calorimetrically by A. Finch, P. J. Gardiner and I. J. Hyams, Trans. Faraday Soc. 51, 649 (1965). The heat of formation of B₂(OH)₄(c) was reported to be -335.1 kcal. mole⁻¹. This value was corrected to be -337.1 ± 2 kcal. mole⁻¹ by use of more recent data on the $\Delta H_f^\circ 298.15$ values used for calculation.

Heat Capacity and Entropy.

The heat capacity for B₂(OH)₄(c) was estimated by comparison with those for B(OH)₃(c). The value of $S_{298.15}^\circ$ was calculated based on 3 cal. deg.⁻¹ mole⁻¹ per atom for B₂(OH)₄(c), which was obtained from the corresponding values for H₂O₂(c) and B(OH)₃(c).

Heat of Sublimation.

The value, $\Delta H_g^\circ 298.15$, was calculated as the difference between $\Delta H_f^\circ 298.15$ for B₂(OH)₄(g) and B₂(OH)₄(c).





Boron Dihydroxide, Dimeric ($\text{B}_2(\text{OH})_4$)
(Ideal Gas) Mol. Wt. = 89.65148

T, °K.	C_p°	$\text{cal. mole}^{-1}\text{deg.}^{-1}$	$S^\circ - (F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0	12.226	64.168	101.205	-3.704	-304.878	-298.086	651.460
100	18.820	74.732	85.444	-2.142	-305.042	-290.852	317.829
200	24.721	83.369	83.369	-0.000	-307.000	-207.963	207.963
300	29.824	83.322	83.369	+0.046	-307.016	-283.043	204.106
400	29.857	91.360	84.407	-2.789	-307.727	-274.937	150.218
500	33.765	98.482	86.523	-5.979	-308.223	-266.679	116.565
600	36.761	104.015	89.061	0.512	-308.550	-258.337	94.099
700	38.113	107.765	91.216	13.216	-308.539	-246.589	79.583
800	41.023	116.117	94.467	17.320	-308.632	-241.546	69.087
900	42.614	121.043	97.149	21.504	-308.632	-233.134	56.613
1000	43.963	125.005	99.770	25.895	-308.761	-224.724	46.113
1100	45.120	129.850	102.314	30.201	-308.643	-216.327	42.860
1200	46.119	133.827	104.775	34.684	-308.482	-207.959	39.551
1300	46.986	137.547	107.154	39.210	-308.286	-199.570	36.251
1400	47.741	141.057	109.452	44.247	-308.089	-191.213	29.850
1500	48.400	144.374	111.671	49.095	-307.877	-182.873	26.645
1600	48.977	147.516	113.814	53.924	-307.664	-174.547	23.842
1700	49.481	150.502	115.880	58.624	-307.450	-166.230	21.470
1800	49.931	153.342	117.887	63.189	-307.239	-157.932	19.170
1900	50.326	156.053	119.825	68.832	-307.034	-149.643	17.213
2000	50.676	158.643	121.702	73.883	-306.831	-141.365	15.448
2100	50.988	161.123	123.520	78.946	-306.636	-133.084	13.851
2200	51.267	163.502	125.280	83.969	-306.450	-124.804	12.351
2300	51.516	165.786	126.996	89.219	-306.271	-116.586	11.078
2400	51.740	167.984	128.658	94.382	-306.106	-108.337	9.965
2500	51.942	170.100	130.274	99.566	-316.730	-99.860	8.732
2600	52.124	172.141	131.845	104.760	-316.571	-91.216	7.667
2700	52.289	174.111	133.363	109.960	-316.427	-82.584	6.667
2800	52.439	176.016	134.863	115.227	-316.279	-73.896	5.766
2900	52.575	177.858	136.314	120.477	-316.137	-65.229	4.916
3000	52.700	179.643	137.729	125.741	-316.007	-56.588	4.122
3100	52.814	181.373	139.109	131.037	-315.881	-47.945	3.380
3200	52.918	183.051	140.496	136.304	-315.764	-39.302	2.691
3300	53.014	184.681	141.772	141.600	-315.660	-30.662	2.031
3400	53.103	186.265	143.057	146.906	-315.562	-22.030	1.416
3500	53.184	187.805	144.314	152.221	-315.473	-13.399	0.837
3600	53.260	189.305	145.543	157.543	-315.393	-4.767	0.280
3700	53.329	190.765	146.743	162.872	-315.323	12.446	-0.219
3800	53.394	192.188	147.923	168.209	-315.263	21.107	-0.719
3900	53.454	193.576	149.075	173.551	-315.213	30.021	-1.183
4000	53.510	194.930	150.205	178.869	-315.151	34.027	-1.659
4100	53.563	196.255	151.312	184.228	-315.087	48.604	-2.001
4200	53.611	197.543	152.397	189.552	-315.028	63.183	-2.301
4300	53.657	198.805	153.462	194.975	-314.975	78.343	-2.562
4400	53.700	200.039	154.507	200.343	-314.928	93.085	-2.792
4500	53.740	201.246	155.532	205.715	-314.881	107.819	-3.026
4600	53.777	202.428	156.539	211.091	-314.839	122.548	-3.263
4700	53.813	203.585	157.527	216.464	-314.798	137.278	-3.502
4800	53.846	204.718	158.499	221.833	-314.758	152.008	-3.742
4900	53.877	205.829	159.453	227.239	-314.718	166.738	-3.982
5000	53.907	206.917	160.392	232.629	-314.678	181.470	-4.222
5100	53.935	207.984	161.314	238.021	-314.638	196.204	-4.462
5200	53.961	209.033	162.222	243.413	-314.598	210.938	-4.702
5300	53.986	210.061	163.115	248.813	-314.558	225.668	-4.942
5400	54.009	211.070	163.994	254.213	-314.518	240.402	-5.182
5500	54.032	212.061	164.859	259.615	-314.478	255.136	-5.422
5600	54.053	213.035	165.710	265.019	-314.438	269.870	-5.662
5700	54.073	213.992	166.549	270.425	-314.398	284.604	-5.902
5800	54.092	214.933	167.375	275.833	-314.358	299.338	-6.142
5900	54.111	215.857	168.189	281.244	-314.318	314.072	-6.382
6000	54.128	216.767	168.991	286.656	-314.278	328.806	-6.622

Mar. 31, 1966

BORON DIHYDROXIDE, DIMERIC ($\text{B}_2(\text{OH})_4$) (IDEAL GAS)

MOL. WT. = 89.65148

Point Group $[C_2]$ $\Delta H^\circ_f 0 = \text{Unknown}$

$S^\circ_{298.15} = [83.37] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H^\circ_f 298.15 = [-307 \pm 5] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega, \text{cm.}^{-1}$	$\omega, \text{cm.}^{-1}$	$\omega, \text{cm.}^{-1}$	$\omega, \text{cm.}^{-1}$
[1390](1)	[1396](1)	[824](2)	
[650](1)	[657](1)	[209](2)	
[304](1)	[325](1)	[3200](4)	
[1378](1)	[1378](1)	[1200](2)	
[862](1)	[862](1)	[880](2)	
[542](1)	[542](1)		

Rotation (1) [1378](1) [862](1) [542](1)

[1155](1) [862](1) [542](1)

Bond Distances: B-B = [1.67] Å B-O = [1.36] Å B-H = [0.96] Å

Bond Angle: H-O-B = [114]° O-B-O = [120]° O-B-B = [120]° $\sigma = 2$

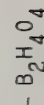
Product of the Moments of Inertia: $I_A I_B I_C = [2.2985 \times 10^{-113}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation ($\Delta H^\circ_f 298.15$) for $\text{B}_2(\text{OH})_4(\text{g})$ was calculated, using bond energies, $D(\text{B-OH}) = 132$ and $D(\text{B-B}) = 76 \text{ kcal. mole}^{-1}$. The bond energy $D(\text{B-OH})$ was taken from that in $\text{B(OH)}_3(\text{g})$ and $D(\text{B-B})$ was estimated by comparison with that in $\text{B}_2\text{P}_4(\text{g})$.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that for $\text{B}_2\text{P}_4(\text{g})$, i.e. the two B(OH)_2 units have staggered configuration, and free rotation about B-B bond. The B-B bond distance was taken as that in B_2P_4 molecule. Those for B-O and B-H bond and bond angles were adopted from H_3BO_3 molecule. Eleven vibrational frequencies were assumed to be the same as those for $\text{B}_2\text{P}_4(\text{g})$. In addition to these were added four OH torsion frequencies, 824(2) and 209(2), four OH stretching, 3200(4), and four B-O-H bending frequencies, 1200(2) and 880(2). The thermodynamic functions were evaluated based on a molecular model having free internal rotation of two B(OH)_2 groups about B-B bond. The reduced moment of inertia for the rotation is calculated as $4.10146 \times 10^{-39} \text{ g. cm.}^2$. The three principal moments of inertia are: $I_A = 1.64037 \times 10^{-38}$ and $I_B = I_C = 3.7441 \times 10^{-38} \text{ g. cm.}^2$.





(IDEAL GAS)

DIBORANE (B₂H₆)

MOL. WT. = 27.668

Diborane (B₂H₆)
(Ideal Gas) Mol. Wt. = 27.668

Point Group D_{3h}
S_{298.15} = 55.703 cal. deg. mole⁻¹
Ground State Quantum Weight = (1)

ΔH_f⁰ = 13.6 ± 4.0 kcal. mole⁻¹
ΔH_f^{298.15} = 9.8 ± 4.0 kcal. mole⁻¹

T, °K.	C _p ⁰	S ⁰ - (F ⁰ -H ₂₉₈)/T	H ⁰ -H ₂₉₈	ΔH _f ⁰	Log K _p
--------	-----------------------------	--------------------------------------------------------	----------------------------------	------------------------------	--------------------

T, °K.	C _p ⁰	S ⁰ - (F ⁰ -H ₂₉₈)/T	H ⁰ -H ₂₉₈	ΔH _f ⁰	Log K _p
0	4.000	INFINITE	2.904	13.552	INFINITE
100	8.268	44.654	2.118	13.552	-15.313
200	10.397	50.934	5.686	11.013	-16.858
298	13.886	55.709	1.185	9.800	-16.082
300	13.957	55.795	1.026	9.777	-16.038
400	17.067	60.473	3.543	9.636	-15.354
500	21.190	64.673	5.745	7.605	-13.600
600	24.219	68.811	5.898	6.890	-12.929
700	26.835	72.746	6.036	6.308	-12.587
800	29.077	76.480	6.152	5.898	-12.348
900	31.000	80.000	6.242	5.636	-12.173
1000	32.600	83.368	6.308	5.493	-12.038
1100	33.966	86.541	6.341	5.437	-11.930
1200	35.123	89.547	6.345	5.453	-11.840
1300	36.100	92.399	6.312	5.516	-11.763
1400	36.941	95.041	6.252	5.614	-11.697
1500	37.656	97.479	6.162	5.724	-11.657
1600	38.271	100.130	6.041	5.841	-11.635
1700	38.802	102.466	5.889	5.965	-11.627
1800	39.262	104.697	5.711	6.087	-11.630
1900	39.654	106.811	5.504	6.210	-11.645
2000	40.016	108.873	5.269	6.332	-11.670
2100	40.325	110.835	5.002	6.447	-11.706
2200	40.599	112.717	4.694	6.557	-11.755
2300	40.834	114.527	4.352	6.663	-11.816
2400	41.031	116.267	3.984	6.765	-11.888
2500	41.195	117.950	3.595	6.863	-11.970
2600	41.325	119.572	3.186	6.957	-12.061
2700	41.421	121.138	2.754	7.047	-12.160
2800	41.481	122.653	2.302	7.133	-12.266
2900	41.507	124.123	1.831	7.215	-12.379
3000	41.566	125.540	1.345	7.291	-12.498
3100	42.072	126.918	9.967	3.423	-11.956
3200	42.169	128.255	9.969	3.353	-11.964
3300	42.261	129.547	9.970	3.289	-11.971
3400	42.348	130.817	9.970	3.229	-11.977
3500	42.413	132.045	9.965	3.177	-11.983
3600	42.462	133.241	9.958	3.132	-11.989
3700	42.506	134.406	10.023	3.097	-11.994
3800	42.546	135.543	10.079	3.066	-11.999
3900	42.581	136.648	10.139	3.036	-12.004
4000	42.710	137.729	10.310	2.955	-12.010
4100	42.758	138.784	10.406	2.874	-12.016
4200	42.802	139.825	10.485	2.794	-12.022
4300	42.842	140.843	10.549	2.715	-12.027
4400	42.881	141.808	10.618	2.637	-12.032
4500	42.917	142.772	10.673	2.560	-12.037
4600	42.951	143.716	10.695	2.485	-12.042
4700	42.981	144.640	10.702	2.411	-12.047
4800	43.013	145.543	10.695	2.338	-12.052
4900	43.040	146.432	10.679	2.266	-12.057
5000	43.067	147.302	10.651	2.195	-12.062
5100	43.092	148.155	10.608	2.125	-12.067
5200	43.117	148.992	10.551	2.056	-12.072
5300	43.143	149.812	10.485	1.988	-12.077
5400	43.158	150.620	10.418	1.921	-12.082
5500	43.178	151.412	10.346	1.856	-12.087
5600	43.197	152.191	10.266	1.792	-12.092
5700	43.217	152.957	10.181	1.729	-12.097
5800	43.232	153.707	10.091	1.667	-12.102
5900	43.248	154.446	10.000	1.606	-12.107
6000	43.264	155.173	9.900	1.546	-12.112

Dec. 31, 1960; Dec. 31, 1964.

Vibrational Frequencies and Degeneracies

W, cm. ⁻¹	W, cm. ⁻¹	W, cm. ⁻¹	W, cm. ⁻¹
2532(1)	2600(1)	1026(1)	2615(1)
2103(1)	919(1)	584(1)	1601(1)
1184(1)	1755(1)	1905(1)	1174(1)
788(1)	942(1)	973(1)	
2612(1)	950(1)	368(1)	

Bond Distance: B-B = 1.775 ± 0.004 Å B-H₂ = 1.196 ± 0.016 Å B-H₃ = 1.339 ± 0.013 Å
Bond Angles: H₂-B-H₂ = 120.2 ± 1.6° H₂-B-H₃ = 118.6 ± 0.6°
Product of the Moments of Inertia: I_AI_BI_C = 2.46622 × 10⁻¹¹⁶ g.³ cm.⁶

Heat of Formation.

ΔH_f^{298.15} is a weighted average of the following data. The older data of W. A. Roth et al. (8) deviates from the rest of the investigations and is not included.

Investigator

Gunn and Green (1) B₂H₆(g) → 2B(am) + 3H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) -5.0 7.4

E. J. Prosen et al. (2) B₂H₆(g) → 2B(am) + 3H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) -6.73 9.13

J. R. Lacher et al. (3) B₂H₆(g) + 6Cl₂ → 2BCl₃(g) + 6HCl(g) ΔH_f^{298.15} (kcal. mole⁻¹) -342.5 17.3

E. J. Prosen et al. (4) B₂H₆(g) + 6H₂O(l) + [2000H₂O(l)] → 2H₃BO₃ + 1000H₂O(soln.) + 6H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) -111.46 ± 0.54 9.32

Gunn and Green (7) (a) B₂H₆(g) + 2000H₂O → 2H₃BO₃ + 1000H₂O + 6H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) -112.22 ± 0.10 10.08

Gunn and Green (7) (b) BCl₃(l) + 130.3H₂O → (H₃BO₃ + 1000H₂O) ΔH_f^{298.15} (kcal. mole⁻¹) -68.14 10.06

(a) -2(b) = (c) B₂H₆(g) + 6(HCl-100H₂O) → 2BCl₃(l) + 6H₂(g) ΔH_f^{298.15} (kcal. mole⁻¹) +24.06 8.3

Gunn (10) (CH₃)₃N(g) + 1/2 B₂H₆(g) → (CH₃)₃NBH₃(c) ΔH_f^{298.15} (kcal. mole⁻¹) -31.40 6.5

McCoey and Bauer (13) (CH₃)₃N(g) + 1/2 B₂H₆(g) → (CH₃)₃NBH₃(c) ΔH_f^{298.15} (kcal. mole⁻¹) -31.40 6.5

Sources of Auxiliary data: From the JANAP tables, ΔH_f^{298.15} = 1.2, -96.31, -22.063 kcal. mole⁻¹ of B(am), BCl₃(g) and HCl(g) respectively. From F. D. Rossini et al. (11) The ΔH_f^{298.15} = 5.6 kcal. mole⁻¹ of BCl₃. From D. D. Wagman (12) the ΔH_f^{298.15} of HCl + 100H₂O = -39.657 kcal. mole⁻¹. From Good et al. (5) the ΔH_f^{298.15} of H₃BO₃(c) = -261.47 ± 0.20 kcal. mole⁻¹ and the H₃BO₃ solution data of Rasolno (6). ΔH_f^{298.15} of (CH₃)₃N(g) = -3.9 ± 0.4 kcal. mole⁻¹ from I Jaffe (10).

(1) S. R. Gunn and L. G. Green, J. Phys. Chem. **65**, 779-83(1961); J. Chem. Phys. **36**, 1118 (1962). Explosive decomposition while mixed with stibine.

(2) E. J. Prosen, W. H. Johnson and F. Y. Fergiel, J. Res. N.B.S. **61**, 247-250 (1958). Decomposition by heating in a flow-type calorimeter.

(3) J. R. Lacher, R. E. Scruby, and J. D. Park, J. Am. Chem. Soc. **74**, 5292-4 (1952). A vapor phase chlorination in a flow-type calorimeter.

(4) E. J. Prosen, W. H. Johnson, and F. Y. Fergiel, J. Res. N.B.S. **62**, 43-47 (1959). Heat of reaction of diborane with water in a flow-type calorimeter.

(5) W. D. Good, W. Mansson, and J. P. McCullough, "Thermochemistry of Boron and Some of its Compounds. The heats of Formation of Trimethylamineborane and Orthoboric Acid" a pre-print from the proceedings of the symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July 1963.

(6) L. G. Rasolno, "Heats of Formation of B₂O₃(c) and B₂O₃(am)" Special Report NMR-360, National Research Corporation, Cambridge, Mass. June 2, 1964.

(7) S. R. Gunn and L. G. Green, J. Phys. Chem. **64**, 61-63(1960). Heats of hydrolysis of diborane and boron trichloride in a sealed rocking bomb type calorimeter.

(8) W. F. O'Leary, R. E. Scruby, and A. Bertman, Ber. **70B**, 49 (1937); Ber. **70B**, 971 (1937) and W. A. Roth, Z. Naturforsch., **1**, 574 (1946). Heat of hydrolysis in a bomb type calorimeter.

(9) S. R. Gunn, abstract (No. 42) of a paper presented at the 19th annual Calorimetry Conference, Washington, D. C., and Bethesda, Maryland, Oct. 13-16, 1964.

(10) I. Jaffe, Thesis University of Maryland, 1959.

(11) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Selected Values of Chemical Thermodynamic Properties, N.B.S. Circ. 500.

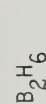
(12) W. H. Evans, Appendix III, National Bureau of Standards Report 8504, July 1, 1964.

(13) R. E. McCoey and S. H. Bauer, J. Am. Chem. Soc. **78**, 2061 (1956).

Heat Capacity and Entropy.

The molecular constants reported by B. L. Carroll, "Electron Diffraction Investigation of Diborane and Boron-alkyls", Thesis, Iowa State University of Science and Technology, 1963, were selected. They agree well with those reported by K. Hedberg, and V. Schomaker, J. Chem. Phys. **22**, 985 (1954). The principal moments are I_A = 1.0578 × 10⁻³⁹, I_B = 4.6416 × 10⁻³⁹, and I_C = 5.0229 × 10⁻³⁹ g. cm.²

The vibrational frequencies for B₂H₆ were those listed by E. C. Wu, Thesis, University of Minn. 1962, "Assignments and Force Constants of Diborane and Isotopic Derivatives" except for ν_8 , ν_{10} and ν_{14} which were taken from the calculated frequency column of table VIII-1 page 55 of the Thesis.



Magnesium Diboride (MgB_2)
(Crystal) Mol. Wt. = 45.96

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0	0.000	0.000	INFINITE	1.425	-21.825	-21.825	INFINITE
100	2.670	9.962	16.482	-1.562	-22.011	-22.011	4.718
200	8.220	4.590	9.950	-1.000	-22.088	-21.664	23.77
298	11.430	8.600	0.000	0.000	-21.980	-21.378	15.670
300	11.440	8.671	0.000	0.021	-21.980	-21.374	15.571
400	13.060	12.150	9.069	1.248	-22.011	-21.170	11.566
500	13.060	15.198	10.002	2.598	-22.129	-20.967	9.156
600	14.670	17.808	11.090	4.030	-22.316	-20.696	7.538
700	15.300	20.117	12.218	5.529	-22.542	-20.407	6.371
800	15.900	22.199	13.337	7.089	-22.797	-20.086	5.497
900	16.500	24.068	14.429	8.711	-23.068	-19.731	4.791
1000	17.140	25.681	15.467	10.394	-23.474	-19.162	4.166
1100	17.705	27.041	16.508	12.137	-23.741	-18.520	3.679
1200	18.270	28.106	17.493	13.935	-24.008	-17.851	3.251
1300	18.835	29.091	18.444	15.780	-24.274	-17.162	2.885
1400	19.400	30.007	19.363	17.672	-24.540	-16.452	2.583
1500	19.961	30.866	20.231	19.602	-24.806	-15.734	2.342
1600	20.550	31.674	21.112	21.669	-25.072	-15.006	2.166
1700	21.071	32.436	21.947	23.760	-25.338	-14.271	2.032
1800	21.570	33.154	22.758	25.913	-25.604	-13.526	1.931
1900	22.046	33.833	23.547	28.124	-25.870	-12.771	1.851
2000	22.500	34.476	24.313	30.391	-26.136	-12.006	1.787

MAGNESIUM DIBORIDE (MgB_2)

(CRYSTAL)

MOL. WT. = 45.96

$$\Delta H^\circ_f 0 = -21.8 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_f 298.15 = -22.0 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 8.60 \pm 0.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = [1320]^\circ\text{K}$$

Heat of Formation.

The equilibrium constants (993 - 1108°K.) for the reaction $2\text{MgB}_2(c) = \text{Mg}(g) + \text{MgB}_4(c)$ were determined by M. Wright and P. N. Walsh, "The Vaporization of $\text{MgB}_4(c)$ ", Technical Research Report OMCO-HEP-55, Jan. 9, 1958, Ohio State University Research Foundation. The corresponding second and third law values of $\Delta H^\circ_f 298.15$ for this reaction were derived as 53.1 ± 4.7 and $54.1 \text{ kcal. mole}^{-1}$, respectively. Using the third law value obtained, i.e. $\Delta H^\circ_f 298.15 = 54.1 \text{ kcal. mole}^{-1}$, for the reaction, the $\Delta H^\circ_f 298.15$ for $\text{MgB}_2(c)$ was evaluated as $-22.0 \pm 2.0 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The low temperature (21.12 - 304.22°K.) heat capacities were measured by R. M. Swift and D. White, J. Am. Chem. Soc. 79, 3641 (1957). Above 298.15°K. the values of C_p were estimated by comparison with those of other related borides. $S^\circ_{298.15}$ was reported by R. M. Swift and D. White, loc. cit., using $S^\circ_{20}(\text{extrap.}) = 0.005 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Decomposition.

T_d was taken from L. Y. Markovskiy, Y. D. Kondrashev, and O. V. Kaputovskaya, Zhur. Obshchei Khim., 25, 409 (1955). On heating to high temperatures $\text{MgB}_2(c)$ decomposes into boride phases A, B, and C with the separation of Mg. The composition of phase A is close to MgB_6 and that of C is close to MgB_{12} .

(Ideal Gas) GFW = 37.6214

DIBORON MONOXIDE (B₂O)

(IDEAL GAS)

OFW = 37.6214

Point Group [C_{2v}]
S_{298.15} = [54.4] gibbs/mol
Ground State Quantum Weight = [1]

ΔHf°₀ = 22 ± 25 kcal/mol

ΔHf°_{298.15} = 23 ± 25 kcal/mol

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹
(1250)(1)
(600)(1)
(1800)(1)

Bond Distance B-O = [1.26] Å
Bond Angle: B-O-B = [150]°

Product of the Moments of Inertia: I_AI_BI_C = [4.7324] X 10⁻¹¹⁷ g³ cm⁶

Heat of Formation.

The heat of formation was calculated from the estimated heat of reaction ΔHf°₀ = 300 ± 25 kcal/mol for B₂O(g) → 2B(g) + O(g), using the JANAF auxiliary data for B(g) and O(g). The value of ΔHf°₀ was assumed to be the sum of the heats of dissociation, 120 kcal/mol for B₂O(g) → B₂O(g) + B(g) and 180 kcal/mol for B₂O(g) → B(g) + O(g). The former was estimated and the latter was derived from the JANAF values.

The possible existence of B₂O(g) in the burning of boron under reducing conditions was discussed by Gilbert S. Bohn in a paper presented at the Combustion Institute, at University of Denver, Apr. 25-27, 1966. He estimated the heat of formation to lie between -27 and +23 kcal/mol, but favored the value of +23 kcal/mol in the theoretical calculations of boron burning in air.

Heat Capacity and Entropy.

The bent molecular structure and the molecular constants were estimated by comparison with those in BO(g), AlO(g) and Al₂O(g). The three principal moments of inertia are I_A = 0.1624 X 10⁻³⁹, I_B = 5.318 X 10⁻³⁹ and I_C = 5.4804 X 10⁻³⁹ g cm².

June 30, 1966

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	Log Kp
0	0.000	0.000	INFINITE	2.480	22.142	INFINITE
100	7.975	45.239	62.085	-	22.578	70.140
200	8.477	50.890	55.222	-	22.888	19.106
298	9.180	54.405	54.405	0.000	23.000	14.921
300	9.193	54.462	54.462	0.017	23.000	14.870
400	9.593	57.205	54.775	0.972	22.950	10.833
500	10.556	59.486	55.495	1.596	22.788	6.145
600	11.121	61.462	56.328	3.080	22.545	2.493
700	11.598	62.713	57.189	5.217	22.261	0.492
800	11.988	63.875	57.982	7.007	21.947	0.198
900	12.269	64.913	58.672	8.607	21.623	0.098
1000	12.514	65.859	59.267	10.000	21.279	0.071
1100	12.712	66.721	60.441	11.108	20.913	0.138
1200	12.875	67.485	61.178	12.043	20.525	1.492
1300	13.012	68.163	61.863	12.838	20.120	2.661
1400	13.115	68.763	62.501	13.500	19.709	2.006
1500	13.206	69.284	63.096	14.044	19.267	1.516
1600	13.284	69.733	63.653	14.569	18.807	1.143
1700	13.349	70.113	64.173	15.068	18.326	0.861
1800	13.405	70.433	64.653	15.533	17.831	0.641
1900	13.445	70.699	65.096	15.962	17.321	0.461
2000	13.475	70.913	65.496	16.359	16.800	0.316
2100	13.501	71.079	65.852	16.720	16.266	0.202
2200	13.521	71.200	66.173	17.053	15.718	0.110
2300	13.536	71.288	66.458	17.359	15.158	0.057
2400	13.546	71.343	66.706	17.633	14.587	0.031
2500	13.553	71.376	66.926	17.874	14.007	0.018
2600	13.558	71.396	67.116	18.084	13.417	0.010
2700	13.562	71.405	67.273	18.263	12.817	0.006
2800	13.565	71.411	67.400	18.413	12.207	0.003
2900	13.567	71.415	67.500	18.538	11.587	0.002
3000	13.570	71.417	67.574	18.641	10.957	0.001
3100	13.571	71.418	67.624	18.724	10.317	0.000
3200	13.572	71.419	67.653	18.788	9.667	0.000
3300	13.573	71.420	67.673	18.838	9.007	0.000
3400	13.574	71.421	67.683	18.874	8.337	0.000
3500	13.575	71.422	67.686	18.898	7.657	0.000
3600	13.576	71.423	67.690	18.913	6.967	0.000
3700	13.577	71.424	67.693	18.919	6.267	0.000
3800	13.578	71.425	67.695	18.922	5.557	0.000
3900	13.579	71.426	67.697	18.924	4.837	0.000
4000	13.580	71.427	67.698	18.925	4.107	0.000
4100	13.581	71.428	67.699	18.926	3.367	0.000
4200	13.582	71.429	67.700	18.927	2.617	0.000
4300	13.583	71.430	67.701	18.928	1.857	0.000
4400	13.584	71.431	67.702	18.929	1.087	0.000
4500	13.585	71.432	67.703	18.930	0.307	0.000
4600	13.586	71.433	67.704	18.931	-0.483	0.000
4700	13.587	71.434	67.705	18.932	-1.263	0.000
4800	13.588	71.435	67.706	18.933	-2.037	0.000
4900	13.589	71.436	67.707	18.934	-2.807	0.000
5000	13.590	71.437	67.708	18.935	-3.572	0.000
5100	13.591	71.438	67.709	18.936	-4.332	0.000
5200	13.592	71.439	67.710	18.937	-5.087	0.000
5300	13.593	71.440	67.711	18.938	-5.837	0.000
5400	13.594	71.441	67.712	18.939	-6.582	0.000
5500	13.595	71.442	67.713	18.940	-7.322	0.000
5600	13.596	71.443	67.714	18.941	-8.057	0.000
5700	13.597	71.444	67.715	18.942	-8.787	0.000
5800	13.598	71.445	67.716	18.943	-9.512	0.000
5900	13.599	71.446	67.717	18.944	-10.232	0.000
6000	13.600	71.447	67.718	18.945	-10.947	0.000

Boron Monoxide, Dimeric ((B₂O)₂)

Mol. Wt. = 53.64

(Ideal Gas)

T, °K	C _p	S° - (H° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	8.000	infinite	infinite	infinite	infinite	infinite	infinite
100	11.528	46.090	2.963	109.304	109.304	109.304	1.971
200	11.528	46.090	2.963	109.304	109.304	109.304	1.971
298	13.655	57.958	3.000	109.000	110.533	110.533	1.239
300	13.725	58.043	3.025	108.998	110.845	110.845	1.247
400	15.027	65.184	3.468	108.910	111.476	111.476	1.005
500	15.947	69.603	3.016	108.917	112.119	112.119	0.605
600	16.688	72.235	2.963	108.989	112.752	112.752	0.168
700	17.307	74.235	2.963	109.098	113.371	113.371	0.308
800	17.824	75.581	2.963	109.229	113.974	113.974	0.135
900	18.255	76.706	2.963	109.370	114.559	114.559	0.186
1000	18.613	77.649	2.963	109.523	115.126	115.126	0.250
1100	18.910	78.437	2.963	109.684	115.680	115.680	0.322
1200	19.157	79.083	2.963	109.856	116.214	116.214	0.394
1300	19.363	79.605	2.963	109.976	116.716	116.716	0.464
1400	19.537	80.013	2.963	110.075	117.190	117.190	0.531
1500	19.683	80.330	2.963	110.159	117.640	117.640	0.593
1600	19.808	80.564	2.963	110.221	118.069	118.069	0.650
1700	19.915	80.720	2.963	110.267	118.476	118.476	0.702
1800	20.007	80.800	2.963	110.297	118.860	118.860	0.749
1900	20.087	80.833	2.963	110.313	119.224	119.224	0.792
2000	20.157	80.833	2.963	110.316	119.570	119.570	0.831
2100	20.216	80.800	2.963	110.306	119.896	119.896	0.865
2200	20.271	80.740	2.963	110.284	120.206	120.206	0.894
2300	20.316	80.660	2.963	110.251	120.496	120.496	0.918
2400	20.356	80.560	2.963	110.209	120.769	120.769	0.937
2500	20.398	80.440	2.963	110.159	121.021	121.021	0.952
2600	20.431	80.300	2.963	110.100	121.256	121.256	0.963
2700	20.456	80.140	2.963	110.033	121.476	121.476	0.970
2800	20.476	80.000	2.963	110.000	121.680	121.680	0.974
2900	20.493	79.840	2.963	109.956	121.868	121.868	0.977
3000	20.508	79.700	2.963	109.900	122.040	122.040	0.979
3100	20.521	79.540	2.963	109.833	122.196	122.196	0.980
3200	20.531	79.380	2.963	109.756	122.336	122.336	0.980
3300	20.538	79.200	2.963	109.668	122.460	122.460	0.980
3400	20.542	79.000	2.963	109.568	122.568	122.568	0.979
3500	20.543	78.780	2.963	109.456	122.656	122.656	0.977
3600	20.541	78.540	2.963	109.332	122.724	122.724	0.974
3700	20.536	78.280	2.963	109.196	122.772	122.772	0.970
3800	20.528	78.000	2.963	109.048	122.800	122.800	0.965
3900	20.517	77.680	2.963	108.888	122.808	122.808	0.959
4000	20.503	77.320	2.963	108.716	122.796	122.796	0.952
4100	20.486	76.920	2.963	108.532	122.764	122.764	0.944
4200	20.466	76.480	2.963	108.336	122.712	122.712	0.935
4300	20.443	76.000	2.963	108.128	122.640	122.640	0.925
4400	20.417	75.560	2.963	107.908	122.548	122.548	0.914
4500	20.388	75.080	2.963	107.676	122.436	122.436	0.901
4600	20.356	74.560	2.963	107.432	122.304	122.304	0.886
4700	20.322	74.000	2.963	107.176	122.152	122.152	0.869
4800	20.286	73.400	2.963	106.904	122.000	122.000	0.850
4900	20.248	72.760	2.963	106.616	121.848	121.848	0.829
5000	20.208	72.080	2.963	106.312	121.684	121.684	0.806
5100	20.166	71.360	2.963	105.996	121.508	121.508	0.781
5200	20.122	70.600	2.963	105.668	121.320	121.320	0.754
5300	20.076	69.800	2.963	105.328	121.120	121.120	0.725
5400	20.028	68.960	2.963	104.976	120.908	120.908	0.694
5500	19.978	68.080	2.963	104.612	120.684	120.684	0.660
5600	19.926	67.160	2.963	104.236	120.448	120.448	0.623
5700	19.872	66.200	2.963	103.848	120.200	120.200	0.584
5800	19.816	65.200	2.963	103.448	120.000	120.000	0.543
5900	19.758	64.160	2.963	103.032	119.784	119.784	0.500
6000	19.698	63.080	2.963	102.600	119.552	119.552	0.454

Point Group D_{2h}

S_{298.15} = 57.958 cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f⁰ = -109.3 ± 2.0 kcal. mole⁻¹

ΔH_f⁰ 298.15 = -109.0 ± 2.0 kcal. mole⁻¹

(IDEAL GAS)

Vibrational Frequencies and Degeneracies

ΔH, cm⁻¹

2065(1)

570(1)

1910(1)

585(2)

285(2)

B-B = 1.70 Å

Bond Angle: O-B-B = 180°

Rotational Constant: B₀ = 0.1125 cm⁻¹

σ = 2

Heat of Formation

The heat of formation (ΔH_f⁰ 298.15) for B₂O₂(g) adopted is the weighted average of three ΔH_f⁰ 298.15 values derived from two different chemical reactions. The chemical reactions related to the production of B₂O₂(g) have been studied by several investigators. Using the equilibrium vapor pressure data, the respective values of ΔH_f⁰ 298.15 were evaluated by both the second and third law methods. The results obtained are based on the latter and presented as follows.

Investigator	Reaction	Third Law Value	Second Law Value	ΔH _f ⁰ 298.15, kcal. mole ⁻¹	ΔH _f ⁰ 298.15, kcal. mole ⁻¹
Inghram, et al. ¹	2/3 B(c) + 2/3 B ₂ O ₃ (l) = B ₂ O ₂ (g)	94.0	91.8 ± 2.2	94.0	-105.5 ± 0.7*
Searcy and Myers ²	2/3 B(c) + 2/3 B ₂ O ₃ (l) = B ₂ O ₂ (g)	24.8	25.4 ± 0.2	24.8	-108.0 ± 0.5
Searcy ³	2B ₂ O(c) + 2B(c) = 2B ₂ O(g) + B ₂ O ₂ (g)	255.4	—	255.4	-102.6 ± 10*
Scheer ⁴	2/3 B(c) + 2/3 B ₂ O ₃ (l) = B ₂ O ₂ (g)	89.3	77.9 ± 0.2	89.3	-110.2 ± 0.9
Rentzepis, et al. ⁴	B ₂ O ₃ (l) + 3C(c) = 3CO(g) + B ₂ O ₂ (g)	—	—	—	-108.5 ± 1.5
Rentzepis, et al. ⁴	B ₂ O ₃ (l) + C(c) = B ₂ O ₂ (g) + CO(g)	—	—	—	—

*The value not used for the calculation of the weighted average of ΔH_f⁰ 298.15 for B₂O₂(g).

¹W. O. Inghram, R. F. Porter and W. A. Chupka, J. Chem. Phys. **25**, 498 (1956).

²A. W. Searcy and C. E. Myers, J. Phys. Chem. **61**, 957 (1957).

³M. D. Scheer, J. Phys. Chem. **62**, 450 (1958).

⁴P. Rentzepis, D. White and P. M. Walsh, J. Phys. Chem. **64**, 1784 (1960). The value of ΔH_f⁰ 298.15 was obtained from derived log K_p(B₂O₂, g) values by the third law method.

Heat Capacity and Entropy

The molecular structure and constants, and vibrational frequencies, corrected to the average isotopic species, were taken from A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys. **32**, 87 (1963). The moment of inertia (I) is 2.4922 × 10⁻³⁸ g. cm².

B₂O₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	4.000	INFINITE	-2.218	-302.162	-302.162	INFINITE
100	4.987	22.984	-2.051	-303.668	-303.668	152.025
200	5.980	14.010	-1.951	-305.921	-305.921	317.688
298	6.950	12.870	-1.900	-308.640	-308.640	208.699
300	15.140	12.963	-0.028	-303.642	-284.608	207.327
400	18.350	17.787	1.712	-303.668	-278.257	152.025
500	20.800	22.148	3.671	-303.631	-271.907	118.845
600	23.250	26.153	5.872	-303.513	-265.571	96.729
700	26.200	29.951	8.239	-303.245	-259.265	80.942
800	29.650	33.673	11.131	-302.740	-253.015	69.117
900	32.050	37.316	14.226	-301.998	-246.843	59.699
1000	34.450	40.789	17.504	-301.130	-240.757	52.615
1100	36.800	44.000	20.895	-300.206	-234.766	46.642
1200	39.100	47.003	24.347	-299.264	-228.857	41.679
1300	41.350	49.789	27.827	-298.337	-223.029	37.493
1400	43.500	52.379	31.323	-297.432	-217.268	33.915
1500	45.500	54.794	34.823	-296.560	-211.576	30.825
1600	47.000	57.053	38.323	-295.722	-205.936	28.128
1700	48.175	59.175	41.823	-294.915	-200.350	25.755
1800	49.175	61.175	45.323	-294.138	-194.810	23.652
1900	50.000	63.068	48.823	-293.387	-189.313	21.775
2000	50.000	64.863	52.323	-292.655	-183.855	20.090

Dec. 31, 1960; Dec. 31, 1964

Heat of Formation.

The heat of formation ($\Delta H_f^\circ 298.15^\circ$) for $B_2O_3(c)$ has been reported by many investigators. However, the values obtained were not in good agreement. The value of $\Delta H_f^\circ 298.15^\circ$ for $B_2O_3(c)$ adopted was taken from L. G. Pasolino, "Heats of Formation of $B_2O_3(c)$ and $B_2O_3(am.)$ ", NMR-5608 (OO), National Research Corporation, Massachusetts, June 2, 1964. The other derived values of $\Delta H_f^\circ 298.15^\circ$ for $B_2O_3(c)$ are listed in the following table.

Investigator	Reaction	$\Delta H_f^\circ 298.15^\circ$ kcal. mole ⁻¹	$\Delta H_f^\circ 298.15^\circ$ kcal. mole ⁻¹
Roth ¹	$B_2O_3(gl.) + 3/2 H_2O(l) = 2 H_3BO_3(c)$	-19.15	-304.2 ± 0.4
Eggerglaess, et al. ²	$2B(am.) + 3/2 O_2(g) = B_2O_3(gl.)$	-281.1 ± 3.1	-283.1 ± 3.1
Artadalen and Anderson ³	$1/2 B_2O_3(am.) + 3/2 H_2O(l) = H_3BO_3(c)$	-9.13 ± 0.04	-304.1 ± 0.4
Ekstein and Artadalen ⁴	$2B(c) + 3/2 O_2(g) = B_2O_3(gl.)$	-304.6 ± 4.2	-309.0 ± 4.2
Gel'chenko et al. ⁵	$2B(am.) + 3/2 O_2(g) = B_2O_3(gl.)$	-299.7 ± 1.8	-300.7 ± 2.0
Pasolino	$B_2O_3(c) + 348 H_2O(l) = 2 H_3BO_3 \cdot 345 H_2O(sol.)$	-3.45 ± 0.05	-303.64 ± 0.40

¹W. A. Roth, Z. Naturforsch., **1**, 574 (1946).

²M. Eggerglaess, A. G. Monroe and W. G. Parker, Trans. Faraday Soc., **45**, 661 (1949).

³G. R. Van Artsdalen and K. F. Anderson, J. Am. Chem. Soc., **73**, 579 (1951).

⁴B. H. Ekstein and E. R. Van Artsdalen, J. Am. Chem. Soc., **80**, 1352 (1958).

⁵S. L. Gel'chenko, A. N. Kornilov and S. M. Skuratov, Russ. J. Inorg. Chem., **5**, 1039 (1960).

In order to evaluate the values of $\Delta H_f^\circ 298.15^\circ$ for $B_2O_3(c)$ from the corresponding $\Delta H_f^\circ 298.15^\circ$ values, the following auxiliary data ($298.15^\circ K$) were used: $\Delta H_f^\circ(B, am.) = 1.2 \pm 0.4$ kcal. mole⁻¹, $\Delta H_f^\circ = 4.36$ kcal. mole⁻¹ for the reaction $B_2O_3(c) = B_2O_3(gl.)$, $\Delta H_f^\circ(H_3BO_3, c) = -261.47 \pm 0.20$ kcal. mole⁻¹, $\Delta H_f^\circ(2 H_3BO_3 \cdot 345 H_2O, sol.) = -512.04 \pm 0.40$ kcal. mole⁻¹ and $\Delta H_f^\circ(H_2O, l) = -68.317$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The low temperature (18.08 - 296.60°K.) heat capacities used were reported by E. C. Kerr, H. N. Hersh and H. L. Johnston, J. Am. Chem. Soc., **72**, 4738 (1950). The high temperature (350.6 - 718.4°K.) heat capacities were derived from the heat content measurements determined by J. C. Southard, J. Am. Chem. Soc., **63**, 3147 (1941). These two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 718.4°K. were estimated by graphical extrapolation. $S_{298.15}^\circ$ was obtained from E. C. Kerr, H. N. Hersh and H. L. Johnston, loc. cit., based on $S_{298}^\circ = 0.027$ cal. deg.⁻¹ mole⁻¹. The specific heats of $B_2O_3(c)$ in the temperature range 51 to 298°K. were also determined by K. K. Kelley, J. Am. Chem. Soc., **63**, 1137 (1941). The C_p values reported are in good agreement with the values adopted.

Melting Data.

Melting temperature (T_m) was taken from P. C. Kracek, O. W. Morey and H. E. Merwin, Am. J. Sci., [5] **35A**, 143 (1938). The heat of melting (ΔH_m°) was converted from $\Delta H_m^\circ 298.15^\circ = 4.36 \pm 0.02$ kcal. mole⁻¹ reported by J. C. Southard, loc. cit.

Heat of Sublimation.

The value of heat of sublimation ($\Delta H_s^\circ 298.15^\circ$) was calculated as the difference in the heats of formation ($\Delta H_f^\circ 298.15^\circ$) for $B_2O_3(g)$ and $B_2O_3(c)$.

Boron Oxide (B₂O₃)

(Liquid) Mol. Wt. = 69.64

BORON OXIDE (B₂O₃)

(LIQUID)

MOL. WT. = 69.64

$$\begin{aligned} S_{298.15}^{\circ} &= 18.739 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \\ T_m &= 725 \pm 2^\circ \text{K.} \\ T_b &= 2316^\circ \text{K.} \\ \Delta H_f^{\circ} 298.15 &= -299.28 \pm 0.40 \text{ kcal. mole}^{-1} \\ \Delta H_m^{\circ} &= 5.26 \pm 0.02 \text{ kcal. mole}^{-1} \\ \Delta H_v^{\circ} &= 87.55 \text{ kcal. mole}^{-1} \end{aligned}$$

Heat of Formation.

$\Delta H_f^{\circ} 298.15$ for B₂O₃(l) was obtained from $\Delta H_f^{\circ} 298.15$ for B₂O₃(c) by adding ΔH_m° and the difference between $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat content ($H_c^{\circ} - H_{298.15}^{\circ}$) measurements on B₂O₃(glass) and B₂O₃(l) were determined, from 381.7 to 1778.8°K., by J. C. Southard, J. Am. Chem. Soc. 65, 3147 (1941) and, from 1015 to 2154°K., by R. M. Krasovitskaya, P. B. Kantor, L. S. Kun, V. V. Kandyba, E. N. Romichev, Russ. J. Phys. Chem. 35, 737 (1961). Based on these data the corresponding heat capacities (C_p) were derived. The C_p values thus obtained were plotted and joined smoothly, assuming a glass transition temperature at 550°K. The heat capacities above 2154°K. were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation. The heat capacities of B₂O₃ glass and liquid have also been measured between 35 and 350°C with a radiation calorimeter by S. B. Thomas and G. S. Parks, J. Phys. Chem. 35, 2091 (1931). The heat capacity curves obtained have been compared and discussed.

Melting Data.

See the B₂O₃(c) table.

Vaporization Data.

The boiling point (T_b) was calculated as the temperature at which the difference in ΔH_f° values for B₂O₃(g) and B₂O₃(l) becomes zero. The corresponding difference in ΔH_f° values at T_b is the heat of vaporization (ΔH_v°).

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0							
100	15.050	18.739	18.739	-	-299.280	-282.115	206.766
200	15.140	18.832	18.739	-0.026	-299.282	-282.009	205.433
300	18.350	23.656	19.475	1.712	-299.308	-276.244	190.926
400	20.800	28.017	20.475	3.471	-299.271	-270.481	118.222
500	28.400	32.354	22.248	6.064	-298.981	-264.739	96.426
600	31.700	37.064	24.068	8.591	-298.571	-258.971	80.291
700	35.650	41.323	25.632	10.693	-297.931	-253.163	67.571
800	39.650	44.068	27.054	12.493	-296.371	-246.192	56.266
900	41.400	48.391	29.744	18.646	-295.628	-242.877	53.078
1000	41.050	51.367	31.578	21.768	-294.973	-237.637	47.212
1100	39.500	53.510	33.030	27.924	-293.881	-227.510	42.373
1200	30.540	58.775	36.646	30.980	-293.414	-222.205	34.666
1300	30.540	60.882	38.193	34.034	-292.989	-217.137	31.635
1400	30.540	62.888	39.673	37.088	-292.596	-212.091	28.969
1500	30.540	64.703	41.105	40.142	-291.912	-207.070	26.534
1600	30.540	66.446	42.452	43.189	-291.606	-202.078	24.669
1700	30.540	68.097	43.759	46.243	-291.320	-197.088	22.669
1800	30.540	69.663	45.015	49.297	-291.054	-192.120	20.993
1900	30.540	71.153	46.224	52.351	-291.054	-187.165	19.478
2000	30.540	72.573	47.392	55.405	-290.578	-182.207	18.111
2100	30.540	73.932	48.515	58.459	-290.367	-177.257	16.844
2200	30.540	75.232	49.601	61.513	-290.367	-172.297	15.696
2300	30.540	76.479	50.652	64.567	-290.947	-167.247	14.620
2400	30.540	77.677	51.669	67.621	-290.751	-162.193	13.609
2500	30.540	78.824	52.649	70.675	-290.384	-157.129	12.654
2600	30.540	79.941	53.609	73.729	-290.384	-152.059	11.753
2700	30.540	81.013	54.536	76.783	-290.212	-146.909	10.995
2800	30.540	82.048	55.436	79.837	-290.048	-141.742	10.242
2900	30.540	83.049	56.310	82.891	-290.889	-136.561	9.537
3000	30.540	84.059	57.169	85.945	-290.788	-131.375	8.876
3100	30.540	85.059	58.009	88.999	-290.458	-126.181	8.259
3200	30.540	85.871	58.786	92.053	-290.458	-120.975	7.673
3300	30.540	86.756	59.583	95.107	-290.323	-115.761	7.123
3400	30.540	87.616	60.349	98.161	-290.196	-110.544	6.604
3500	30.540	88.459	61.082	101.215	-289.958	-105.320	6.113
3600	30.540	89.267	61.828	104.269	-289.958	-100.095	5.654
3700	30.540	90.050	62.542	107.323	-289.846	-94.866	5.208
3800	30.540	90.833	63.239	110.377	-289.846	-89.636	4.773
3900	30.540	90.833	63.239	110.377	-289.846	-84.406	4.355
4000	30.540	90.833	63.239	110.377	-289.846	-79.176	3.955

Point Group C_{2v}
S_{298.15} = 67.798 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1

ΔH_f⁰ = -198.87 ± 0.50 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -199.14 ± 0.50 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies
ω, cm.⁻¹ ω, cm.⁻¹ ω, cm.⁻¹
2073(1) 1240(1) 172(1)
730(1) 457(1) 460(1)
521(1) 2073 (1) 480(1)

Bond Distance: O-B = 1.36 ± 0.02 Å B-O = 1.20 ± 0.03 Å
Bond Angle: O-B-O = 180° B-O-B = 120°
Product of the Moments of Inertia: I_AI_BI_C = 3.15283 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation (ΔH_f⁰ 298.15) for B₂O₃(g) was calculated from the values of ΔH_f⁰ 298.15 and ΔH_f⁰ 298.15 for B₂O₃(l). The ΔH_f⁰ 298.15 value was obtained from the analyses of the vapor pressure data of B₂O₃(l) by both the second and third law methods. Ten sets vapor pressure data were employed for examination. The results obtained are as follows.

Investigator	Temperature, °K.	Third Law Value	Second Law Value
Cole and Taylor ¹	1473 - 1673	87.77	72.92 ± 2.3
Speiser, et al. ²	1331 - 1642	99.25	87.10 ± 1.8
Soulen, et al. ³	1567 - 1808	98.49	65.87 ± 7.8
Searcy and Myers ⁴	1501 - 1586	98.70	101.3 ± 2.5
Scheer ⁵	1414 - 1621	101.89	95.25 ± 0.9
Nesseyanov and Firsova ⁶	1299 - 1515	98.86	82.36 ± 2.9
White, et al. ⁷	1220 - 1641	99.36	90.52 ± 0.6
Sommer ⁸	1228 - 1641	99.63	93.08 ± 0.7
Blackburn ⁹	1325 - 1547	99.43	92.78 ± 1.4
Hildenbrand, et al. ¹⁰	1436 - 1584	100.14	100.75 ± 1.1
Büchler, et al. ¹¹	1300	—	100.2 ± 3.0

*All calculations based on the third law values listed except the last one.

1. S. S. Cole and N. W. Taylor, J. Am. Ceram. Soc. **18**, 82 (1935).
2. R. Speiser, S. Naiditch and H. L. Johnston, J. Am. Chem. Soc. **72**, 2578 (1950).
3. R. Soulen, P. Schapinonda and J. L. Margrave, J. Phys. Chem. **59**, 132 (1955).
4. A. W. Searcy and C. E. Myers, J. Phys. Chem. **61**, 957 (1957).
5. M. D. Scheer, J. Phys. Chem. **61**, 1184 (1957).
6. A. N. Nesseyanov and L. P. Firsova, Russ. J. Phys. Chem. **34**, 490 (1960).
7. D. White, P. N. Welsh, H. W. Goldstein and D. P. Dever, J. Phys. Chem. **65**, 1404 (1961).
8. A. Sommer, Ph. D. Thesis, The Ohio State University, 1962.
9. S. E. Blackburn, "Research on Thermodynamics of the Al-B-O and Be-B-O Systems," Quarterly Report No. 4, Mar. 1 - May 31, 1963, Arthur D. Little, Inc.
10. L. Hildenbrand, W. P. Hall and N. D. Potter, J. Chem. Phys. **39**, 296 (1963).
11. A. Büchler and J. B. Berkowitz-Mattuck, J. Chem. Phys. **39**, 286 (1963).

The free energy functions of B₂O₃(g) used for calculation are obtained using two estimated vibrational frequencies, 172 and 460 cm.⁻¹. Smaller evaluations were made using 259 and 460 cm.⁻¹ instead, each corresponding third law values of ΔH_f⁰ obtained was lower by more than 1 kcal. mole⁻¹ than that of the previous ones. The value of ΔH_f⁰ 298.15 for B₂O₃(g) adopted is the third law value based on the vapor pressures reported by D. L. Hildenbrand, W. P. Hall and N. D. Potter, loc. cit.

Heat Capacity and Entropy.
The bond distances were reported by P. A. Akshin and V. P. Spridinov, Doklady Akad. Nauk. S.S.S.R. **131**, 557 (1960). The bond angle was taken from W. Weltner, Jr. and J. R. W. Mann, J. Chem. Phys. **37**, 292 (1962). The vibrational frequencies were obtained from A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys. **39**, 87 (1963) and corrected to the average isotopic species. The three principal moments of inertia are: I_A = 3.10959 X 10⁻³⁸, I_B = 2.9768 X 10⁻³⁹ and I_C = 3.40717 X 10⁻³⁸ g.² cm.²

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	9.500	94.229	147.016	-198.870	-198.870	IMFANTE
200	13.224	69.160	1.443	-199.148	-197.386	413.316
298	15.979	67.798	67.798	-199.140	-196.402	215.738
300	16.020	67.799	0.30	-199.140	-196.566	144.106
400	17.861	72.774	67.431	-195.151	-194.586	143.204
500	19.207	76.911	69.740	-199.217	-194.874	106.939
600	20.272	80.510	72.241	-199.324	-195.995	85.175
700	21.136	82.573	74.343	-199.382	-196.982	70.659
800	21.858	84.253	76.049	-199.401	-197.883	58.490
900	22.427	85.191	77.649	-199.426	-198.649	46.439
1000	22.903	85.569	77.303	-199.446	-199.286	37.615
1100	23.293	85.771	78.702	-200.025	-199.333	29.089
1200	23.649	85.912	80.040	-200.189	-199.352	27.002
1300	23.979	86.005	81.259	-200.356	-199.352	25.172
1400	24.116	86.063	82.369	-200.526	-199.332	23.359
1500	24.307	86.103	83.750	-200.763	-199.288	21.674
1600	24.469	86.237	84.888	-200.985	-199.224	20.039
1700	24.597	86.355	85.705	-201.224	-199.146	18.448
1800	24.690	86.455	86.049	-201.752	-199.051	16.884
1900	24.750	86.535	86.049	-201.752	-199.051	15.359
2000	24.820	86.595	86.049	-201.752	-199.051	13.869
2100	24.909	86.648	86.049	-202.032	-199.008	12.419
2200	24.999	86.688	86.049	-202.323	-198.966	11.007
2300	25.089	86.719	86.049	-202.628	-198.924	9.627
2400	25.179	86.742	86.049	-202.942	-198.882	8.287
2500	25.231	86.758	86.049	-203.268	-198.840	6.987
2600	25.275	86.768	86.049	-203.605	-198.800	5.727
2700	25.314	86.773	86.049	-203.952	-198.760	4.507
2800	25.348	86.775	86.049	-204.309	-198.720	3.327
2900	25.378	86.775	86.049	-204.676	-198.680	2.187
3000	25.409	86.775	86.049	-205.052	-198.640	1.087
3100	25.435	86.775	86.049	-205.438	-198.600	0.027
3200	25.456	86.775	86.049	-205.834	-198.560	-0.933
3300	25.473	86.775	86.049	-206.240	-198.520	-1.883
3400	25.486	86.775	86.049	-206.656	-198.480	-2.823
3500	25.518	86.775	86.049	-207.082	-198.440	-3.753
3600	25.535	86.775	86.049	-207.518	-198.400	-4.673
3700	25.548	86.775	86.049	-207.964	-198.360	-5.583
3800	25.558	86.775	86.049	-208.420	-198.320	-6.483
3900	25.578	86.775	86.049	-208.886	-198.280	-7.373
4000	25.591	86.775	86.049	-209.362	-198.240	-8.253
4100	25.602	86.775	86.049	-209.848	-198.200	-9.123
4200	25.613	86.775	86.049	-210.344	-198.160	-9.983
4300	25.623	86.775	86.049	-210.850	-198.120	-10.833
4400	25.632	86.775	86.049	-211.366	-198.080	-11.673
4500	25.641	86.775	86.049	-211.892	-198.040	-12.503
4600	25.649	86.775	86.049	-212.428	-198.000	-13.323
4700	25.657	86.775	86.049	-212.974	-197.960	-14.133
4800	25.664	86.775	86.049	-213.530	-197.920	-14.933
4900	25.671	86.775	86.049	-214.096	-197.880	-15.723
5000	25.677	86.775	86.049	-214.672	-197.840	-16.503
5100	25.683	86.775	86.049	-215.258	-197.800	-17.273
5200	25.689	86.775	86.049	-215.854	-197.760	-18.033
5300	25.694	86.775	86.049	-216.460	-197.720	-18.783
5400	25.699	86.775	86.049	-217.076	-197.680	-19.523
5500	25.704	86.775	86.049	-217.702	-197.640	-20.253
5600	25.709	86.775	86.049	-218.338	-197.600	-20.973
5700	25.714	86.775	86.049	-218.984	-197.560	-21.683
5800	25.719	86.775	86.049	-219.640	-197.520	-22.383
5900	25.724	86.775	86.049	-220.306	-197.480	-23.073
6000	25.725	86.775	86.049	-220.982	-197.440	-23.753

Mar. 31, 1961; Dec. 31, 1964.

Lead Diborate (PbB_2O_4)
(Crystal) Mol. Wt. = 292.85

T, °K.	C_p	S°	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{-(F^\circ - H^\circ_{298})/T}$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0							
100							
200							
298	25.600	31.200	31.200	0.000	-372.000	-346.628	254.073
300	25.700	31.359	31.200	0.047	-372.001	-346.671	252.392
400	30.980	39.501	32.275	2.890	-371.876	-337.972	184.651
500	35.180	46.875	34.469	6.203	-371.524	-329.533	144.032
600	38.830	53.623	37.107	9.909	-370.968	-321.183	116.985
700	42.000	59.717	40.000	13.640	-370.180	-312.831	91.640
800	44.140	65.578	42.770	18.246	-370.090	-304.480	69.934
900	45.970	70.886	45.603	22.755	-369.461	-296.239	71.933
1000	47.420	75.807	48.380	27.427	-368.319	-288.160	62.974
1100	48.570	80.383	51.084	32.228	-367.103	-280.206	55.609
1200	49.480	84.639	53.726	37.156	-365.526	-272.461	49.681
1300	50.210	88.639	56.291	42.118	-363.506	-264.925	44.186
1400	50.830	92.383	58.680	47.170	-363.161	-256.992	40.116
1500	51.420	95.911	61.055	52.283	-361.796	-249.458	36.344
1600	51.930	99.246	63.339	57.451	-360.415	-242.012	33.056
1700	52.400	102.416	65.525	62.675	-359.022	-234.580	30.165
1800	52.800	105.444	67.597	67.926	-357.622	-227.160	27.606
1900	53.200	108.279	69.739	73.226	-356.219	-219.183	25.326
2000	53.580	111.018	71.735	78.565	-354.801	-213.061	23.281



MOL. WT. = 292.85

(CRYSTAL)

LEAD DIBORATE (PbB_2O_4)

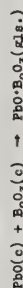
$\Delta H^\circ_f 0 = \text{Unknown}$

$\Delta H^\circ_f 298.15 = -372 \pm 1.5 \text{ kcal. mole}^{-1}$

$S^\circ_{298.15} = [31.2 \pm 3] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Heat of Formation.

W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system. L. Shartsis and E. Newman, J. Am. Ceram. Soc. 31, 213 (1948) measured heats of solution of the lead borate glasses in 2 N HNO_3 . In their phase studies C. Mazzetti and P. De Carli, Gazz. chim. Ital. 56, 19 (1926) established that the compounds formed were $\text{PbO} \cdot \text{B}_2\text{O}_3$, $\text{PbO} \cdot 2\text{B}_2\text{O}_3$, $\text{PbO} \cdot 3\text{B}_2\text{O}_3$ and 2 $\text{PbO} \cdot 5\text{B}_2\text{O}_3$. From the Shartsis and Newman paper loc. cit. Evans obtained the following:



$\Delta H^\circ_f = -16.2 \text{ kcal. mole}^{-1}$

and estimated a $\Delta H^\circ_f 298.15$ of 7.0 kcal. mole⁻¹ for the conversion to the $\text{PbO} \cdot \text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the $\Delta H^\circ_f 298.15$ was calculated to be -372 kcal./mole. The results of B. M. Lepinskikh and O. A. Eain, Zhur. Neorg. Khim. 5, 1223 (1961) studying the lead borate system at 1000°K. with cells of the type $\text{Pb}(\text{liq.})/\text{PbO} \cdot \text{B}_2\text{O}_3/\text{Pt}/\text{O}_2(g)$ were in fair agreement with the results of Shartsis and Newman.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities for B_2O_3 and PbO .

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate for the reaction:



that the simple addition of entropies will give values at least 2.7 e.u. too low for the reaction. The reason for this is probably structural, the $\text{B}_2\text{O}_4^{--}$ ion is a flexible chain. Therefore, the $S^\circ_{298.15}$ for PbB_2O_4 was obtained from the summation of JANAF $S^\circ_{298.15}$ for constituent oxides and the addition of 2.7 e.u.



Titanium Diboride (TiB₂)

(Crystal)

Mol. Wt. = 69.522

T, °K	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	-1.333	-66.399	-66.399	INFINITE
100	1.798	13.472	-1.287	-66.347	-66.347	144.095
200	6.802	7.662	-1.061	-66.601	-66.601	72.245
298	10.583	6.808	0.000	-66.608	-66.608	46.236
300	10.641	6.808	0.020	-66.801	-66.802	47.034
400	13.119	10.310	7.260	-66.865	-66.865	35.763
500	14.739	13.422	2.618	-66.942	-66.949	28.453
600	15.814	16.208	0.296	-67.036	-67.121	23.073
700	16.810	18.708	0.465	-67.139	-67.328	20.083
800	17.225	20.066	7.462	-67.247	-67.919	17.461
900	17.814	22.791	9.214	-67.352	-68.496	15.418
1000	18.377	25.936	13.912	-67.452	-68.962	13.782
1100	18.914	29.713	14.995	-67.549	-69.420	12.441
1200	19.427	28.380	16.042	-67.646	-69.876	11.315
1300	19.914	29.955	17.052	-67.743	-70.336	10.334
1400	20.375	31.448	18.768	-67.834	-70.801	9.528
1500	20.810	32.868	20.648	-67.926	-71.269	8.813
1600	21.219	34.225	22.960	-68.012	-71.737	8.186
1700	21.602	35.523	25.090	-68.092	-72.205	7.633
1800	21.959	36.768	27.269	-68.164	-72.673	7.141
1900	22.290	37.964	29.481	-68.231	-73.141	6.700
2000	22.595	39.115	31.726	-68.297	-73.608	6.293
2100	22.874	40.224	34.000	-68.363	-74.076	5.915
2200	23.127	41.294	36.300	-68.429	-74.544	5.571
2300	23.354	42.327	38.624	-68.496	-75.012	5.258
2400	23.555	43.326	40.969	-68.564	-75.480	4.971
2500	23.733	44.291	43.335	-68.633	-75.948	4.698
2600	23.955	45.227	45.720	-68.695	-76.416	4.440
2700	24.155	46.135	48.126	-68.759	-76.884	4.151
2800	24.335	47.017	50.551	-68.824	-77.352	3.912
2900	24.555	47.875	52.997	-68.888	-77.820	3.690
3000	24.733	48.711	55.462	-68.953	-78.288	3.483
3100	24.955	49.526	57.948	-69.017	-78.756	3.290
3200	25.155	50.321	60.453	-69.082	-79.224	3.110
3300	25.355	51.098	62.979	-69.146	-79.692	2.940
3400	25.555	51.856	65.524	-69.211	-80.160	2.782
3500	25.733	52.602	68.090	-69.275	-80.628	2.633
3600	25.955	53.330	70.675	-69.339	-81.096	2.495
3700	26.155	54.044	73.281	-69.404	-81.564	2.365
3800	26.355	54.744	75.906	-69.468	-82.032	2.241
3900	26.555	55.431	78.552	-69.532	-82.500	2.121
4000	26.733	56.100	81.217	-69.596	-82.968	2.005

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

TITANIUM DIBORIDE (TiB₂)

(CRYSTAL)

B₂Ti

MOL. WT. = 69.522

$$\Delta H_f^0 = -66.4 \pm 4.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -68.8 \pm 4.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [24] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 6.808 \pm 0.1 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

$$T_m = 3193^\circ \text{K.}$$

Heat of Formation.

G. M. Kibler, T. P. Lyon, M. J. Linevsky, and V. J. DeSantis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vapor pressure of the reaction $\text{TiB}_2(c) + 1/2 \text{C}(c) = \text{Ti}(g) + 1/2 \text{B}_2(c)$ by comparing the absorption intensity of the 3371-Å Ti resonance line of the above reaction at temperature T_1 to Ti (g) over pure titanium metal at temperature T_2 . Using JANAF auxiliary data $\Delta H_{2475}^0 = 91.612 \text{ kcal. mole}^{-1}$ for the above reaction and $\Delta H_{298}^0(\text{TiB}_2(c)) = -66.9 \text{ kcal. mole}^{-1}$ were calculated.

W. S. Williams, J. Phys. Chem. **65**, 2213 (1961) found 2150 ± 25°K. to be the temperature at which $\text{TiB}_2(c)$ was formed from a mixture of $\text{Ti}(c)$ and $\text{B}(c)$. If $\Delta H_{2150}^0 = 0$ is assumed for the reaction $\text{Ti}(c) + 2\text{B}(c) = \text{TiB}_2(c) + 3/2 \text{N}_2(g)$ then $\Delta H_{298}^0(\text{TiB}_2(c)) = -70.7 \text{ kcal. mole}^{-1}$. If, however, $\text{N}_2(g)$ is $1/2 \text{ atm.}$ then $\Delta H_{2150}^0 = 4.4 \text{ kcal. mole}^{-1}$ and $\Delta H_{298}^0(\text{TiB}_2(c)) = -66.3 \text{ kcal. mole}^{-1}$. He has also shown by stability comparisons that ΔF and $\Delta H > 0$ for the reaction $\text{TiB}_2 + 3/2 \text{C} = \text{TiC} + 1/2 \text{B}_2$. Thus $\Delta H_{298}^0(\text{TiB}_2) < -51 \text{ kcal. mole}^{-1}$.

F. O. Schiesel and O. C. Truison, J. Phys. Chem. **68**, 1492 (1962) used a mass spectrometer with Knudsen cells to study the vaporization of the titanium-boron system. Only the set of measurements without excess boron or titanium was used. The value $\Delta H_{2651}^0 = 194.9 \text{ kcal. mole}^{-1}$ for the reaction $\text{TiB}_2(c) = \text{Ti}(g) + 2\text{B}(g)$ was obtained. This corresponds to $\Delta H_{298}^0(\text{TiB}_2(c)) = -62.9 \text{ kcal. mole}^{-1}$ using JANAF auxiliary data.

V. A. Epel'baum and M. I. Starostina, Bor Trudy Konf. Khim. Bora 1 Ego Soedinenii **97** (1955-pub.1956) report $\Delta H_{298}^0(\text{TiB}_2(c)) = -66.85 \pm 2.7 \text{ kcal. mole}^{-1}$ from combustion calorimetry.

C. E. Lowell and W. S. Williams, Rev. Sci. Instr. **32**, 1120 (1961) used high temperature calorimetry to obtain the heat of formation of $\text{TiB}_2(c)$. From their data and JANAF auxiliary data $\Delta H_{298}^0(\text{TiB}_2(c)) = -48.2 \pm 5 \text{ kcal. mole}^{-1}$ was calculated. We question the adiabaticity of the experiment and believe their value is an upper limit.

$\Delta H_{298}^0(\text{TiB}_2(c)) = -66.8 \pm 4 \text{ kcal. mole}^{-1}$ was chosen as representative of the first four investigations.

Heat Capacity and Entropy.

The heat capacity of $\text{TiB}_2(c)$ has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum ¹	Adiabatic Calorimetry	5- 850°K.
Walker et al. ²	Drop calorimeter	373- 877°K.
Southern Research Institute ³	Drop type ice calorimeter	588-2689°K.
Mezaki ⁴	Copper-block drop calorimeter	420-1180°K.
Prophet ⁵	Arc-heating furnace	1300-2150°K.
Barriault et al. ⁶	Pulse-method	1733-2417°K.

¹L. Kaufman and E. V. Clougherty, Technical Documentary Report No. RPD-TDR-63-4096 Part 1 p. 239 (Dec. 1963).

²R. E. Walker, C. T. Ewing, and R. R. Miller, J. Phys. Chem. **61**, 1882 (1957).

³Southern Research Institute, Technical Documentary Report No. ASD-TDR-62-675 p. 253 (Jan. 1963).

⁴R. Mezaki, M. S. Thesis, University of Wisconsin (1961).

⁵H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.

⁶R. J. Barriault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).

The low temperature data of Westrum¹ and the medium range data of Walker et al.² were used to obtain the C_p of this tabulation. Their data were fitted to a Shomate plot and extrapolated to 4000°K.

$$S_{298.15}^0 = 6.808 \text{ cal. deg}^{-1} \text{ mole}^{-1} \text{ was determined by Westrum}^1.$$

Melting Data.

The melting point has been reported as 3063°, 3193°, and 3203°K. by P. W. Glaser, Trans. AIME **194**, 391 (1952), B. Post, F. W. Glaser, and D. Moskowitz, Acta. Met. **20** (1954), and by G. V. Samsonov and O. V. Petrushin, Metalloved. Obrabotka Metalov No. **5**, 19 (1955) respectively. The heat of melting is derived from an estimated $\Delta S_m = 2.5 \text{ cal. deg}^{-1} \text{ g. atom}^{-1}$. It should be pointed out that an error of 0.5 cal. deg⁻¹ g. atom⁻¹ in the estimation of ΔS_m is 5 kcal. mole⁻¹ in ΔH_m^0 .

B₂Ti

Titanium Diboride (TiB₂)

(Liquid) Mol. Wt. = 69.522

T, °K.	C _p ^a	S ^b	cal. mole ⁻¹ deg. ⁻¹	(H ^c - H ₂₉₈ ^c)/T	cal. mole ⁻¹	ΔH _f ^d	ΔF _f ^e	Log K _f
0								
100								
200								
298	10.583	13.455	13.455	.000	- 44.993	- 45.983		33.705
300	10.641	13.455	13.455	.020	- 44.994	- 45.989		33.401
400	13.119	16.957	13.907	1.220	- 45.058	- 46.311		25.302
500	14.739	20.069	14.834	2.618	- 45.135	- 46.615		20.375
600	15.814	22.855	15.943	4.147	- 45.229	- 46.902		17.083
700	17.225	27.613	18.286	7.462	- 45.440	- 47.129		14.429
800	17.814	29.676	19.438	9.214	- 45.545	- 47.271		12.956
900	18.377	31.583	20.559	11.024	- 45.645	- 47.502		11.576
1000	18.914	33.350	21.642	12.889	- 45.742	- 48.125		9.561
1100	19.417	35.007	23.602	15.778	- 45.825	- 48.235		8.140
1200	19.914	36.602	25.609	18.778	- 45.927	- 48.540		7.577
1300	20.375	38.095	26.675	20.848	- 46.989	- 48.554		7.089
1400	20.810	39.515	27.617	22.949	- 47.045	- 48.762		6.660
1500	21.219	40.872	28.528	25.094	- 47.133	- 48.973		6.282
1600	21.959	43.415	28.255	27.260	- 47.137	- 49.073		5.959
1700	22.290	44.611	29.094	29.461	- 47.172	- 49.078		5.644
1800	22.595	45.762	29.899	31.726	- 50.870	- 49.078		5.363
1900	26.000	46.871	30.661	34.000	- 50.826	- 48.987		5.098
2000	26.000	49.237	32.133	36.200	- 50.116	- 48.847		4.851
2100	26.000	50.343	32.927	41.800	- 49.776	- 48.797		4.443
2200	26.000	51.405	33.645	44.400	- 60.218	- 48.546		4.244
2300	26.000	52.424	34.347	47.000	- 59.878	- 48.087		4.042
2400	26.000	54.351	35.708	52.200	- 59.198	- 47.506		3.856
2500	26.000	55.263	36.367	54.800	- 58.858	- 46.777		3.525
2600	26.000	56.145	37.012	57.400	- 58.518	- 46.371		3.378
2700	26.000	56.997	37.653	60.000	- 58.178	- 45.971		3.241
2800	26.000	57.823	38.285	62.600	- 57.838	- 45.571		3.104
2900	26.000	58.623	38.905	65.200	- 57.498	- 45.203		2.993
3000	26.000	59.399	39.458	67.800	- 57.158	- 44.837		2.882
3100	26.000	60.153	40.039	70.400	- 56.818	- 44.484		2.778
3200	26.000	60.885	40.608	73.000	- 56.480	- 44.136		2.691
3300	26.000	62.291	41.712	75.600	- 56.141	- 43.793		2.591
3400	26.000	62.249	42.249	78.200	- 55.802	- 43.456		2.500
3500	26.000	63.625	42.775	80.800	- 55.462	- 43.120		2.411
3600	26.000	64.267	43.291	83.400	- 55.122	- 42.784		2.324
3700	26.000	64.893	43.798	86.000	- 54.782	- 42.448		2.242
3800	26.000	65.505	44.296	88.600	- 54.442	- 42.112		2.160
3900	26.000	66.103	44.785	91.200	- 54.102	- 41.776		2.078
4000	26.000	66.687	45.265	93.800	- 53.762	- 41.440		1.996
4100	26.000	67.258	45.737	96.400	- 53.422	- 41.104		1.914
4200	26.000	67.818	46.200	99.000	- 53.082	- 40.768		1.832
4300	26.000	68.365	46.657	101.600	- 52.742	- 40.432		1.750
4400	26.000	68.901	47.105	104.200	- 52.402	- 40.096		1.668
4500	26.000	69.426	47.546	106.800	- 52.062	- 39.760		1.586
4600	26.000	69.941	47.981	109.400	- 51.722	- 39.424		1.504
4700	26.000	70.444	48.408	112.000	- 51.382	- 39.088		1.422
4800	26.000	70.941	48.828	114.600	- 51.042	- 38.752		1.340
4900	26.000	71.427	49.242	117.200	- 50.702	- 38.416		1.258
5000	26.000	71.904	49.650	119.800	- 50.362	- 38.080		1.176
5100	26.000	72.373	50.052	122.400	- 50.022	- 37.744		1.094
5200	26.000	72.833	50.452	125.000	- 49.682	- 37.408		1.012
5300	26.000	73.285	50.852	127.600	- 49.342	- 37.072		0.930
5400	26.000	73.730	51.251	130.200	- 49.002	- 36.736		0.848
5500	26.000	74.167	51.600	132.800	- 48.662	- 36.400		0.766
5600	26.000	74.597	51.949	135.400	- 48.322	- 36.064		0.684
5700	26.000	75.021	52.298	138.000	- 47.982	- 35.728		0.602
5800	26.000	75.440	52.647	140.600	- 47.642	- 35.392		0.520
5900	26.000	75.854	52.996	143.200	- 47.302	- 35.056		0.438
6000	26.000	76.263	53.345	145.800	- 46.962	- 34.720		0.356

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

B₂Ti

MOL. WT. = 69.522

(LIQUID)

TITANIUM DIBORIDE (TiB₂)ΔH_f^{298.15} = [13.455] cal. deg.⁻¹ mole⁻¹ΔH_m^{298.15} [24] kcal. mole⁻¹T_m = 3193°K.T_d = [4250]°K.

Heat of Formation.

ΔH_f^{298.15}(l) was calculated from ΔH_f^{298.15}(c) by adding ΔH_m^{298.15} and the difference between ΔH_m^{298.15} for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2100°K. C_p(l) at and below 2100°K. were assumed to be equal to those of TiB₂(c). Above 2100°K. the heat capacities were estimated to be constant. S_{298.15}^{298.15}(l) is calculated based on S_{298.15}^{298.15}(c) and an estimated ΔS_m^{298.15} = 2.5 cal. deg.⁻¹ gm. atom⁻¹.

Melting Data.

See TiB₂(c) table for details.

Decomposition Data.

T_d estimated from ΔH_f^{298.15} = 0 for the reaction TiB₂(l) = Ti(g) + 2B(g).B₂Ti

T, °K.	C _p	S°	-(F°-H° ₃₉₈)/T	H°-H° ₃₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	-1.580	-76.789	-76.789	INFINITE	
100	2.870	16.207	-1.503	-76.524	-76.524	18.749	
200	7.117	29.523	-1.417	-76.258	-76.258	16.946	
298	11.530	38.590	-1.330	-76.000	-76.000	15.743	
300	11.589	8.662	8.590	0.021	-77.100	55.394	
400	13.744	12.328	8.076	1.301	-77.099	41.354	
500	14.970	15.358	7.576	2.742	-77.155	32.027	
600	15.729	18.338	7.120	4.279	-77.272	27.302	
700	16.259	20.804	6.705	5.879	-77.429	23.278	
800	16.661	23.002	6.326	7.526	-77.610	20.253	
900	16.991	24.984	6.000	9.220	-77.804	17.495	
1000	17.245	26.788	5.667	10.951	-78.016	15.003	
1100	17.489	28.443	5.326	12.657	-78.258	12.737	
1200	17.733	29.975	5.000	14.419	-78.524	10.651	
1300	17.977	31.404	4.687	16.204	-78.816	8.728	
1400	18.221	32.735	4.387	18.014	-79.134	6.956	
1500	18.465	34.011	4.100	19.846	-79.479	5.321	
1600	18.709	35.210	3.826	21.707	-79.852	3.826	
1700	18.953	36.352	3.565	23.590	-80.254	2.461	
1800	19.197	37.442	3.316	25.498	-80.683	1.218	
1900	19.441	38.486	3.079	27.432	-81.134	0.081	
2000	19.685	39.490	2.854	29.396	-81.610	-0.780	
2100	19.929	40.456	2.640	31.366	-82.110	-1.663	
2200	20.173	41.389	2.437	33.332	-82.634	-2.568	
2300	20.417	42.291	2.244	35.301	-83.184	-3.494	
2400	20.661	43.165	2.061	37.265	-83.759	-4.441	
2500	20.905	44.013	1.887	39.220	-84.359	-5.409	
2600	21.149	44.838	1.722	41.166	-84.984	-6.398	
2700	21.393	45.641	1.565	43.100	-85.634	-7.408	
2800	21.637	46.423	1.416	45.020	-86.309	-8.439	
2900	21.881	47.184	1.273	46.926	-86.999	-9.491	
3000	22.125	47.924	1.136	48.819	-87.704	-10.554	
3100	22.369	48.642	1.004	50.699	-88.434	-11.628	
3200	22.613	49.338	0.877	52.565	-89.189	-12.712	
3300	22.857	50.016	0.754	54.418	-89.959	-13.806	
3400	23.101	50.677	0.636	56.258	-90.744	-14.910	
3500	23.345	51.323	0.522	58.084	-91.544	-16.024	
3600	23.589	51.954	0.412	59.896	-92.359	-17.148	
3700	23.833	52.570	0.306	61.694	-93.189	-18.282	
3800	24.077	53.171	0.204	63.478	-94.034	-19.426	
3900	24.321	53.757	0.106	65.248	-94.894	-20.579	
4000	24.565	54.328	0.012	67.004	-95.769	-21.741	

Sept. 30, 1962; Mar. 31, 1963; June 30, 1965

ZIRCONIUM DIBORIDE (ZrB₂)
(CRYSTAL)

MOL. WT. = 112.842

$\Delta H_f^\circ = -76.8 \pm 1.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 298.15 = -77.1 \pm 1.6 \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = [25] \text{ kcal. mole}^{-1}$
 $T_m = 3323^\circ\text{K.}$

Heat of Formation.

G. K. Johnson, Argonne National Laboratory, private communication, May 1965, reported ΔH_f° 298 (ZrB₂)₉₉₉ + 0.006 = -78.7 ± 1.5 kcal. mole⁻¹. Their value was obtained by fluorine bomb calorimetry and was based on their recently redetermined value of ΔH_f° 298(BF₃)₉₉₉ = -271.80 ± 0.20 kcal. mole⁻¹.
G. M. Kibler, T. F. Lyon, M. J. Linevsky, and V. J. De Santis, General Electric Co., report No. WADD-TR-60-646, Part IV (August 1964) studied the vaporization of ZrB₂ 931 by the Knudsen effusion method. Over the range 280 to 2500°K., $\log K_p = 22.038 - 10.115 \times 10^4/T$. For the reaction ZrB₂ 931 (c) = Zr (g) + 1.931 B (g). JANAP auxiliary data were used to calculate ΔH_f° 298 = 478.5 ± 1.5 kcal. mole⁻¹ by the 3rd law method and ΔH_f° 298 (ZrB₂)₉₃₁ (c) = -76.7 ± 3.2 kcal. mole⁻¹.
O. C. Trullson and H. W. Goldstein, Union Carbide Res. Inst., report No. C-25 (October 1964), investigated the decomposition vapor pressure of the reaction ZrB₂ (c) = Zr (g) + 2B (g) and reported ΔH_f° 298 (ZrB₂)₉₃₁ (c) = -72.1 ± 5.3 kcal. mole⁻¹. They also reported ΔH_f° 298 (ZrB₂)₉₃₁ (c) = -47.0 ± 3 kcal. mole⁻¹, ΔH_f° 298 (ZrB₂)₉₃₁ (c) = -76.1 ± 3 kcal. mole⁻¹ was calculated. JANAP values for ΔH_f° 298 B (g) and Zr (g) were not used since their independent determinations serve to cancel instrumental constants.
From oxygen bomb calorimetry, E. J. Huber, Jr., E. L. Head, and C. E. Holley, Jr., J. Phys. Chem. 68, 3040 (1964) reported ΔH_f° 298 (ZrB₂)₉₃₁ (c) = -77.2 ± 1.2 kcal. mole⁻¹.
 ΔH_f° 298 (ZrB₂)₉₃₁ (c) = -77.1 ± 1.6 was chosen as a value representative of the above.

Heat Capacity and Entropy.

The heat capacity of ZrB₂ (c) has been determined by the following investigators:

Investigator	Method	Temperature Range
Westrum and Feick ¹	Adiabatic calorimetry	5-350°K.
Valentine et al. ²	Copper-block drop calorimeter	410-1125°K.
Mezaki ³	Copper-block drop calorimeter	430-1170°K.
Prophet ⁴	Arc-heating furnace	1300-2150°K.
Barriault et al. ⁵	Pulse-method	1740-2520°K.
Southern Research Institute ⁶	Drop type ice calorimeter	500-2500°K.

¹ E. P. Westrum, Jr. and O. Feick, J. Chem. Eng. Data 6(2), 193 (1963).
² R. H. Valentine, T. P. Jambois, and J. L. Margrave, J. Chem. Eng. Data 9(2), 182 (1964).
³ R. Mezaki, M. S. Thesis, University of Wisconsin (1961).
⁴ H. Prophet, Annual Report for 1962 of the Dow Chemical Co. to ARPA under Contract AF 04(611)7554.
⁵ K. J. Barriault et al., Thermodynamics of Certain Refractory Compounds, AVCO Corporation, report ASD-TR-61-260, Part I, Vol. 1, (May 1962).
⁶ D. Neel, C. Pears, and S. Ogleasby, Southern Research Institute, report ASD-TR-62-675 (August 1962).
Westrum and Feick's ¹ C_p values were adopted to 350°K. The disparities in heat capacities above room temperatures seem too great to be errors in measurement and are probably due to sample differences. Since the samples used by Westrum and Feick¹ and by Valentine et al.² were from the same batch, Valentine's data were used above 350°K. The two sets of data were fitted to a Shomate plot which was extrapolated to 4000°K. However, in consideration of the results of Mezaki³, Prophet⁴ and Southern Research Institute⁶, the C_p extrapolation ran somewhat higher than a direct extrapolation of Valentine's data would yield.
 ΔH_f° 298.15 (ZrB₂)₉₃₁ = 6.59 cal. mole⁻¹ K⁻¹ was determined by Westrum¹.

Melting Data.

The melting point has been reported as 3313°, 3323°, and 3265°K. by P. Glaeser and B. Post, J. of Metals, 5, 1117 (1953), B. Post, P. Glaeser, and D. W. Moskowitz, Acta. Met. 2, 70 (1954) and H. Greenwood, Engineer 187, 349 (1949) respectively. The heat of melting is derived from an estimated $\Delta S_m^\circ = 2.5 \text{ cal. deg.}^{-1} \text{ g. atom}^{-1}$ at 3323°K. It should be pointed out that an error of 0.5 cal. deg⁻¹ g. atom⁻¹ in the estimation of ΔS_m° is 5 kcal. mole⁻¹ in ΔH_m° .

Zirconium Diboride (ZrB₂)

(Liquid) Mol. Wt. = 112.842

B₂Zr

MOL. WT. = 112.842

ZIRCONIUM DIBORIDE (ZrB₂) (LIQUID)

$$\Delta H_f^{298.15} = [15.448] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = [-54.194] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [25] \text{ kcal. mole}^{-1}$$

$$T_m = 3323^\circ\text{K.}$$

$$T_d = [4466]^\circ\text{K.}$$

Heat of Formation.

$\Delta H_f^{298.15}(l)$ was calculated from $\Delta H_f^{298.15}(c)$ by adding ΔH_m^0 and the difference between ΔH_m^0 and ΔH_m^0 for crystal and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2200°K. $C_p(l)$ at and below 2200°K. were assumed to be equal to those of ZrB₂(c). Above 2200°K. the heat capacities were estimated to be constant. $S_{298.15}^0(c)$ and an estimated $\Delta S_m^0 = 2.5 \text{ cal. deg.}^{-1} \text{ gm. atom}^{-1}$.

Melting Data.

See ZrB₂(c) table for details.

Decomposition Data.

T_d estimated from $\Delta F_{Td}^0 = 0$ for the reaction $2\text{ZrB}_2(l) = \text{Zr}(g) + 2\text{B}(g)$.

T, °K.	C _p ⁰	cal. mole ⁻¹ deg. ⁻¹	S ⁰	-(F ⁰ -H ₂₉₈ ⁰)/T	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
100								
200	11.530	15.448	15.448	0.000	54.194	55.187	40.452	
298								
300	11.589	15.520	15.448	1.021	54.194	55.194	40.207	
400	12.344	16.184	15.448	2.762	54.194	55.259	40.336	
500	14.970	22.398	16.912	4.279	54.259	55.657	24.414	
600	15.729	25.196	18.065	4.279	54.366	56.168	20.458	
700	16.259	27.662	18.263	5.879	54.523	56.456	17.625	
800	16.661	29.860	20.453	7.526	54.704	56.720	15.495	
900	16.961	31.462	21.610	10.591	54.898	56.951	13.831	
1000	17.245	33.446	22.725	10.591	55.110	57.177	12.449	
1100	17.489	35.301	23.794	12.657	55.352	57.374	11.399	
1200	17.733	36.833	24.817	14.419	56.566	57.498	10.471	
1300	17.977	38.262	25.797	16.204	56.823	57.567	9.677	
1400	18.221	39.736	26.736	18.014	57.089	57.613	8.993	
1500	18.465	40.869	27.658	19.846	57.365	57.644	8.398	
1600	18.709	42.068	28.501	21.707	57.647	57.649	7.874	
1700	18.953	43.210	29.333	23.590	57.937	57.643	7.410	
1800	19.197	44.300	30.134	25.498	58.228	57.616	6.995	
1900	19.441	45.344	30.908	27.429	58.519	57.574	6.622	
2000	19.685	46.348	31.655	29.386	58.804	57.518	6.285	
2100	19.929	47.314	32.378	31.366	59.084	57.446	5.978	
2200	20.000	48.247	33.078	33.372	64.258	57.196	5.682	
2300	20.000	49.269	33.760	35.672	64.258	56.875	5.404	
2400	20.000	50.286	34.426	37.772	64.258	56.552	5.150	
2500	20.000	51.187	35.078	40.272	75.000	56.013	4.896	
2600	20.000	52.089	35.715	42.572	75.070	55.253	4.644	
2700	20.000	52.957	36.338	44.872	75.080	54.487	4.410	
2800	20.000	53.793	36.946	47.172	75.080	53.726	4.193	
2900	20.000	54.601	37.541	49.472	75.100	52.959	3.991	
3000	20.000	55.380	38.123	51.772	75.110	52.196	3.802	
3100	20.000	56.134	38.692	54.072	75.120	51.436	3.626	
3200	20.000	56.865	39.249	56.372	75.130	50.673	3.461	
3300	20.000	57.572	39.793	58.672	75.140	49.902	3.305	
3400	20.000	58.259	40.326	60.972	75.150	49.137	3.158	
3500	20.000	58.926	40.848	63.272	75.160	48.378	3.021	
3600	20.000	59.574	41.359	65.572	75.170	47.612	2.890	
3700	20.000	60.204	41.860	67.872	75.180	46.846	2.767	
3800	20.000	60.817	42.351	70.172	75.190	46.075	2.650	
3900	20.000	61.415	42.832	72.472	75.200	45.315	2.539	
4000	20.000	61.997	43.304	74.772	317.568	40.256	2.199	
4100	20.000	62.565	43.767	77.072	317.116	33.331	1.777	
4200	20.000	63.119	44.221	79.372	316.662	26.405	1.374	
4300	20.000	63.660	44.667	81.672	316.210	19.502	0.991	
4400	20.000	64.189	45.105	83.972	315.760	12.609	0.626	
4500	20.000	64.708	45.535	86.272	315.310	5.728	0.278	
4600	20.000	65.212	45.957	88.572	314.860	1.146	0.054	
4700	20.000	65.706	46.372	90.872	314.412	8.017	0.373	
4800	20.000	66.190	46.780	93.172	450.399	16.401	0.747	
4900	20.000	66.655	47.181	95.472	450.010	26.108	1.164	
5000	20.000	67.129	47.575	97.772	449.626	35.829	1.566	
5100	20.000	67.595	47.963	100.072	449.250	45.531	1.951	
5200	20.000	68.031	48.345	102.372	448.879	55.235	2.321	
5300	20.000	68.470	48.720	104.672	448.515	64.912	2.677	
5400	20.000	68.899	49.090	106.972	448.158	74.605	3.019	
5500	20.000	69.321	49.454	109.272	447.804	84.288	3.349	
5600	20.000	69.736	49.812	111.572	447.458	93.950	3.666	
5700	20.000	70.143	50.165	113.872	447.118	103.616	3.973	
5800	20.000	70.543	50.513	116.172	446.784	113.275	4.268	
5900	20.000	70.936	50.856	118.472	446.453	122.932	4.553	
6000	20.000	71.323	51.194	120.772	446.128	132.578	4.820	

Sept. 30, 1962; Dec. 31, 1962; June 30, 1965

B₂Zr

Boron Oxide Chloride, Trimeric ((BOCl)₃)₃

(Ideal Gas) Mol. Wt. = 186.831



BORON OXIDE CHLORIDE, TRIMERIC ((BOCl)₃)₃ (IDEAL GAS) MOL. WT. = 186.831

Point Group [D_{3h}]
 $\Delta H_f^\circ 0 = -389 \pm 2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [91.367] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -390 \pm 2 \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies		
$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$	$\omega_e, \text{cm.}^{-1}$
[807] (1)	[980] (2)	[600] (1)
[690] (1)	[1300] (2)	[140] (1)
[333] (1)	[920] (2)	[400] (2)
[1037] (1)	[390] (2)	[120] (2)
[400] (1)	[150] (2)	

Bond Distance: B-Cl = [1.75]Å B-O = [1.36]Å

Bond Angle: Cl-B-O = [120°] B-O-B = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [1.86850 \times 10^{-11}] \text{ g.}^3 \text{ cm.}^6$

$\sigma = 6$

Heat of Formation.

The equilibrium constants for the reaction $\text{B}_2\text{O}_3(1) + \text{BCl}_3(g) = (\text{BOCl})_3(g)$ were determined in the temperature range 536-825°K. by a transpiration method by J. Blauer and M. Farber, J. Chem. Phys. 39, 158 (1963); and in the temperature range 1234-1309°K. by an effusion method by the same investigators, Trans. Faraday Soc. 60, 301 (1964). Using the reported equilibrium constants, the enthalpy changes for this reaction were evaluated by both the second and third law methods. The results obtained are given in the following table.

Method Used	$\Delta H_f^\circ 298.15, \text{kcal. mole}^{-1}$	
	Third Law Value	Second Law Value
Transpiration	5.31	5.07 ± 0.4
Effusion	12.57	5.85 ± 3.3
*Based on the third law values		

By a mass spectroscopic method the enthalpy change, $\Delta H_f^\circ 1000 = 16.6 \pm 2.5 \text{ kcal. mole}^{-1}$, for the reaction $\text{BCl}_3(g) + \text{B}_2\text{O}_3(1) = (\text{BOCl})_3(g)$ was determined by R. P. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964). The $\Delta H_f^\circ 298.15$ value for $(\text{BOCl})_3(g)$ was derived as $-377 \pm 5 \text{ kcal. mole}^{-1}$. However, it is possible that the intensity of $\text{B}_2\text{O}_3\text{Cl}_3$, employed to plot the ion ratios $(\text{B}_2\text{O}_3\text{Cl}_3^+)/(\text{BCl}_2^+)$ versus $\frac{1}{M}$, does not fully reflect the concentration of $\text{B}_2\text{O}_3\text{Cl}_3$ especially at the highest temperatures, due to changes in the fragmentation pattern with temperature.

The value of $\Delta H_f^\circ 298.15$ adopted for $(\text{BOCl})_3(g)$ is $-390 \pm 2 \text{ kcal. mole}^{-1}$ derived from transpiration data. The effusion data were measured in the temperature range where Porter and Gupta, loc. cit. found the presence of $(\text{BOCl})_4(g)$. However, this point was not taken into consideration in the report. Hence, the corresponding $\Delta H_f^\circ 298.15$ value was not adopted.

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with related molecules such as $\text{B}_3\text{O}_3(g)$ and $(\text{BH}_2\text{O})_3(g)$. The B-Cl bond distance was assumed to be the same as that in $\text{BCl}_3(g)$. The B-O bond distance and all bond angles were estimated. The three principal moments of inertia are: $I_A = I_B = 9.7785 \times 10^{-38}$ and $I_C = 1.95517 \times 10^{-37} \text{ g. cm.}^2$

Dec. 31, 1960; Mar. 31, 1963; Sept. 30, 1963; June 30, 1964; Mar. 31, 1965



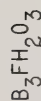
T, °K.	C _p	S°	-($\int_0^T \frac{C_p}{T^2} dT$)	H° - H° ₂₉₈	ΔH_f°	ΔF_f°	Log K _p
0	+0.00	INFINITE	-	6.057	-388.778	-388.778	INFINITE
100	16.750	65.733	114.858	4.912	-389.772	-389.772	837.693
200	25.139	80.088	94.052	2.793	-389.994	-376.742	411.064
298	31.436	91.367	91.367	+0.000	-390.000	-370.238	271.379
300	31.538	91.562	91.367	+0.098	-389.999	-370.117	269.617
400	36.260	101.318	92.666	3.461	-389.874	-363.505	198.600
500	39.618	109.792	95.262	7.265	-389.685	-356.933	156.008
600	41.975	117.236	98.317	11.351	-389.459	-350.402	127.628
700	43.645	123.839	100.000	15.337	-389.196	-343.922	107.969
800	44.894	129.750	104.669	20.065	-388.908	-337.463	92.186
900	45.747	135.087	107.757	24.597	-388.660	-331.045	80.385
1000	46.421	139.943	110.736	29.207	-388.387	-324.655	70.950
1100	46.940	144.393	113.497	33.876	-388.134	-318.298	63.937
1200	47.347	148.486	115.336	38.591	-387.898	-311.958	58.613
1300	47.672	152.299	118.058	43.343	-387.687	-305.640	54.380
1400	47.934	155.842	121.668	48.124	-387.499	-299.334	46.726
1500	48.149	159.156	125.871	52.928	-387.343	-293.045	42.695
1600	48.327	162.270	129.674	57.762	-387.215	-286.761	39.169
1700	48.476	165.206	133.183	62.597	-387.115	-280.483	36.149
1800	48.602	167.978	136.508	67.447	-387.047	-274.215	33.293
1900	48.709	170.646	139.550	72.312	-387.001	-267.946	30.819
2000	48.802	173.110	143.516	77.188	-386.975	-261.682	28.594
2100	48.881	175.493	147.411	82.072	-386.966	-255.417	26.480
2200	48.951	177.769	151.240	86.974	-386.974	-249.134	24.750
2300	49.012	179.946	155.006	91.862	-387.008	-242.868	23.079
2400	49.065	182.033	161.714	96.766	-387.059	-236.616	21.546
2500	49.113	184.037	168.367	101.675	-387.129	-230.374	20.108
2600	49.155	185.964	174.968	106.588	-387.215	-224.151	18.752
2700	49.193	187.821	181.556	111.506	-387.315	-217.934	17.474
2800	49.227	189.610	188.027	116.427	-387.430	-211.724	16.250
2900	49.257	191.337	194.492	121.351	-387.556	-205.520	15.073
3000	49.285	193.008	199.915	126.278	-387.692	-199.324	13.923
3100	49.310	194.624	205.299	131.208	-387.839	-193.138	12.791
3200	49.332	196.190	210.646	136.140	-387.996	-186.964	11.674
3300	49.353	197.709	215.959	141.074	-388.164	-180.802	10.570
3400	49.372	199.182	221.238	146.011	-388.342	-174.652	9.476
3500	49.389	200.614	226.485	150.949	-388.529	-168.519	8.391
3600	49.405	202.005	231.703	155.888	-388.724	-162.394	7.316
3700	49.419	203.359	236.892	160.829	-388.926	-156.276	6.254
3800	49.433	204.677	242.053	165.772	-389.134	-150.164	5.202
3900	49.445	205.961	247.188	170.716	-389.347	-144.056	4.160
4000	49.457	207.213	252.298	175.661	-389.564	-137.952	3.127
4100	49.468	208.435	257.384	180.607	-389.786	-131.852	2.102
4200	49.478	209.627	262.447	185.555	-389.999	-125.756	1.086
4300	49.487	210.791	267.488	190.503	-390.196	-119.664	0.079
4400	49.496	211.929	272.508	195.452	-390.384	-113.576	-0.929
4500	49.504	213.041	277.508	200.402	-390.564	-107.492	-1.938
4600	49.512	214.129	282.488	205.353	-390.736	-101.412	-2.952
4700	49.519	215.194	287.449	210.304	-390.899	-95.336	-3.970
4800	49.525	216.237	292.392	215.257	-391.056	-89.264	-4.990
4900	49.532	217.258	297.317	220.209	-391.206	-83.196	-6.012
5000	49.538	218.259	302.226	225.163	-391.352	-77.132	-7.036
5100	49.543	219.240	307.119	230.117	-391.494	-71.072	-8.062
5200	49.548	220.202	311.996	235.072	-391.632	-65.016	-9.088
5300	49.553	221.146	316.858	240.027	-391.766	-58.964	-10.114
5400	49.558	222.072	321.705	244.982	-391.896	-52.916	-11.140
5500	49.562	222.982	326.538	249.938	-392.022	-46.872	-12.166
5600	49.567	223.875	331.365	254.895	-392.144	-40.828	-13.192
5700	49.571	224.752	336.186	259.852	-392.262	-34.784	-14.218
5800	49.574	225.614	340.995	264.809	-392.376	-28.738	-15.244
5900	49.578	226.462	345.799	269.766	-392.486	-22.692	-16.270
6000	49.581	227.295	350.598	274.724	-392.592	-16.646	-17.296

Monofluoroboroxin ($B_3O_3H_2F$)

(Ideal Gas) Mol. Wt. = 101.4554

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	11.162	57.652	91.583	1.393	-376.205	-376.205	-376.205	INFINITE
200	22.744	75.225	106.635	1.000	-375.520	-375.520	-375.520	820.744
298	22.744	75.225	106.635	1.000	-382.000	-382.000	-382.000	267.532
300	22.863	75.367	106.635	1.042	-382.012	-382.012	-382.012	265.616
400	27.749	82.635	76.184	2.890	-382.586	-382.586	-382.586	195.996
500	31.713	89.269	78.147	5.561	-383.043	-383.043	-383.043	154.167
600	34.866	95.341	80.514	8.806	-383.381	-383.381	-383.381	126.291
700	37.367	100.911	83.036	12.512	-383.608	-383.608	-383.608	106.296
800	39.354	106.035	85.595	16.352	-383.739	-383.739	-383.739	91.324
900	40.941	110.766	88.132	20.370	-383.790	-383.790	-383.790	79.676
1000	42.218	115.148	90.617	24.530	-383.786	-383.786	-383.786	70.356
1100	43.234	119.222	93.095	28.806	-383.753	-383.753	-383.753	62.732
1200	44.100	123.023	95.537	33.175	-383.695	-383.695	-383.695	56.378
1300	44.769	126.581	97.662	37.621	-383.632	-383.632	-383.632	51.004
1400	45.380	129.923	99.830	42.131	-383.567	-383.567	-383.567	46.397
1500	45.867	133.071	101.942	46.694	-383.515	-383.515	-383.515	42.406
1600	46.279	136.045	103.981	51.301	-383.477	-383.477	-383.477	38.914
1700	46.630	138.861	105.951	55.947	-383.455	-383.455	-383.455	35.833
1800	46.930	141.535	107.854	60.626	-383.453	-383.453	-383.453	33.095
1900	47.190	144.080	109.694	65.332	-383.466	-383.466	-383.466	30.645
2000	47.415	146.506	111.475	70.063	-383.491	-383.491	-383.491	28.439
2100	47.612	148.824	113.199	74.814	-383.531	-383.531	-383.531	26.463
2200	47.785	151.043	114.869	79.584	-383.588	-383.588	-383.588	24.639
2300	47.937	153.171	116.488	84.370	-383.657	-383.657	-383.657	22.972
2400	48.072	155.214	118.059	89.171	-383.746	-383.746	-383.746	21.453
2500	48.192	157.179	119.595	93.984	-400.013	-400.013	-400.013	20.027
2600	48.299	159.071	121.068	98.809	-400.108	-400.108	-400.108	18.682
2700	48.396	160.896	122.509	103.644	-400.209	-400.209	-400.209	17.436
2800	48.482	162.657	123.912	108.488	-400.316	-400.316	-400.316	16.279
2900	48.561	164.360	125.277	113.340	-400.429	-400.429	-400.429	15.201
3000	48.632	166.009	126.608	118.200	-400.549	-400.549	-400.549	14.195
3100	48.696	167.603	127.905	123.066	-400.673	-400.673	-400.673	13.254
3200	48.755	169.150	129.169	127.939	-400.806	-400.806	-400.806	12.374
3300	48.809	170.651	130.404	132.817	-400.946	-400.946	-400.946	11.541
3400	48.858	172.109	131.609	137.700	-401.092	-401.092	-401.092	10.760
3500	48.903	173.526	132.787	142.588	-401.246	-401.246	-401.246	10.024
3600	48.945	174.904	133.937	147.481	-401.406	-401.406	-401.406	9.327
3700	48.983	176.246	135.063	152.377	-401.576	-401.576	-401.576	8.669
3800	49.019	177.553	136.164	157.277	-401.750	-401.750	-401.750	8.044
3900	49.052	178.826	137.242	162.181	-401.933	-401.933	-401.933	7.452
4000	49.082	180.069	138.297	167.088	-402.126	-402.126	-402.126	6.897
4100	49.110	181.281	139.330	171.997	-402.330	-402.330	-402.330	6.377
4200	49.137	182.465	140.343	176.910	-402.543	-402.543	-402.543	5.887
4300	49.162	183.621	141.337	181.825	-402.766	-402.766	-402.766	5.426
4400	49.184	184.752	142.310	186.742	-403.000	-403.000	-403.000	4.991
4500	49.206	185.857	143.266	191.661	-403.243	-403.243	-403.243	4.579
4600	49.226	186.939	144.204	196.583	-403.496	-403.496	-403.496	4.190
4700	49.245	187.998	145.124	201.507	-403.758	-403.758	-403.758	3.831
4800	49.263	189.035	146.028	206.432	-404.029	-404.029	-404.029	3.491
4900	49.280	190.051	146.916	211.359	-404.308	-404.308	-404.308	3.166
5000	49.295	191.047	147.789	216.288	-404.594	-404.594	-404.594	2.854
5100	49.310	192.023	148.657	221.218	-404.886	-404.886	-404.886	2.554
5200	49.324	192.981	149.500	226.150	-405.184	-405.184	-405.184	2.264
5300	49.337	193.920	150.320	231.083	-405.488	-405.488	-405.488	1.984
5400	49.350	194.843	151.136	236.017	-405.798	-405.798	-405.798	1.714
5500	49.362	195.748	151.939	240.953	-406.114	-406.114	-406.114	1.454
5600	49.373	196.638	152.729	245.890	-406.436	-406.436	-406.436	1.204
5700	49.383	197.512	153.507	250.827	-406.764	-406.764	-406.764	0.964
5800	49.394	198.371	154.273	255.766	-407.098	-407.098	-407.098	0.734
5900	49.404	199.215	155.028	260.706	-407.438	-407.438	-407.438	0.514
6000	49.412	200.045	155.771	265.647	-407.784	-407.784	-407.784	0.304

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965; Dec. 31, 1965



MOL. WT. = 101.44554

(IDEAL GAS)

MONOFUOROBOROXIN ($B_3O_3H_2F$)

$$\Delta H_f^o = -379 \pm 6 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = -382 \pm 6 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = [75.225] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
[2100] (1)	[880] (1)	[350] (1)	[550] (1)
[870] (1)	[1460] (1)	[225] (1)	[225] (1)
[670] (1)	[520] (1)	[800] (1)	[800] (1)
[2200] (1)	[2230] (1)	[225] (1)	[225] (1)
[1390] (1)	[1390] (1)	[840] (1)	[840] (1)
[1200] (1)	[1200] (1)	[800] (1)	[800] (1)
[880] (1)	[350] (1)	[260] (1)	[260] (1)

Bond Distances B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å

Bond Angles B-O-B = [120°] O-B-H = [120°] O-B-F = [120°]

Product of the Moments of Inertia $I_A I_B I_C = [2.1854] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

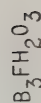
Heat of Formation.

The equilibrium constants (K), 1246-1396°K. for the two reactions $2B_3O_3 \cdot 2H_2O(g) = B_3O_3 \cdot 2H_2O(g) + B_3O_3 \cdot 2H_2O(g)$ and $2B_3O_3 \cdot 2H_2O(g) = B_3O_3 \cdot 2H_2O(g) + B_3O_3 \cdot 2H_2O(g)$ were reported by F. R. Porter and W. F. Sholette, J. Chem. Phys. 37, 198 (1962). The ΔH_f^o 298.15 for $B_3O_3 \cdot 2H_2O(g)$ adopted was evaluated by use of K values slightly outside the ranges given by Porter and Sholette. See the table for $B_3O_3 \cdot 2H_2O(g)$ for details.

Heat Capacity and Entropy.

The structure was assumed to be a planar six membered ring structure of C_{2v} symmetry, which has 21 vibrations of the type θ_{11} , θ_{12} , θ_{13} , θ_{14} , θ_{15} , and θ_{16} . These frequencies were estimated from the values for boroxin and trifluoroboroxin, the symmetry being reduced from D_{3h} as follows: $3A_1 \rightarrow 3A_1$, $2A_1 \rightarrow 2A_1$, $5E' \rightarrow 5A_1 + 5B_1$, $2A_2 \rightarrow 2B_2$ and $2E'' \rightarrow 2A_2 + 2B_2$.

The B-F distance was taken as approximately equal to that in $(CH_3)_2O \cdot BF_3$ reported by S. H. Bauer, O. R. Finckley and A. W. Leubengayer, J. Am. Chem. Soc. 57, 339 (1935). The other bond lengths and angles were taken equal to those in boroxin. The individual moments of inertia were calculated to be $I_A = 32.985 \times 10^{-39}$, $I_B = 13.973 \times 10^{-39}$, and $I_C = 46.868 \times 10^{-39} \text{ g. cm.}^2$.



Point Group [C_{2v}]
 $\Delta H_f^\circ = -472 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = -475 \pm 5 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [78.6] \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

λ , cm. ⁻¹	λ , cm. ⁻¹	λ , cm. ⁻¹
[1650] (1)	[660] (1)	[300] (1)
[830] (1)	[1370] (1)	[220] (1)
[610] (1)	[490] (1)	[710] (1)
[1800] (1)	[1840] (1)	[220] (1)
[1385] (1)	[1395] (1)	[780] (1)
[1080] (1)	[1080] (1)	[700] (1)
[690] (1)	[310] (1)	[230] (1)

Bond Distances: B-O = [1.36] Å B-H = [1.18] Å B-F = [1.41] Å
 Bond Angle: B-O-B = [120°] O-B-H = [120°] O-B-F = [120°]
 Product of the Moments of Inertia: $I_A I_B I_C = [7.5869] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$

$\sigma^- = [2]$

Heat of Formation.

The stabilities of gaseous boroxin (B₃O₃H₂) and its fluoro derivatives have been studied by R. F. Porter and W. P. Shollette, J. Chem. Phys. 37, 199 (1962). From the mass spectra of the gaseous reaction products generated by reaction of an H₂-B₃O₃ mixture on B₂O₃ at 1250°K, the equilibrium constants (K) for the following proposed reactions were reported.

Reaction	Temperature, °K.	K	ΔH_f° 298.15, kcal. mole ⁻¹
(1) H ₂ (g) + B ₃ O ₃ H ₂ (g) = HF(g) + B ₃ O ₃ H ₂ H(g)	1246 - 1326	4.2×10^{-3}	20.45 - 17.17
(2) 2B ₃ O ₃ H ₂ (g) = B ₃ O ₃ PH ₂ (g) + B ₃ O ₃ PH ₂ (g)	1246 - 1326	0.62 - 0.46	1.28 - 2.15
(3) 2B ₃ O ₃ PH ₂ (g) = B ₃ O ₃ H ₂ (g) + B ₃ O ₃ PH ₂ (g)	1246 - 1326	1.0 - 0.63	-2.56 - -1.51

Using these reported K values the corresponding enthalpy changes (ΔH_f° 298.15) were evaluated by the third law method. The results obtained are listed in the above table. Based on ΔH_f° 298.15 = -565.3 and -64.8 kcal. mole⁻¹ for B₃O₃H₂(g) and HF(g), respectively, the value of ΔH_f° 298.15 for B₃O₃PH₂(g) was calculated from Reaction (1) as -482 kcal. mole⁻¹. From Reaction (2), the ΔH_f° 298.15 value for B₃O₃PH₂(g) was calculated as -397 kcal. mole⁻¹. However, employing ΔH_f° 298.15(B₃O₃H₂, g) = -591 kcal. mole⁻¹, the values of ΔH_f° 298.15 for B₃O₃PH₂(g) and B₃O₃PH₂(g) thus obtained do not fit properly for Reaction (3). Therefore the ΔH_f° 298.15 for B₃O₃PH₂(g) and B₃O₃PH₂(g) adopted were evaluated by use of K values slightly outside the ranges given by Porter and Shollette.

Heat Capacity and Entropy.

The vibrational frequencies were obtained by comparison with B₃O₃F₂(g) and B₃H₃O₃(g). The types of vibration and symmetry are identical to those given for B₃O₃F₂(g). The bond angles and lengths were taken equal to those for B₃O₃F₂(g). The individual moments of inertia were calculated to be $I_A = 22.051 \times 10^{-39}$, $I_B = 46.659 \times 10^{-39}$ and $I_C = 70.710 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C _p	S°	(-F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	Log K _p
0	0.000	INFINITE	-	-4.571	-472.461	INFINITE
100	11.771	59.365	-	-3.672	-468.147	1023.084
200	18.724	69.975	-	-2.162	-474.435	505.117
298	24.744	78.608	0.000	-	-475.000	334.365
300	24.847	78.608	0.046	-	-475.009	332.219
400	29.837	86.619	79.646	2.789	-475.415	449.669
500	33.785	93.719	81.762	5.979	-475.718	545.076
600	36.857	100.162	86.301	9.517	-475.919	633.219
700	39.230	106.030	89.992	13.327	-476.026	715.706
800	41.066	111.394	92.712	17.345	-476.059	789.098
900	42.495	116.316	94.398	21.526	-476.029	854.441
1000	43.618	120.854	95.020	25.834	-475.960	902.243
1100	44.512	125.055	97.662	30.242	-475.878	938.896
1200	45.230	128.960	100.018	34.731	-475.782	965.700
1300	45.814	132.604	102.386	39.284	-475.692	983.823
1400	46.294	136.017	104.667	43.860	-475.607	998.988
1500	46.692	139.225	106.865	48.500	-475.540	1011.779
1600	47.026	142.250	108.983	53.226	-475.492	1022.275
1700	47.308	145.109	111.025	57.943	-475.465	1030.710
1800	47.548	147.820	112.994	62.686	-475.441	1037.238
1900	47.755	150.397	114.896	67.452	-475.474	1042.456
2000	47.933	152.851	116.733	72.236	-475.501	1046.561
2100	48.088	155.193	118.509	77.038	-475.544	1049.593
2200	48.223	157.434	120.228	81.853	-475.605	1051.547
2300	48.342	159.580	121.892	86.682	-475.680	1052.437
2400	48.448	161.640	123.506	91.521	-475.775	1052.278
2500	48.541	163.619	125.071	96.371	-475.889	1051.067
2600	48.625	165.525	126.590	101.229	-476.012	1048.823
2700	48.699	167.361	128.067	106.095	-476.145	1045.548
2800	48.766	169.134	129.502	110.969	-476.287	1041.268
2900	48.827	170.846	130.898	115.848	-476.437	1036.000
3000	48.882	172.502	132.257	120.734	-476.626	1029.752
3100	48.931	174.106	133.582	125.625	-476.829	1022.529
3200	48.976	175.660	134.872	130.520	-477.040	1014.329
3300	49.018	177.168	136.131	135.420	-477.256	1005.161
3400	49.055	178.632	137.360	140.323	-477.481	995.033
3500	49.086	180.054	138.560	145.231	-477.716	983.955
3600	49.122	181.437	139.732	150.141	-477.961	971.928
3700	49.151	182.784	140.877	155.055	-478.216	958.953
3800	49.178	184.095	141.997	159.972	-478.481	945.033
3900	49.204	185.373	143.093	164.891	-478.756	929.161
4000	49.227	186.619	144.166	169.812	-479.041	912.343
4100	49.248	187.834	145.216	174.736	-479.337	894.577
4200	49.269	189.021	146.245	179.662	-479.644	875.868
4300	49.287	190.181	147.253	184.590	-479.961	856.212
4400	49.305	191.314	148.242	189.519	-480.287	835.612
4500	49.321	192.423	149.211	194.451	-480.623	814.068
4600	49.337	193.507	150.162	199.384	-480.969	791.577
4700	49.351	194.568	151.096	204.318	-481.326	768.141
4800	49.364	195.607	152.013	209.254	-481.694	742.762
4900	49.377	196.625	152.913	214.191	-482.072	716.441
5000	49.389	197.623	153.797	219.129	-482.461	689.161
5100	49.400	198.601	154.666	224.069	-482.861	660.921
5200	49.411	199.560	155.520	229.009	-483.271	631.721
5300	49.421	200.502	156.360	233.951	-483.691	601.561
5400	49.431	201.425	157.186	238.893	-484.121	570.441
5500	49.441	202.332	158.000	243.837	-484.561	538.361
5600	49.449	203.223	158.798	248.781	-485.011	505.321
5700	49.456	204.099	159.585	253.726	-485.471	471.341
5800	49.464	204.959	160.360	258.672	-485.941	436.421
5900	49.471	205.804	161.123	263.619	-486.421	400.541
6000	49.478	206.636	161.875	268.567	-486.911	363.661

Mar. 31, 1965; Sept. 30, 1965; Mar. 31, 1965; Dec. 31, 1965

Boron Oxide Fluoride, Trimeric ((BOF)₃)

(Crystal) Mol. Wt. = 137.46

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0						
100						
200						
298	30.000	52.000	0.000	-586.500	-557.166	408.304
300	30.085	52.186	0.001	-586.500	-556.986	408.744
400	34.000	61.262	3.267	-586.500	-556.986	398.935
500	39.000	69.666	6.976	-586.500	-556.986	386.860
600	42.725	77.113	11.066	-586.029	-527.569	372.158
700	46.000	83.951	15.506	-585.580	-517.858	358.875
800	48.000	89.959	20.251	-584.966	-508.227	346.835
900	50.000	95.173	25.251	-584.184	-498.679	335.090
1000	51.100	101.671	30.474	-583.299	-489.251	323.614
1100	54.400	106.806	35.862	-582.319	-479.864	312.336
1200	56.400	111.600	41.277	-581.279	-470.592	301.202
1300	58.000	116.090	46.822	-580.114	-461.412	290.202
1400	59.400	120.288	52.547	-578.848	-452.312	279.402
1500	60.600	124.217	58.342	-577.490	-443.292	268.802

B₃F₃O₃

MOL. WT. = 137.46

BORON OXIDE FLUORIDE, TRIMERIC ((BOF)₃)

(CRYSTAL)

ΔH_f⁰ 0 = Unknown
 ΔH_f⁰ 298.15 = -586.5 ± 3.0 kcal. mole⁻¹
 ΔG_f⁰ = Unknown
 ΔG_f⁰ 298.15 = 21.2 ± 3.2 kcal. mole⁻¹
 T_m = 353°K.

Heat of Formation.

The heats of solution of the compounds B₂O₃(gl), BF₃(g) and (BOF)₃(c) in water and methanol, respectively, were reported by E. M. Magee, J. Inorg. Nucl. Chem. 22, 156 (1961). The corresponding enthalpy changes for the reaction B₂O₃(gl) + BF₃(g) = (BOF)₃(c) were derived as -19.8 and -14.4 kcal. mole⁻¹, yielding ΔH_f⁰ 298.15 for (BOF)₃(c) -589.18 and -585.78 kcal. mole⁻¹, respectively. The adopted value of ΔH_f⁰ 298.15 for (BOF)₃(c) is the average of these two values obtained.

Heat Capacity and Entropy.

The heat capacities (C_p) for (BOF)₃(c) were estimated from the C_p values for B₂O₃(c) and BF₃(g), according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York, 1958. S° 298.15 for (BOF)₃(c) was estimated by E. M. Magee, loc. cit.

Melting Data.

The value of T_m was reported by E. M. Magee, loc. cit.

Heat of Sublimation.

The heat of sublimation (ΔH_g⁰ 298.15) for (BOF)₃(c) is calculated as the difference between ΔH_f⁰ 298.15 for crystal and gas.

B₃F₃O₃

Boron Oxide Fluoride, Trimeric ((BOF)₃)
(Ideal Gas) Mol. Wt. = 137.46

BORON OXIDE FLUORIDE, TRIMERIC ((BOF)₃) (IDEAL GAS)

MOL. WT. = 137.46

Point Group {D_{3h}}
S_{298.15}° = [81.8] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

ΔH_f⁰ = -563.3 ± 1.0 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -565.3 ± 1.0 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies
ω_j cm.⁻¹ ω_j cm.⁻¹ ω_j cm.⁻¹

(1233) (1)	1450 (2)	714 (1)
(790) (1)	1381 (2)	(170) (1)
(570) (1)	966 (2)	(630) (2)
(1280) (1)	(420) (2)	(185) (2)
(440) (1)	(220) (2)	

Bond Distance: B-F = [1.3] Å. B-O = [1.36] Å

Bond Angle: F-B-O = [120°] B-O-B = [120°] O-B-O = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [1.9254 X 10⁻¹¹²] g.³ cm.⁶

σ⁻ = 6

Heat of Formation.

The enthalpy changes (ΔH_f⁰) of the reaction B₂O₃(l) + BF₃(g) = (BOF)₃(g) were derived by both the second and third law methods, using the equilibrium constant data reported by several investigators. The results are given as follows.

Investigator	Third Law Value	Second Law Value	ΔH _f ⁰ 298.15 ⁰ kcal. mole ⁻¹
Hildenbrand, et al. ¹	4.06	4.01 ± 0.3	-565.32 ± 1.0
Fisher, et al. ²	3.41	6.45 ± 0.6	-565.97 ± 1.5
Smith and Lawrence ³	4.03	—	-565.35 ± 1.3
Farber ⁴	5.25	—	-564.13 ± 2.0
Porter, et al. ⁵	—	7.58 ± 0.2	-565.82 ± 2.0
	—	4.33 ± 0.30	-565.05 ± 1.0

*Calculation based on the third law values available.

- 1 D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. **33**, 1973 (1963).
- 2 H. D. Fisher, J. Kishi and A. Cane, Report HVC-61-90, June 1961, Hughes Tool Company, Culver City, California
- 3 D. D. Smith and R. W. Lawrence, Aerojet Report No. 1952, February 1961, Aerojet-General Corporation.
- 4 M. Farber, J. Chem. Phys. **35**, 661 (1962). The first ΔH_f⁰ 298.15 value was evaluated based on K₁₀₀₀ = 1280 and 1233 from Fisher, et al., can be assigned to the reaction B₂O₃(c) + BF₃(g) = (BOF)₃(g).
- 5 R. P. Porter, D. R. Biddisat and K. P. Watterson, J. Chem. Phys. **35**, 2104 (1962). The ΔH_f⁰ 298.15 value was derived from ΔH_f⁰ 700 = 3.46 ± 0.30 kcal. mole⁻¹.

The adopted value of ΔH_f⁰ 298.15 for (BOF)₃(g) is the weighted average of the six ΔH_f⁰ 298.15 values listed above.

Heat Capacity and Entropy.

The infra-red spectrum has been reported by D. D. Smith and R. L. Lawrence, loc. cit., and by H. D. Fisher, W. J. Lehmann, and I. Shapiro, J. Phys. Chem. **65**, 1166 (1961) who also made a partial assignment. The unassigned bands at 1280 and 1233 from Fisher, et al., can be assigned to the A₂⁺ and A₁⁺ species which may be observed if the selection rules are not rigorously obeyed in the solid. All the unobserved frequencies were estimated by comparison with B₂O₃(OH)₃, B₂O₃(OD)₃ from J. L. Parsons, J. Chem. Phys. **33**, 1860 (1960) and B₂O₃-H₂O from S. K. Gupta and R. P. Porter, J. Phys. Chem. **57**, 1266 (1953) and O. H. Lee, W. H. Bauer and S. E. Wiberley, J. Phys. Chem. **67**, 1742 (1963). The D_{3h} assumed symmetry has 14 vibrations of the type 3A₁⁺, 2A₂⁺, 5E₁⁺, 2A₂⁻ and 2E₁⁻ which are given in order above. The B-F bond distance was assumed to be the same as that in BF₃. The B-O bond distance was estimated by comparison with other related compounds. The three principal moments of inertia are: I_A = I_B = 4.5832 X 10⁻³⁸ g. cm.²

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1962; Sept. 30, 1963; Sept. 31, 1965

T. °K.	C _p	S ⁰	cal. mole ⁻¹ deg. ⁻¹	-(F ⁰ -H ₂₉₈ ⁰)/T	H ⁰ -H ₂₉₈ ⁰	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	-	5.184	-563.331	-563.331	INFINITE
100	13.862	60.014	102.010	4.200	564.676	-564.676	-564.676	1219.713
200	21.489	71.426	116.818	4.000	565.840	-565.840	-565.840	1564.653
298	27.499	81.825	126.757	3.805	566.984	-566.984	-566.984	1890.373
300	27.500	81.995	126.757	3.805	566.984	-566.984	-566.984	1890.373
400	32.456	90.626	135.073	3.617	568.164	-568.164	-568.164	2366.819
500	36.226	98.282	142.250	3.443	569.403	-569.403	-569.403	2793.851
600	39.066	105.161	148.429	3.287	570.698	-570.698	-570.698	3180.053
700	41.189	111.350	153.638	3.147	572.050	-572.050	-572.050	3536.422
800	42.783	116.959	158.000	3.020	573.458	-573.458	-573.458	3873.952
900	43.994	122.071	161.605	2.904	574.922	-574.922	-574.922	4192.188
1000	44.927	126.757	164.676	2.800	576.442	-576.442	-576.442	4492.600
1100	45.657	131.074	167.214	2.706	578.018	-578.018	-578.018	4777.231
1200	46.237	135.073	169.250	2.621	579.650	-579.650	-579.650	5048.504
1300	46.703	138.793	170.800	2.545	581.338	-581.338	-581.338	5307.960
1400	47.083	142.268	171.950	2.478	583.082	-583.082	-583.082	5556.176
1500	47.396	145.528	172.750	2.419	584.882	-584.882	-584.882	5794.626
1600	47.657	148.595	173.214	2.366	586.738	-586.738	-586.738	6023.856
1700	47.876	151.491	173.458	2.318	588.650	-588.650	-588.650	6244.419
1800	48.062	154.232	173.458	2.275	590.618	-590.618	-590.618	6456.879
1900	48.221	156.836	173.209	2.237	592.642	-592.642	-592.642	6661.688
2000	48.358	159.313	172.650	2.203	594.722	-594.722	-594.722	6859.271
2100	48.477	161.675	172.819	2.172	596.858	-596.858	-596.858	7049.999
2200	48.581	163.933	172.687	2.144	599.050	-599.050	-599.050	7234.219
2300	48.672	166.094	172.397	2.119	601.298	-601.298	-601.298	7402.384
2400	48.752	168.169	171.950	2.096	603.602	-603.602	-603.602	7564.956
2500	48.823	170.159	171.350	2.075	605.962	-605.962	-605.962	7722.384
2600	48.886	172.075	170.614	2.056	608.378	-608.378	-608.378	7875.119
2700	48.943	173.921	169.750	2.039	610.850	-610.850	-610.850	8023.619
2800	48.994	175.702	168.750	2.024	613.378	-613.378	-613.378	8168.449
2900	49.040	177.422	167.619	2.010	615.962	-615.962	-615.962	8309.159
3000	49.081	179.086	166.350	2.000	618.602	-618.602	-618.602	8446.299
3100	49.118	180.696	165.050	1.992	621.298	-621.298	-621.298	8580.419
3200	49.153	182.256	163.719	1.986	624.050	-624.050	-624.050	8712.159
3300	49.184	183.769	162.350	1.981	626.858	-626.858	-626.858	8842.159
3400	49.212	185.237	160.950	1.977	629.722	-629.722	-629.722	8970.059
3500	49.238	186.664	160.519	1.974	632.642	-632.642	-632.642	9096.519
3600	49.262	188.052	160.050	1.972	635.618	-635.618	-635.618	9221.299
3700	49.284	189.402	160.545	1.970	638.650	-638.650	-638.650	9345.059
3800	49.305	190.716	160.000	1.969	641.738	-641.738	-641.738	9467.459
3900	49.324	191.997	160.420	1.968	644.882	-644.882	-644.882	9589.059
4000	49.341	193.246	160.810	1.968	648.082	-648.082	-648.082	9709.519
4100	49.357	194.465	161.167	1.968	651.338	-651.338	-651.338	9828.519
4200	49.373	195.654	161.500	1.968	654.650	-654.650	-654.650	9946.719
4300	49.387	196.816	161.816	1.968	658.018	-658.018	-658.018	10063.879
4400	49.400	197.952	162.116	1.968	661.442	-661.442	-661.442	10179.659
4500	49.412	199.062	162.400	1.968	664.922	-664.922	-664.922	10293.819
4600	49.424	200.148	162.674	1.968	668.458	-668.458	-668.458	10406.999
4700	49.434	201.211	162.938	1.968	672.050	-672.050	-672.050	10518.959
4800	49.444	202.252	163.192	1.968	675.698	-675.698	-675.698	10629.459
4900	49.454	203.272	163.436	1.968	679.402	-679.402	-679.402	10738.259
5000	49.463	204.271	163.670	1.968	683.162	-683.162	-683.162	10846.019
5100	49.471	205.251	163.900	1.968	687.078	-687.078	-687.078	10952.519
5200	49.479	206.211	164.126	1.968	691.050	-691.050	-691.050	11057.619
5300	49.487	207.154	164.350	1.968	695.078	-695.078	-695.078	11161.159
5400	49.494	208.082	164.574	1.968	699.162	-699.162	-699.162	11263.119
5500	49.501	208.987	164.798	1.968	703.302	-703.302	-703.302	11363.459
5600	49.507	209.879	165.022	1.968	707.498	-707.498	-707.498	11462.119
5700	49.513	210.755	165.246	1.968	711.750	-711.750	-711.750	11559.059
5800	49.519	211.617	165.470	1.968	716.058	-716.058	-716.058	11654.219
5900	49.525	212.466	165.694	1.968	720.422	-720.422	-720.422	11748.459
6000	49.529	213.298	165.918	1.968	724.842	-724.842	-724.842	11841.719



MOL. WT. = 83.484

(CRYSTAL)

BOROXIN ($\text{B}_3\text{O}_3\text{H}_3$)



(Crystal) Mol. Wt. = 83.484

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0								
100								
200								
298	23.500	40.000	40.000	0.000	0.000	-301.700	-276.498	202.689
300	23.600	40.146	40.000	0.044	0.044	-301.710	-276.343	201.306
400	28.700	47.631	40.987	2.658	2.658	-302.170	-267.813	146.319
500	33.900	54.598	43.019	5.789	5.789	-302.422	-259.190	113.286
600	38.900	61.234	45.506	9.437	9.437	-302.382	-250.541	91.255
700	43.000	67.546	48.208	13.537	13.537	-302.050	-241.921	75.528
800	46.500	73.525	51.002	18.018	18.018	-301.460	-233.373	63.751
900	49.138	79.100	53.821	22.805	22.805	-300.660	-224.908	54.612
1000	51.200	84.449	56.622	27.827	27.827	-299.711	-216.538	47.322
1100	52.517	89.392	59.379	33.014	33.014	-298.683	-208.272	41.378
1200	53.600	94.010	62.075	38.322	38.322	-297.605	-200.098	36.441
1300	54.203	98.324	64.696	43.713	43.713	-296.518	-192.018	32.280
1400	54.738	102.361	67.247	49.161	49.161	-295.438	-184.018	28.725
1500	55.203	106.154	69.715	54.658	54.658	-294.379	-176.099	25.656
1600	55.600	109.730	72.105	60.199	60.199	-293.340	-168.268	22.980
1700	55.928	113.111	74.419	65.776	65.776	-292.321	-160.459	20.627
1800	56.188	116.315	76.658	71.382	71.382	-291.329	-152.733	18.545
1900	56.378	119.396	78.826	77.011	77.011	-290.360	-145.059	16.685
2000	56.500	122.254	80.926	82.656	82.656	-289.415	-137.437	15.018

ΔH_f° 0 = Unknown
 ΔH_f° 298.15 = -301.7 ± 10 kcal. mole⁻¹
 ΔH_f° = Unknown
 ΔH_g° 298.15 = 10.7 ± 0.5 kcal. mole⁻¹

Heat of Formation.

The value of ΔH_f° 298.15 for $\text{B}_3\text{O}_3\text{H}_3(\text{c})$ was calculated from the ΔH_f° 298.15 for $\text{B}_3\text{O}_3\text{H}_3(\text{g})$ and ΔH_g° 298.15 for $\text{B}_3\text{O}_3\text{H}_3(\text{c})$ reported by R. F. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964).

Heat Capacity and Entropy.

The heat capacities (C_p) were estimated from those for $\text{P}_2\text{O}_5(\text{c})$ and 1/2 $\text{P}_2\text{H}_6(\text{g})$, according to the method suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. The value of S°_{298.15} for $\text{B}_3\text{O}_3\text{H}_3(\text{c})$ was calculated based on ΔS°_{298.15} = 6.6 cal. deg.⁻¹ mole⁻¹ for the reaction $\text{B}_3\text{O}_3\text{H}_3(\text{c}) = \text{P}_2\text{O}_5(\text{am}) + 1/2 \text{P}_2\text{H}_6(\text{g})$, which was obtained from the calculated ΔH_f° 298.15 and measured ΔH_f° 298.15 evaluated from the vapor pressure reported by W. F. Sholette and R. F. Porter, J. Phys. Chem. 67, 177 (1963).

Heat of Sublimation.

ΔH_g° 298.15 was taken from R. F. Porter and S. K. Gupta, loc. cit.



T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(-F°-H°) ₂₉₈	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	10.000	53.000	4.026	-288.002	-288.002	-288.002	-288.002	INFINITE
200	15.050	74.500	3.862	-289.363	-289.363	-289.363	-289.363	922.4785
300	18.600	86.400	3.750	-290.000	-290.000	-290.000	-290.000	1540.326
400	20.992	96.744	3.656	-291.000	-291.000	-291.000	-291.000	201.326
500	21.084	106.874	3.574	-291.015	-291.015	-291.015	-291.015	200.012
600	25.753	126.594	3.386	-291.742	-291.742	-291.742	-291.742	146.951
700	29.706	146.776	3.185	-292.346	-292.346	-292.346	-292.346	115.041
800	32.920	168.490	2.970	-292.817	-292.817	-292.817	-292.817	93.728
900	35.514	193.767	2.751	-293.156	-293.156	-293.156	-293.156	78.482
1000	37.614	218.415	2.538	-293.389	-293.389	-293.389	-293.389	67.038
1100	39.326	243.183	2.339	-293.526	-293.526	-293.526	-293.526	58.130
1200	40.751	267.402	2.154	-293.594	-293.594	-293.594	-293.594	51.001
1300	41.891	291.340	1.992	-293.620	-293.620	-293.620	-293.620	45.169
1400	42.856	315.028	1.852	-293.612	-293.612	-293.612	-293.612	40.307
1500	43.664	338.491	1.733	-293.588	-293.588	-293.588	-293.588	36.194
1600	44.355	361.752	1.633	-293.554	-293.554	-293.554	-293.554	32.669
1700	44.923	384.832	1.552	-293.529	-293.529	-293.529	-293.529	29.614
1800	45.416	407.748	1.487	-293.513	-293.513	-293.513	-293.513	26.942
1900	45.839	430.514	1.436	-293.508	-293.508	-293.508	-293.508	24.583
2000	46.205	453.145	1.390	-293.519	-293.519	-293.519	-293.519	22.487
2100	46.523	475.651	1.348	-293.543	-293.543	-293.543	-293.543	20.611
2200	46.800	498.045	1.310	-293.576	-293.576	-293.576	-293.576	18.923
2300	47.044	520.334	1.276	-293.622	-293.622	-293.622	-293.622	17.495
2400	47.259	542.528	1.246	-293.683	-293.683	-293.683	-293.683	16.206
2500	47.440	564.634	1.219	-293.755	-293.755	-293.755	-293.755	15.038
2600	47.586	586.651	1.195	-293.845	-293.845	-293.845	-293.845	14.000
2700	47.709	608.681	1.173	-293.951	-293.951	-293.951	-293.951	13.074
2800	47.805	630.729	1.152	-294.072	-294.072	-294.072	-294.072	12.254
2900	47.876	652.794	1.132	-294.208	-294.208	-294.208	-294.208	11.533
3000	47.923	674.874	1.113	-294.358	-294.358	-294.358	-294.358	10.904
3100	48.008	696.969	1.095	-294.522	-294.522	-294.522	-294.522	10.364
3200	48.083	719.079	1.078	-294.699	-294.699	-294.699	-294.699	9.904
3300	48.152	741.194	1.062	-294.889	-294.889	-294.889	-294.889	9.524
3400	48.215	763.314	1.047	-295.091	-295.091	-295.091	-295.091	9.224
3500	48.273	785.439	1.032	-295.304	-295.304	-295.304	-295.304	8.994
3600	48.327	807.569	1.018	-295.528	-295.528	-295.528	-295.528	8.824
3700	48.376	829.694	1.004	-295.763	-295.763	-295.763	-295.763	8.704
3800	48.421	851.814	0.990	-296.008	-296.008	-296.008	-296.008	8.624
3900	48.462	873.929	0.977	-296.263	-296.263	-296.263	-296.263	8.574
4000	48.500	896.049	0.964	-296.528	-296.528	-296.528	-296.528	8.544
4100	48.534	918.164	0.952	-296.803	-296.803	-296.803	-296.803	8.524
4200	48.574	940.279	0.940	-297.088	-297.088	-297.088	-297.088	8.514
4300	48.610	962.394	0.928	-297.383	-297.383	-297.383	-297.383	8.514
4400	48.643	984.509	0.916	-297.688	-297.688	-297.688	-297.688	8.524
4500	48.673	1006.624	0.904	-298.003	-298.003	-298.003	-298.003	8.544
4600	48.700	1028.739	0.892	-298.328	-298.328	-298.328	-298.328	8.574
4700	48.724	1050.854	0.880	-298.663	-298.663	-298.663	-298.663	8.614
4800	48.745	1072.969	0.868	-299.008	-299.008	-299.008	-299.008	8.664
4900	48.763	1095.084	0.856	-299.363	-299.363	-299.363	-299.363	8.724
5000	48.778	1117.199	0.844	-299.728	-299.728	-299.728	-299.728	8.794
5100	48.790	1139.314	0.832	-300.103	-300.103	-300.103	-300.103	8.874
5200	48.800	1161.429	0.820	-300.488	-300.488	-300.488	-300.488	8.964
5300	48.808	1183.544	0.808	-300.883	-300.883	-300.883	-300.883	9.064
5400	48.814	1205.659	0.796	-301.288	-301.288	-301.288	-301.288	9.174
5500	48.818	1227.774	0.784	-301.703	-301.703	-301.703	-301.703	9.294
5600	48.820	1249.889	0.772	-302.128	-302.128	-302.128	-302.128	9.424
5700	48.823	1271.994	0.760	-302.563	-302.563	-302.563	-302.563	9.564
5800	48.825	1294.109	0.748	-303.008	-303.008	-303.008	-303.008	9.714
5900	48.826	1316.224	0.736	-303.463	-303.463	-303.463	-303.463	9.874
6000	48.827	1338.339	0.724	-303.928	-303.928	-303.928	-303.928	10.044

Mar. 31, 1963; Sept. 30, 1963; Mar. 31, 1965

(IDEAL GAS)

Point Group [D_{3h}]
ΔH_f⁰ = -288 ± 10 kcal. mole⁻¹
S_{298.15}⁰ = [69.7] cal. deg⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
2530 (1)	2620 (2)	303 (1)	
[920] (1)	1404 (2)	[300] (1)	
[735] (1)	1335 (2)	1115 (2)	
[1560] (1)	940 (2)	[250] (2)	
[1550] (1)	[400] (2)		

Bond Distance: B-O = [1.36] Å B-H = [1.18] Å

Bond Angle: B-O-B = [120°] O-B-H = [120°]

Product of the Moments of Inertia: I_AI_BI_C = [5.4563] X 10⁻¹¹⁴ g.³ cm.³

Heat of Formation.

The equilibrium constants (1290-1481°K.) for the reaction (1) 3/2 H₂(g) + B(am) + B₂O₃(l) = B₃O₃H₃(g) were determined by W. F. Sholette and R. F. Porter, J. Phys. Chem. 67, 177 (1963). The equilibrium pressures of B₂H₆(g) and B₃O₃H₃(g) for the reaction (2) B₃O₃H₃(g) = 1/2 B₂H₆(g) + B₂O₃(c) were measured at 300°K. by R. F. Porter and S. K. Gupta, J. Phys. Chem. 68, 280 (1964). The equilibrium constants (1246-1326°K.) for the reaction (3) 2B₂O₃PH₂(g) = B₃O₃H₃(g) + B₂O₃H₃(g) were reported by R. F. Porter and W. F. Sholette, J. Chem. Phys. 37, 188 (1962). Using these data the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Reaction	Third Law Value	Second Law Value	ΔH _f ⁰ 298.15° kcal. mole ⁻¹
(1)	-5.90	+6.52 ± 4.5	-304.0 ± 5.0
(2)**	-11.11	—	-287.6 ± 2.0
(3)	-12.21	—	-282.5 ± 2.0
	-2.0	—	-314 ± 12.0

*Calculation based on the third law values.

**The initial system for the first set of measurements was B₂H₆(g) + B(OH)₃(c).

That for the second set was B₂H₆(g) + B₂O₃(g).

The value of ΔH_f⁰ 298.15 for B₃O₃H₃(g) adopted is a weighted average of these ΔH_f⁰ 298.15 values listed.

Heat Capacity and Entropy.

The infra-red spectrum of solid boroxin has been determined by S. K. Gupta and R. F. Porter, J. Phys. Chem. 67, 1286 (1963) and a partial assignment was made. The infra-red spectra of the gas has also been reported by G. H. Lee, W. H. Bauer, and S. E. Miberley, J. Phys. Chem. 67, 1742 (1963) and is in essential agreement with the solid. The assignment of the frequencies has been changed slightly due to the non-appearance of the band at 1115 cm⁻¹ in the gas phase. The assumed D_{3h} symmetry has 14 vibrations of the type 3A₁, 2A₂, 5E₁, 2A₂, and 2E₂, the 7 estimated frequencies were obtained by comparison with B₃O₃H₃ by J. L. Parsons, J. Chem. Phys. 33, 1860 (1960).

The point group, bond angles and bond lengths were assumed to be the same as for (BOP)₃(g). The B-H bond length was taken as the sum of the single covalent radii of the atoms. The individual moments of inertia were calculated to be I_A = I_B = 13.973 X 10⁻³⁹, and I_C = 27.949 X 10⁻³⁹ g.² cm.²

B₃H₃O₃

Metaboric Acid, Trimeric ((HBO₂)₃)
(Ideal Gas) Mol. Wt. = 131.484



T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	23.148	60.120	5.440	-538.303	-538.303	INFINITE
200	23.148	71.939	4.530	-530.688	-530.688	1159.485
298	32.807	83.047	2.762	-542.105	-542.105	568.032
300	32.969	83.250	2.762	-542.105	-542.105	372.882
400	32.969	83.250	2.762	-542.105	-542.105	370.428
500	32.969	83.250	2.762	-542.105	-542.105	212.100
600	49.633	112.174	12.868	-473.601	-473.601	172.501
700	52.405	120.044	18.363	-461.951	-461.951	144.221
800	54.310	125.752	23.827	-450.326	-450.326	123.021
900	55.722	130.695	29.251	-438.727	-438.727	101.821
1000	57.522	135.695	34.627	-427.127	-427.127	80.621
1100	58.648	145.231	40.361	-415.527	-415.527	59.421
1200	59.602	150.377	46.274	-403.927	-403.927	38.221
1300	60.482	155.114	52.187	-392.327	-392.327	17.021
1400	61.303	159.650	58.056	-380.727	-380.727	5.821
1500	61.735	163.923	63.884	-369.127	-369.127	4.621
1600	62.270	167.924	69.699	-357.527	-357.527	3.421
1700	62.715	171.514	75.514	-345.927	-345.927	2.221
1800	63.159	174.736	81.329	-334.327	-334.327	1.021
1900	63.519	177.736	87.144	-322.727	-322.727	0.821
2000	63.844	180.003	92.959	-311.127	-311.127	0.621
2100	64.133	181.125	102.369	-302.285	-302.285	0.421
2200	64.392	181.115	108.772	-293.062	-293.062	0.221
2300	64.623	180.982	115.224	-283.839	-283.839	0.021
2400	64.833	180.736	121.736	-274.616	-274.616	0.001
2500	65.020	180.387	128.300	-265.393	-265.393	0.000
2600	65.190	180.941	134.913	-256.170	-256.170	0.000
2700	65.344	201.404	149.008	-246.947	-246.947	0.000
2800	65.481	203.083	161.555	-237.724	-237.724	0.000
2900	65.603	204.588	174.679	-228.501	-228.501	0.000
3000	65.728	208.310	184.679	-219.278	-219.278	0.000
3100	65.835	210.466	196.444	-210.055	-210.055	0.000
3200	65.933	212.588	208.165	-200.832	-200.832	0.000
3300	66.023	214.588	219.845	-191.609	-191.609	0.000
3400	66.108	216.478	231.476	-182.386	-182.386	0.000
3500	66.183	218.248	243.058	-173.163	-173.163	0.000
3600	66.254	220.344	254.590	-163.940	-163.940	0.000
3700	66.319	222.100	266.180	-154.717	-154.717	0.000
3800	66.379	223.654	277.820	-145.494	-145.494	0.000
3900	66.437	225.054	289.410	-136.271	-136.271	0.000
4000	66.490	227.337	301.049	-127.048	-127.048	0.000
4100	66.539	229.979	312.739	-117.825	-117.825	0.000
4200	66.585	232.583	324.480	-108.602	-108.602	0.000
4300	66.628	235.151	336.180	-99.379	-99.379	0.000
4400	66.668	237.684	347.830	-90.156	-90.156	0.000
4500	66.706	240.184	359.430	-80.933	-80.933	0.000
4600	66.742	242.648	371.000	-71.710	-71.710	0.000
4700	66.775	245.084	382.530	-62.487	-62.487	0.000
4800	66.807	247.490	394.020	-53.264	-53.264	0.000
4900	66.836	249.864	405.470	-44.041	-44.041	0.000
5000	66.864	252.218	416.880	-34.818	-34.818	0.000
5100	66.890	254.543	428.250	-25.595	-25.595	0.000
5200	66.915	256.842	439.580	-16.372	-16.372	0.000
5300	66.939	259.114	450.870	-7.149	-7.149	0.000
5400	66.961	261.368	462.120	2.074	2.074	0.000
5500	66.982	263.597	473.330	11.301	11.301	0.000
5600	67.003	265.804	484.500	20.528	20.528	0.000
5700	67.022	267.990	495.630	29.755	29.755	0.000
5800	67.039	270.154	506.720	38.982	38.982	0.000
5900	67.057	272.297	517.770	48.209	48.209	0.000
6000	67.074	274.429	528.780	57.436	57.436	0.000

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1964

METABORIC ACID, TRIMERIC ((HBO₂)₃) (IDEAL GAS)

MOL. WT. = 131.484

Point Group C_{3h}

ΔH_f⁰ = [-538 ± 3] kcal. mole⁻¹

ΔF_f⁰ 298.15 = [-543 ± 3] kcal. mole⁻¹

S° 298.15 = [83.047] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies			
ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
[550](1)	[250](1)	[600](2)	[600](2)
[1150](1)	[500](1)	[450](2)	[450](2)
[950](1)	[3500](1)	[3500](2)	[3500](2)
[3500](1)	[750](2)	[3500](2)	[3500](2)
[1100](1)	[900](2)	[200](2)	[200](2)
[1600](1)	[1300](2)	[1000](2)	[1000](2)
[500](1)	[1000](2)		

Bond Distance: B-O = [1.36] Å O-H = [1.0] Å

Bond Angle: H-O-B = [120]° O-B-O = [120]° B-O-B = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [1.7712 X 10⁻¹¹²] g.³ cm.⁶

Heat of Formation.

The equilibrium constant, K_p 1451 = 0.9, for the reaction H₃BO₃(l) + B₂O₃(l) = (HBO₂)₃(g) was reported by D. J. Meschi, W. A. Chupka and J. Berkowitz, J. Chem. Phys. 33, 530 (1960), which was determined by means of mass spectrometry. The equilibrium constants of the reactions between water vapor and liquid B₂O₃ were determined at 1147°K. by J. A. Blauer and M. Farber, J. Phys. Chem. 68, 2357 (1964), by use of a transpiration method. From the reported value, 1.5 K₂ + 0.5 K₃ = 0.0342 ± 0.0095, the equilibrium constant, K₂, for the reaction 1.5 B₂O₃(l) + 1.5 H₂O(g) = (HBO₂)₃(g) was derived as 0.0168, using K₃ = 0.0181 for the reaction 0.5 B₂O₃(l) + 1.5 H₂O(g) = H₂BO₃(g) evaluated by use of JANAF values of ΔH_f⁰ for B₂O₃(l), H₂O(g) and H₂BO₃(g). Employing the equilibrium constants obtained the respective enthalpy changes (ΔH_f⁰ 298.15) for the two reactions were calculated by the third law method. The corresponding values of ΔF_f⁰ 298.15 for (HBO₂)₃(g) were also derived. The results are presented as follows.

Investigator	Chemical Reaction	ΔH _f ⁰ 298.15 kcal. mole ⁻¹	ΔF _f ⁰ 298.15 kcal. mole ⁻¹
Meschi, et al.	H ₃ BO ₃ (l) + B ₂ O ₃ (l) = (HBO ₂) ₃ (g)	-7.31	-543.8
Blauer and Farber	1.5 B ₂ O ₃ (l) + 1.5 H ₂ O(g) = (HBO ₂) ₃ (g)	-6.67	-542.3

The adopted value of ΔH_f⁰ 298.15 for (HBO₂)₃(g) is the average of these two listed in the above table. The equilibrium constants for the same reactions between B₂O₃(l) and H₂O(g) were also determined by a transpiration method in the temperature region 1000°-1275°K. by S. F. Randall and J. L. Margrave, J. Inorg. Nucl. Chem. 16, 29 (1960). The reported value, ΔH_f⁰ 0 = -537.5 ± 3 kcal. mole⁻¹ for (HBO₂)₃(g), is in good agreement with the value adopted.

Heat Capacity and Entropy.

All the molecular and spectroscopic constants were estimated by D. White, D. E. Mann, P. N. Walsh and A. Sommer, J. Chem. Phys. 32, 468 (1960). The three principal moments of inertia are: I_A = I_B = 4.4823 X 10⁻³⁸ and I_C = 8.9247 X 10⁻³⁸ g.² cm.². The infrared absorption spectra for B₃O₃(OH)₃(c) in the 430 to 4000 cm.⁻¹ was reported by L. J. Parsons, J. Chem. Phys. 33, 1860 (1960). A partial Raman spectrum was also given.





MOL. WT. = 80.532

(IDEAL GAS)

BORAZINE (B₃N₃H₆)

Point Group D_{3h}
 $\Delta H_f^\circ 0 = -115.8 \pm 3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -121.9 \pm 3 \text{ kcal. mole}^{-1}$
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$

3450 (1)	3400 (2)
2535 (1)	2519 (2)
958 (1)	1610 (2)
851 (1)	1466 (2)
[1650](1)	917 (2)
[1110](1)	717 (2)
[900](1)	525 (2)
1098 (1)	1070 (2)
822 (1)	798 (2)
415 (1)	288 (2)

$\sigma^- = 6$

Bond Distances: B-N = 1.44 Å B-H = 1.20 Å H-N = 1.02 Å
Bond Angle: N-B-N = 120° B-N-B = 120° N-B-H = 120°
Product of Moments of Inertia: $I_{AB} I_{BC} = 8.3303 \times 10^{-14} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of combustion for the reaction $B_3N_3H_6(l) + 15/4 O_2(g) = 3 H_2BO_3(c) + 3/2 N_2(g)$ was reported to be $-552.9 \pm 3.0 \text{ kcal. mole}^{-1}$ by M. V. Kilday, W. H. Johnson and E. J. Prosen, J. Res. Natl. Bur. Std. 65A, 101 (1961). $\Delta H_f^\circ 298.15 H_2O(l) = -68.317 \text{ kcal. mole}^{-1}$ from Natl. Bur. Std. Circ. 500, "Selected Values of Chemical Thermodynamic Properties", 1952 and $\Delta H_f^\circ 298.15 H_2BO_3(c) = -261.47 \text{ kcal. mole}^{-1}$ from JANAF tables were used to calculate $\Delta H_f^\circ 298.15 B_3N_3H_6(l) = -129.0 \pm 3.0 \text{ kcal. mole}^{-1}$. Vapor pressure data on $B_3N_3H_6(l)$ reported by A. Stock and E. Fohland, Ber. 59, 2215 (1926) were fitted to a linear least squares. $\Delta C_p(1-g)$ for borazine was approximated by benzene to calculate a 2nd law $\Delta H_v 298 = 7.1 \pm 0.1 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The fundamental frequency assignment was made by B. L. Crawford, Jr. and J. T. Edsall, J. Chem. Phys. 17, 223 (1949). The three frequencies enclosed by brackets are calculated values. The moments of inertia were calculated from molecular constants given by S. H. Bauer, J. Am. Chem. Soc. 80, 524 (1958). The three principal moments of inertia are: $I_A = I_B = 16.09 \times 10^{-39}$ and $I_C = 32.18 \times 10^{-39} \text{ g. cm.}^2$.

Dec. 31, 1960; Mar. 31, 1965



(Ideal Gas) Mol. Wt. = 80.532

T, °K.	C _p ^o	S ^o - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	ΔF ^o	Log K _p
0	0.000	INFINITE	-	-115.791	-115.791	INFINITE
100	9.046	83.056	3.947	-115.791	-115.791	INFINITE
150	15.548	70.465	3.869	-120.169	-107.080	211.543
200	21.166	68.083	3.800	-121.900	-92.482	68.042
300	23.307	66.084	3.743	-121.931	-92.650	67.492
400	30.302	64.821	3.734	-123.333	-82.667	45.165
500	35.867	64.215	3.727	-124.369	-72.373	31.653
600	40.486	61.187	3.705	-125.161	-61.890	22.542
700	44.137	57.712	3.670	-125.670	-51.300	16.016
800	47.140	53.806	3.629	-125.969	-40.655	11.106
900	49.645	49.509	3.576	-126.098	-29.981	7.280
1000	51.756	44.852	3.511	-126.095	-18.300	4.218
1100	53.554	39.872	3.437	-125.999	-5.826	1.714
1200	55.089	34.596	3.353	-125.826	2.041	-3.72
1300	56.407	29.052	3.260	-125.600	12.684	-9.132
1400	57.545	23.285	3.158	-125.335	23.314	-14.546
1500	58.531	17.409	3.046	-125.035	33.921	-19.962
1600	59.389	11.415	2.924	-124.705	44.509	-25.379
1700	60.138	5.406	2.792	-124.348	55.083	-30.798
1800	60.795	-0.595	2.649	-123.966	65.631	-36.219
1900	61.374	-6.595	2.500	-123.566	76.154	-41.644
2000	61.885	-12.595	2.346	-123.151	86.652	-47.071
2100	62.338	-18.595	2.187	-122.722	97.128	-52.500
2200	62.742	-24.595	2.024	-122.280	107.589	-57.930
2300	63.102	-30.595	1.857	-121.826	118.034	-63.361
2400	63.426	-36.595	1.686	-121.351	128.465	-68.793
2500	63.716	-42.595	1.511	-120.856	138.882	-74.226
2600	63.978	-48.595	1.332	-120.341	149.287	-79.661
2700	64.215	-54.595	1.149	-119.806	159.682	-85.096
2800	64.430	-60.595	0.962	-119.251	169.967	-90.531
2900	64.623	-66.595	0.771	-118.676	180.142	-95.966
3000	64.803	-72.595	0.576	-118.081	190.207	-101.401
3100	64.966	-78.595	0.377	-117.466	200.162	-106.836
3200	65.115	-84.595	0.174	-116.831	210.007	-112.271
3300	65.252	-90.595	-0.031	-116.176	219.742	-117.706
3400	65.378	-96.595	-0.224	-115.501	229.367	-123.141
3500	65.494	-102.595	-0.411	-114.806	238.882	-128.576
3600	65.602	-108.595	-0.592	-114.091	248.287	-134.011
3700	65.701	-114.595	-0.767	-113.356	257.582	-139.446
3800	65.793	-120.595	-0.936	-112.601	266.767	-144.881
3900	65.878	-126.595	-1.100	-111.826	275.842	-150.316
4000	65.958	-132.595	-1.259	-111.031	284.807	-155.751
4100	66.033	-138.595	-1.413	-110.216	293.662	-161.186
4200	66.102	-144.595	-1.562	-109.381	302.407	-166.621
4300	66.167	-150.595	-1.706	-108.526	311.042	-172.056
4400	66.227	-156.595	-1.845	-107.651	319.567	-177.491
4500	66.284	-162.595	-1.979	-106.756	327.982	-182.926
4600	66.337	-168.595	-2.108	-105.841	336.287	-188.361
4700	66.387	-174.595	-2.232	-104.906	344.482	-193.796
4800	66.434	-180.595	-2.351	-103.951	352.567	-199.231
4900	66.478	-186.595	-2.465	-102.976	360.542	-204.666
5000	66.521	-192.595	-2.574	-101.981	368.407	-210.101
5100	66.560	-198.595	-2.678	-100.966	376.162	-215.536
5200	66.597	-204.595	-2.777	-99.931	383.807	-220.971
5300	66.633	-210.595	-2.871	-98.876	391.342	-226.406
5400	66.666	-216.595	-2.960	-97.801	398.767	-231.841
5500	66.698	-222.595	-3.044	-96.706	406.082	-237.276
5600	66.728	-228.595	-3.123	-95.591	413.287	-242.711
5700	66.756	-234.595	-3.197	-94.456	420.382	-248.146
5800	66.782	-240.595	-3.266	-93.301	427.367	-253.581
5900	66.809	-246.595	-3.330	-92.126	434.242	-259.016
6000	66.834	-252.595	-3.389	-90.931	441.007	-264.451

Dipotassium Tetraborate ($K_2B_4O_7$)

(Crystal) Mol. Wt. = 233.44

$B_4K_2O_7$

MOL. WT. = 233.44

DIPOTASSIUM TETRABORATE ($K_2B_4O_7$)

(CRYSTAL)

$\Delta H_f^\circ =$ Unknown

$\Delta H_f^\circ 298.15 = -796.9 \text{ kcal. mole}^{-1}$

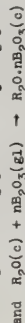
$\Delta H_m^\circ = 24.9 \pm 1 \text{ kcal. mole}^{-1}$

$S^\circ_{298.15} = [49.8 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 1088^\circ K.$

Heat of Formation.

$\Delta H_f^\circ 298.15$ was recalculated from the experimental data of L. Sharts and W. Capps, J. Am. Ceram. Soc. **37**, 27-32 (1954). They studied the heat of solution of various alkali borates in 2N nitric acid. Average molecular weights were used for physical mixtures of the oxides B_2O_3 and R_2O (where R is either Li, Na, or K) rather than for the borate compounds $R_2O \cdot nB_2O_3$ present. These incorrect molecular weights led to spurious correlations and faulty conclusions. In reinterpreting the data, the steps followed were: (1) The calculation of the correct molecular weights and molar heats of reaction; (2) The establishment that the heat of formation of the borates from the oxides is linear with the mole fraction of B_2O_3 in the total original moles of oxides for the reactions



with the heat of formation being zero at 100 percent R_2O ; (3) The evaluation of the least square fit of the line through the heat of reaction data for reaction I and for reaction II; (4) The use of the proper weighting factors in applying least squares to adjust for both the sample size and the molecular weight of the mixture of borates used in each solution experiment.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mc. 59-2916, in the range 298-973°K were smoothed graphically and were used to obtain a smooth set of C_p data. The heat capacity was extrapolated smoothly above this region. The entropy at 298°K was estimated from that of $Na_2B_4O_7(c)$ by using an average entropy change of $4.5 \pm 1.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ on substituting Na by K.

Melting Data.

T_m was given by A. F. Rollet, Comp. Rend. **200**, 1763 (1955). The heat of melting was obtained from the heats of formation of the crystal and glass at 298°K combined with the enthalpy differences between 298 and 1088°K. This involves a slight extrapolation of the crystal data and an uncertainty of about $1.0 \text{ kcal. mole}^{-1}$.

T. °K.	C_p°	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔF_f°	Log K _P
0							
100	40.750	49.800	49.800	0.000	-796.900	-749.734	549.543
200							
298							
300	40.950	50.053	49.801	-0.076	-796.916	-749.440	549.940
400	49.300	63.092	51.522	4.628	-798.828	-733.276	400.624
500	55.640	74.813	55.028	9.893	-799.288	-716.829	313.311
600	59.880	85.364	59.221	15.686	-799.485	-700.314	255.077
700	62.800	94.917	63.643	24.562	-799.500	-682.739	204.444
800	64.800	103.517	67.243	36.763	-799.621	-650.688	156.001
900	66.300	111.059	72.434	51.664	-799.664	-634.137	136.584
1000	67.700	118.118	76.654				
1100	68.901	124.629	80.723	48.296	-837.935	-615.933	122.289
1200	69.706	130.599	84.637	62.520	-837.918	-575.240	106.703
1300	70.400	136.050	88.370	76.526	-835.320	-555.140	86.657
1400	71.318	141.560	92.008	90.373	-835.945	-535.068	77.956
1500	71.720	146.495	95.478				
1600	72.279	151.142	98.813	83.727	-835.588	-515.023	70.346
1700	72.775	155.709	102.022	100.275	-835.584	-479.984	57.653
1800	73.210	160.100	105.077	112.966	-834.574	-455.011	52.336
1900	73.467	163.673	108.000				
2000	73.700	167.448	110.965		-834.265	-435.043	47.537

$B_4K_2O_7$

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _F
0						
100						
200						
298						
300	40.750	56.700	0.000	-786.100	-740.991	543.135
400	40.950	56.701	0.076	-786.116	-740.710	530.581
500	49.300	69.992	56.422	-786.026	-728.236	396.232
600	55.650	81.715	61.928	-786.487	-709.479	310.008
700	59.880	92.267	66.121	-788.483	-693.454	252.651
800	64.200	101.840	75.354	-788.327	-672.818	211.114
900	66.200	115.041	79.350	-788.253	-662.257	180.912
1000	101.880	126.708	80.418	-781.923	-647.074	157.124
1100	104.730	137.700	85.602	-778.230	-632.284	136.179
1200	109.706	149.048	90.812	-772.349	-615.831	122.349
1300	115.180	166.810	101.087	-762.745	-599.190	108.940
1400	117.512	175.433	106.093	-757.817	-580.938	97.660
1500	119.600	183.613	110.990	-752.737	-564.059	88.049
1600	121.444	191.392	115.774	-747.537	-547.536	79.772
1700	123.048	198.894	120.442	-742.199	-531.361	72.577
1800	124.408	205.876	124.993	-736.780	-515.513	66.271
1900	125.526	212.634	129.430	-731.293	-499.981	60.703
2000	126.400	219.096	133.752	-725.745	-484.755	55.757
2100	127.196	225.282	137.965	-720.164	-469.818	51.337
2200	127.924	231.216	142.069	-714.554	-455.157	47.364
2300	128.584	236.918	146.070	-708.912	-440.760	43.783
2400	129.176	242.403	149.970	-703.240	-426.629	40.537
2500	129.700	247.687	153.774	-697.544	-411.935	37.510
2600	130.156	252.783	157.485	-691.808	-397.689	34.747
2700	130.544	257.703	161.106	-686.044	-383.253	32.214
2800	130.864	262.456	164.641	-680.254	-369.248	29.887
2900	131.116	267.053	168.084	-674.448	-355.448	27.743
3000	131.300	271.501	171.467	-668.622	-341.850	25.761
				-662.782	-328.447	23.926

$S_{298.15}^o = [56.7 \pm 2.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o 298.15 = -786.1 \text{ kcal. mole}^{-1}$
 $\Delta H_m = 24.9 \pm 1 \text{ kcal. mole}^{-1}$
 $T_m = 1088^\circ \text{K.}$

Heat of Formation.

The heat of formation was obtained from reaction (1) given on the crystal table.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2918 in the range 298 to 1373°K on the glass and liquid were smoothed graphically and used to determine C_p . There is a discontinuity (glass transition) in the C_p curve at 678°K. Above 1373°K the C_p values were extrapolated smoothly.

The entropy at 298°K was obtained from that of the crystal by adding ΔS_m^o and the difference between S_{1088}^o and S_{298}^o for crystal and liquid.

Melting Data.

See the crystal table.

Dilithium Tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$)
(Crystal) Mol. Wt. = 169.1178

T, °K	C _p	$\int_{298}^T C_p dT$ cal. mole ⁻¹ deg ⁻¹	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$ kcal. mole ⁻¹	ΔH_f°	ΔF_f°	Log K _p
0							
100							
200							
298							
400	43.750	37.200	37.200	0.000	-803.600	-757.734	555.408
500	43.761	37.471	37.471	0.081	-803.507	-757.452	551.777
600	47.239	50.492	38.053	4.616	-804.090	-741.998	405.390
700	52.567	61.610	42.194	9.600	-806.144	-726.257	317.431
800	57.625	71.653	46.446	15.124	-806.597	-710.231	258.689
900	61.950	80.869	50.715	21.108	-806.800	-694.151	216.713
1000	65.586	89.384	55.023	27.489	-806.776	-678.063	185.229
1100	68.766	97.294	59.285	34.208	-806.552	-661.985	160.744
1200	71.803	104.695	63.460	41.234	-806.140	-645.937	141.163
1300	75.052	111.691	67.529	48.578	-805.525	-629.948	125.153
1400	78.198	118.357	71.489	56.240	-805.665	-614.021	111.623
1500	81.344	124.740	75.342	64.218	-805.613	-598.176	100.558
1600	84.490	130.883	79.091	72.509	-802.303	-582.417	90.915
1700	87.636	136.820	82.743	81.116	-800.755	-566.770	82.574
1800	90.782	142.576	86.303	90.036	-798.958	-551.222	75.290
1900	93.928	148.174	89.779	99.272	-787.004	-533.145	68.537
2000	97.074	153.632	93.175	108.822	-764.339	-513.581	62.354
2100	100.220	158.965	96.498	118.687	-741.413	-494.172	56.840
2200	103.366	164.195	99.752	128.866	-718.215	-474.927	51.895



MOL. WT. = 169.1178

(CRYSTAL)

DILITHIUM TETRABORATE ($\text{Li}_2\text{B}_4\text{O}_7$)

$\Delta H_f^\circ 0$ = Unknown

$\Delta H_f^\circ 298.15 = -803.6 \pm 1.5$ kcal. mole⁻¹

$\Delta H_m^\circ = 28.6 \pm 1.5$ kcal. mole⁻¹

$S_{298.15}^\circ = [37.2 \pm 1.0]$ cal. deg⁻¹ mole⁻¹

$T_m = 1190 \pm 2^\circ\text{K}$.

Heat of Formation.

The heat of formation was calculated from $\Delta H_f^\circ 298 = -12.2$ kcal. for the reaction $\text{Li}_2\text{B}_4\text{O}_7(\text{c}) + 2\text{HNO}_3(\text{aq.}) + 5\text{H}_2\text{O}(\text{l.}) = 4\text{H}_3\text{BO}_3(\text{aq.}) + 2\text{LiNO}_3(\text{aq.})$. The heat of solution (ΔH_s°) was interpolated from the heat of solution data of L. Shartels and W. Ceppe, J. Am. Ceram. Soc. 37, 27 (1954). Auxiliary data are from National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1190°K. were smoothed graphically and used to determine C_p . A linear extrapolation of C_p was used from 1190 to 2000°K.

S_{298}° was estimated by three routes: (1) $S_{298}^\circ (\text{Li}_2\text{B}_4\text{O}_7) = 37.3$ cal. mole⁻¹ deg⁻¹ based on JANAF S_{298}° ($\text{Na}_2\text{B}_4\text{O}_7$) = 45.3 and $\Delta S_{298}^\circ (2\text{Na} - 2\text{Li}) = 8$ cal. deg⁻¹ from W. M. Latimer, J. Am. Chem. Soc. 73, 1480 (1951); (2) $S_{298}^\circ (\text{Li}_2\text{B}_4\text{O}_7) = 36.7$ cal. mole⁻¹ deg⁻¹ in a similar manner based on $\Delta S_{298}^\circ (2\text{Na} - 2\text{Li}) = 8.6$ cal. deg⁻¹ from K. K. Kelley, Bureau of Mines, private communication, June 1960; and (3) $S_{298}^\circ (\text{Li}_2\text{B}_4\text{O}_7) = 37.6$ cal. mole⁻¹ deg⁻¹ based on addition of the JANAF entropies for 2LiBO_2 and B_2O_3 . The value adopted is an average of these estimates.

Melting Data.

The value for T_m is from B. S. R. Sastry and F. A. Hummel, J. Am. Chem. Soc. 42, 216 (1959). A. P. Rollet and R. Bousziz, Compt. rend. 240, 2417 (1955) earlier reported $T_m = 1188^\circ\text{K}$. $\Delta H_m^\circ = 28.6$ kcal. mole⁻¹ is from G. S. Smith loc. cit.



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
100	43.295	41.564	•000	- 748.226	- 748.438	548.438
200	43.400	41.832	41.565	- 747.797	- 747.951	548.456
300	43.400	42.001	41.565	- 747.797	- 747.951	548.456
400	43.400	42.169	41.565	- 747.797	- 747.951	548.456
500	43.400	42.338	41.565	- 747.797	- 747.951	548.456
600	43.400	42.507	41.565	- 747.797	- 747.951	548.456
700	43.400	42.676	41.565	- 747.797	- 747.951	548.456
800	43.400	42.845	41.565	- 747.797	- 747.951	548.456
900	43.400	43.014	41.565	- 747.797	- 747.951	548.456
1000	43.400	43.183	41.565	- 747.797	- 747.951	548.456
1100	43.400	43.352	41.565	- 747.797	- 747.951	548.456
1200	43.400	43.521	41.565	- 747.797	- 747.951	548.456
1300	43.400	43.690	41.565	- 747.797	- 747.951	548.456
1400	43.400	43.859	41.565	- 747.797	- 747.951	548.456
1500	43.400	44.028	41.565	- 747.797	- 747.951	548.456
1600	43.400	44.197	41.565	- 747.797	- 747.951	548.456
1700	43.400	44.366	41.565	- 747.797	- 747.951	548.456
1800	43.400	44.535	41.565	- 747.797	- 747.951	548.456
1900	43.400	44.704	41.565	- 747.797	- 747.951	548.456
2000	43.400	44.873	41.565	- 747.797	- 747.951	548.456
2100	43.400	45.042	41.565	- 747.797	- 747.951	548.456
2200	43.400	45.211	41.565	- 747.797	- 747.951	548.456
2300	43.400	45.380	41.565	- 747.797	- 747.951	548.456
2400	43.400	45.549	41.565	- 747.797	- 747.951	548.456
2500	43.400	45.718	41.565	- 747.797	- 747.951	548.456
2600	43.400	45.887	41.565	- 747.797	- 747.951	548.456
2700	43.400	46.056	41.565	- 747.797	- 747.951	548.456
2800	43.400	46.225	41.565	- 747.797	- 747.951	548.456
2900	43.400	46.394	41.565	- 747.797	- 747.951	548.456
3000	43.400	46.563	41.565	- 747.797	- 747.951	548.456

DILITHIUM TETRABORATE (Li₂B₄O₇) (LIQUID)

MOL. WT. = 169.1178

$S_{298.15}^o = [41.564 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^o 298.15 = -792.79 \pm 1.5 \text{ kcal. mole}^{-1}$

$\Delta F_f^o 298.15 = -792.79 \pm 1.5 \text{ kcal. mole}^{-1}$

$T_m = 1190 \pm 2^\circ\text{K.}$

Heat of Formation.

$\Delta H_f^o 298.15(1)$ was calculated from $\Delta H_f^o 298.15(c)$ by adding ΔH_m^o and the difference between H_m^o and H_l^o for crystal and liquid.

$\Delta H_m^o = 26.3 \pm 1.5 \text{ kcal. mole}^{-1}$

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph. D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. M10 59-2916 in the range 298 to 1373°K. were smoothed graphically and used to determine C_p . The C_p data have a discontinuity at about 756°K. A linear extrapolation of C_p was used from 1373 to 3000°K.

The entropy at 298°K. is set so that ΔF is equal at T_m for the crystal and liquid.

Melting Data.

See crystal table for details.

Magnesium Tetraboride (MgB_4)
(Crystal) Mol. Wt. = 67.60

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	$-(F^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	ΔH°_f	ΔF°_f	Log K _p
0	•000	•000	INFINITE	- 2.275	- 25.011	- 25.011	INFINITE
100	4.120	1.920	23.300	- 2.138	- 25.052	- 24.984	54.601
200	11.060	6.860	13.775	- 1.383	- 25.179	- 24.974	27.289
298	16.810	12.410	12.410	•000	- 25.100	- 24.797	18.176
300	16.900	12.514	12.410	•031	- 25.100	- 24.796	18.063
400	19.000	17.671	13.099	1.829	- 25.204	- 24.685	13.487
500	20.800	22.104	14.487	3.820	- 25.507	- 24.523	10.718
600	22.500	26.054	16.075	5.987	- 25.909	- 24.290	9.847
700	24.000	29.520	17.885	8.255	- 26.311	- 23.817	9.182
800	25.270	32.607	19.850	10.766	- 26.792	- 23.417	8.682
900	26.540	35.959	21.117	13.357	- 27.226	- 23.166	8.293
1000	27.660	38.814	22.745	16.069	- 27.773	- 22.840	7.926
1100	28.610	41.296	24.382	18.894	- 28.177	- 22.602	7.631
1200	29.430	43.450	26.020	21.836	- 28.586	- 22.360	7.397
1300	30.144	45.407	27.595	24.767	- 28.986	- 22.109	7.182
1400	30.800	47.165	28.768	27.814	- 29.382	- 21.882	6.987
1500	31.450	48.665	30.194	30.928	- 29.797	- 21.624	6.805
1600	32.000	50.000	31.567	34.101	- 30.213	- 21.355	6.635
1700	32.500	51.164	32.859	37.321	- 30.630	- 21.069	6.476
1800	32.900	52.176	34.081	40.581	- 31.044	- 20.768	6.326
1900	33.200	53.040	35.245	43.881	- 31.454	- 20.455	6.182
2000	33.600	53.773	36.363	47.221	- 31.848	- 20.123	6.053

MAGNESIUM TETRABORIDE (MgB_4)
(CRYSTAL)

MOL. WT. = 67.60

$$\Delta H^\circ_f 0 = -25.0 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$\Delta H^\circ_f 298.15 = -25.1 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 12.41 \pm 0.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = [1100]^\circ\text{K.}$$

Heat of Formation.

The equilibrium pressures (1169-1177°K.) of the reaction $\text{MgB}_4(\text{c}) \rightarrow \text{Mg}(\text{g}) + 4\text{B}(\text{c})$ were measured by M. Wright and F. N. Walsh, "The Vaporization of $\text{MgB}_4(\text{c})$ ", Technical Research Report OMCC-HEP-55, Jan. 9, 1958, Ohio State University Research Foundation. The third law value of $\Delta H^\circ_f 298.15$ for this reaction was derived as 60.40 ± 1.5 kcal. mole⁻¹. This leads to a $\Delta H^\circ_f 298.15 = -25.1 \pm 2.0$ kcal. mole⁻¹ for $\text{MgB}_4(\text{c})$. The unit of equilibrium pressures reported should be in atmosphere not in mm Hg as printed. The diameter of the hole drilled through the center of the lid served as the effusion orifice should be 1/16 inch rather than the reported value 1/8 inch.

Heat Capacity and Entropy.

The low temperature (17.34-299.53°K.) heat capacities were measured by R. M. Swift and D. White, J. Am. Chem. Soc. 79, 3641 (1957). Above 298.15°K. the C_p values were estimated by comparison with those of other related borides. $S^\circ_{298.15}$ was reported by R. M. Swift and D. White, loc. cit., using $S^\circ_{20}(\text{extrap.}) = 0.022 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Decomposition.

T_d was estimated from the decomposition reaction reported by M. Wright and F. N. Walsh, loc. cit.

B_4Mg

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	18.290	12.145	76.954	-778.909	-778.909	INFINITE
200	33.400	20.772	48.027	-781.288	-766.799	1678.756
298	44.640	28.289	34.851	-782.532	-751.763	821.440
300	44.801	28.566	34.580	-783.160	-736.520	539.857
400	51.100	35.383	26.201	-783.167	-736.230	536.316
500	54.621	41.172	20.791	-783.216	-736.284	307.827
600	57.720	46.111	15.811	-785.580	-688.061	250.614
700	60.396	50.215	11.720	-785.870	-671.785	200.731
800	62.822	53.680	8.260	-786.058	-655.471	170.059
900	64.822	56.536	5.404	-786.160	-639.121	146.646
1000	66.850	58.917	3.023	-786.228	-622.794	136.105
1100	68.734	60.831	1.063	-786.192	-606.459	120.466
1200	70.474	62.387	-0.808	-832.554	-569.205	107.304
1300	72.077	63.687	-2.512	-832.554	-532.854	94.656
1400	73.522	64.787	-4.112	-831.290	-506.744	82.555
1500	74.830	65.692	-5.609	-830.552	-480.754	71.012
1600	76.085	66.474	-7.006	-829.742	-454.883	60.452
1700	77.295	67.155	-8.303	-828.754	-429.134	50.769
1800	78.453	67.755	-9.507	-827.684	-403.503	41.917
1900	79.567	68.282	-10.622	-826.682	-377.983	33.857
2000	80.640	68.747	-11.652	-825.421	-352.563	26.537

$\Delta H_f^o = -778.91 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o 298.15 = -783.16 \pm 2.0 \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = 19.4 \pm 1.5 \text{ kcal. mole}^{-1}$
 $T_m = 1015.6^\circ\text{K}$

$S_{298.15}^o = 45.269 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1015.6^\circ\text{K}$

Heat of Formation.

The heat of the reaction $\text{Na}_2\text{O}(c) + 2\text{B}_2\text{O}_3(l) \rightarrow \text{Na}_2\text{B}_4\text{O}_7(c)$ was reported by L. Shartais and W. Capps, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAP values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and for $\text{Na}_2\text{O}(c)$ (June 30, 1962). The above $\Delta H_f^o = -85.2 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

In the low temperature region (5-344°K) the C_p values are those determined by E. P. Westrum, Jr., and G. Grenier, J. Am. Chem. Soc. 79, 1799 (1957). The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1015.6°K were smoothed graphically and used to determine C_p ; the values did not join smoothly with those of Westrum and Grenier and the low temperature values were given greater weight. Above T_m the heat capacity was extrapolated. $S_{298.15}^o$ was derived from low temperature heat capacities.

Melting.

The value for T_m is from G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. 59, 2248 (1936). Other reported values for T_m are: $1008 \pm 5^\circ\text{K}$ by S. S. Coles, S. R. Scholes, and C. R. Amberg, J. Am. Ceram. Soc. 19, 58 (1935); 1011°K by H. Menzel, Z. anorg. Chem., 224, 1 (1935); 1005°K by J. P. Ponomareff, Z. anorg. Chem. 89, 383 (1924); 1015°K by A. L. Day and E. T. Allen, "The Isomorphism and Thermal Properties of the Feldspars", Carnegie Inst. of Washington, Publ. No. 31 (1905) p. 23; and 1064°K by C. H. Burgess and A. Holt, Proc. Roy. Soc. (London) 74, 285 (1904). ΔH_m^o was obtained from the values of ΔH_f^o for $\text{Na}_2\text{B}_4\text{O}_7(c)$ and $\text{Na}_2\text{B}_4\text{O}_7(l)$ at 298°K as described above and the difference between $H_{1015-H_{298}}$ for crystal and liquid.

Disodium Tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$)
(Liquid) Mol. Wt. = 201.262

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K_p
0							
100							
200							
298	44.800	47.513	47.513	0.000	-778.360	-732.383	536.825
300	44.967	47.791	47.614	+083	-778.366	-732.098	539.307
400	53.000	61.873	49.379	4.497	-776.917	-716.527	391.473
500	59.100	74.374	53.152	10.611	-779.996	-700.664	306.245
600	64.200	85.601	57.640	16.777	-779.814	-684.609	249.430
700	69.200	95.874	62.378	23.447	-779.343	-669.009	208.864
800	106.330	107.921	67.260	32.529	-776.624	-653.374	178.485
900	106.330	120.445	72.467	43.162	-772.484	-638.217	154.973
1000	106.330	131.648	77.853	55.795	-768.465	-623.509	136.261
1100	106.330	141.783	83.212	69.428	-764.577	-609.211	121.033
1200	106.330	151.035	88.484	84.061	-760.768	-594.337	108.238
1300	106.330	159.545	93.627	98.694	-757.037	-579.894	96.957
1400	106.330	167.425	98.620	113.327	-753.474	-565.894	87.337
1500	106.330	174.761	103.455	127.960	-750.069	-552.420	79.041
1600	106.330	181.624	108.128	142.593	-746.795	-539.573	71.817
1700	106.330	188.070	112.643	157.226	-743.649	-527.319	65.474
1800	106.330	194.148	117.004	171.859	-740.622	-515.647	59.864
1900	106.330	199.897	121.217	186.492	-737.713	-504.647	54.867
2000	106.330	205.351	125.288	201.125	-734.920	-494.299	50.391
2100	106.330	210.538	129.225	215.758	-732.235	-484.609	46.460
2200	106.330	215.485	133.034	230.391	-729.659	-475.588	42.713
2300	106.330	220.212	136.723	245.024	-727.184	-467.129	39.199
2400	106.330	224.737	140.296	259.657	-724.813	-458.323	35.873
2500	106.330	229.077	143.761	274.290	-722.538	-449.073	32.706
2600	106.330	233.248	147.124	288.923	-720.359	-440.378	29.688
2700	106.330	237.261	150.380	303.556	-718.276	-432.228	26.835
2800	106.330	241.128	153.560	318.189	-716.289	-424.633	24.128
2900	106.330	244.859	156.644	332.822	-714.398	-417.598	21.568
3000	106.330	248.464	159.645	347.455	-712.603	-411.023	19.058

$\text{B}_4\text{Na}_{207}$
MOL. WT. = 201.262

DISODIUM TETRABORATE ($\text{Na}_2\text{B}_4\text{O}_7$) (LIQUID)

$S_{298.15}^\circ = 47.513 \pm 1.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = 19.4 \pm 1.5 \text{ kcal. mole}^{-1}$
 $T_m = 1015.6^\circ\text{K.}$

Heat of Formation.

The heat of reaction $\text{Na}_2\text{O}(c) + 2\text{B}_2\text{O}_3(l) \rightarrow \text{Na}_2\text{B}_4\text{O}_7(l)$ was reported by L. Shartsis and W. Cappe, J. Am. Ceram. Soc. 57, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and for $\text{Na}_2\text{O}(c)$ (June 30, 1962). The above $\Delta H_f^\circ = -80.4 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916, in the range 298 to 1373°K, were smoothed graphically and used to determine C_p . These were joined smoothly with the low temperature data of E. P. Westrum and G. Grenier, J. Am. Chem. Soc. 79, 1799 (1957). At 743°K a glass transition was observed and above this temperature the C_p adopted as constant.

The entropy at 298°K obtained from that of the crystal by adding ΔS_m° and the difference between S_{1015}° and S_{298}° for crystal and liquid.

Melting.

See the crystal for details.

$\text{B}_4\text{Na}_{207}$

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° cal. mole ⁻¹ deg. ⁻¹	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0							
100							
200							
298	40.200	39.900	39.900	+0.00	-683.000	-637.470	467.255
300	40.400	39.001	39.001	+0.75	-683.003	-637.188	466.169
400	47.800	41.000	41.000	+4.00	-683.003	-637.188	464.582
500	57.020	45.089	45.089	+9.902	-682.487	-606.706	265.176
600	63.470	75.875	49.112	15.948	-681.684	-591.616	215.486
700	68.630	86.060	53.644	22.551	-681.728	-576.499	179.982
800	72.780	93.504	58.468	39.659	-680.344	-561.561	153.404
900	76.000	100.000	64.000	56.000	-678.000	-546.000	127.000
1000	78.880	112.436	67.009	44.827	-676.913	-532.241	116.316
1100	81.140	120.064	72.035	52.832	-674.960	-517.873	102.687
1200	82.940	127.205	76.338	61.040	-672.687	-503.679	91.728
1300	84.290	133.187	80.511	69.782	-670.746	-489.666	82.316
1400	85.200	138.000	84.459	77.802	-668.456	-475.868	73.680
1500	86.180	142.096	88.459	86.456	-666.366	-462.131	67.529
1600	86.860	151.680	92.237	95.109	-664.162	-448.583	61.271
1700	87.400	156.963	95.691	103.823	-661.964	-435.176	55.943
1800	87.800	161.770	99.000	112.584	-659.788	-421.901	51.223
1900	88.120	166.000	102.000	121.000	-657.600	-408.000	46.500
2000	88.370	171.253	104.150	130.206	-655.497	-395.701	43.238

Heat of Formation.

See lead diborate table for the complete writeup. W. H. Evans in NBS Report 7192, July 1, 1961, analyzed the heats of formation of the lead borate system based upon Shartsis and Newman's heats of solution and Mazzetti and DeCarli's phase studies. From the Shartsis and Newman paper Evans obtained the following:



and estimated a ΔH_{298}° of 11.4 kcal. mole⁻¹ for the conversion to the $\text{PbO} \cdot 2\text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the ΔH_f° 298.15 was calculated to be -683.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. O. King, Bureau of Mines Bull. 592 (1961). These indicate for the reaction:



that the simple addition of entropies will give values at least 2.7 e.u. in the case of Na borates and 5.7 e.u. for Ca borates too high for the reaction. The reason for this is probably structural, the $\text{B}_4\text{O}_7^{--}$ ion is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the average entropy difference of 4.2 for the reaction was assumed to hold for each additional mole of B_2O_3 . Therefore the entropy at 298.15 was obtained from $S_{298.15}^\circ$ for PbB_2O_4 and B_2O_3 and the subtraction of 4.2 e.u.

Pentaborane (B₅H₉)

(Liquid) Mol. Wt. = 63.172

T, °K.	C _p ^a	S° ^b	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^c	ΔF _f ^c	Log K _p
100							
200							
298	36.120	44.056	44.056	0.000	10.240	41.067	-30.102
300	36.200	44.280	44.057	0.067	10.224	41.057	-30.084
400	38.200	46.280	46.067	2.067	8.157	41.110	-28.552
500	40.200	48.280	48.081	4.081	6.203	41.328	-27.242
600	50.200	74.520	52.276	13.346	8.034	73.110	-26.620
700	58.400	82.942	56.056	18.820	7.769	83.980	-26.221
800	61.300	90.494	59.923	24.809	7.656	104.570	-25.916
900	63.500	97.277	63.790	31.277	7.584	125.160	-25.611
1000	65.800	103.139	67.582	37.557	7.514	145.750	-25.475
1100	66.987	111.468	71.288	44.108	7.468	166.340	-25.304
1200	68.000	117.341	74.884	50.949	7.421	186.930	-25.157
1300	68.840	122.618	78.363	57.792	7.375	207.520	-25.010
1400	69.500	127.395	81.741	64.635	7.330	228.110	-24.863
1500	70.000	132.759	84.967	71.468	7.282	248.700	-24.808



MOL. WT. = 63.172

(LIQUID)

PENTABORANE (B₅H₉)

$$\Delta H_f^{298.15} = 10.240 \pm 1.6 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 1.466 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = 6.79 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{\circ} = 44.056$$

$$T_m = 226.3^{\circ}\text{K.}$$

$$T_b = 335^{\circ}\text{K.}$$

Heat of Formation.

The vapor pressures of B₅H₉(l) were measured by H. E. Wirth and E. D. Palmer, J. Phys. Chem. 60, 914 (1956) and H. L. Johnston, E. C. Kerr, J. T. Clarke and N. C. Hallett, "Calorimetric Investigation with the Condensed Gas Calorimeter. IV. The Heat Capacities, Latent Heats and Entropies of Pentaborane from 15 to 298°K.; Heats of Transition, Fusion and Vaporization; Vapor Pressures of the Liquid", TR-6, July 8, 1949, The Ohio State University. By use of both the second and third law methods, the respective heats of vaporization (ΔH_v^{298.15}) were evaluated. The ΔH_f^{298.15} values for B₅H₉(l) were calculated from ΔH_f^{298.15} for B₅H₉(g) and ΔH_v^{298.15} for B₅H₉(l) obtained previously. The results are presented as follows.

Investigator	ΔH _f ^{298.15} , kcal. mole ⁻¹		ΔH _f ^{298.15} , kcal. mole ⁻¹
	Second Law Value	Third Law Value	
Wirth and Palmer	7.26 ± 0.02	7.26	10.24 ± 1.6
Johnston, et al.	7.23 ± 0.04	7.25	10.23 ± 1.6

*Calculation based on the third law ΔH_f^{298.15} values.

The adopted value is the average of the two ΔH_f^{298.15} values obtained.

Heat Capacity and Entropy.

The heat capacities (C_p), 231.34 - 230.19°K., for B₅H₉(l) were measured by Johnston, Kerr, Clarke and Hallett, loc. cit. The C_p values above 230.19°K. were estimated by graphical extrapolation of the C_p curve plotted using the experimental data. The value of S_{298.15}^o was derived based on the low temperature C_p, 13.29 - 221.61°K., and ΔH_m^o for B₅H₉(c) reported by Johnston, Kerr, Clarke and Hallett, loc. cit. and C_p values, 226.34 - 238.15°K., for B₅H₉(l), using S_{13.29}^o = 0.236 cal. deg.⁻¹ mole⁻¹ for B₅H₉(c).

Melting Data.

The values of T_m and ΔH_m^o were taken from Johnston, Kerr, Clarke and Hallett, loc. cit.

Vaporization Data.

The boiling point (T_b) is calculated as the temperature at which the free energy change of the reaction B₅H₉(l) → B₅H₉(g) becomes zero. The enthalpy change of the reaction at T_b is heat of vaporization (ΔH_v^o).

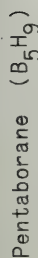




MOL. WT. = 63.172

(IDEAL GAS)

PENTABORANE (B_5H_9)



Mol. Wt. = 63.172

(Ideal Gas)

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	24.444	24.444	INFINITE
100	8.289	51.631	79.877	2.758	21.796	21.796	- 80.425
200	18.289	51.631	79.877	2.758	19.040	19.040	- 15.426
300	22.423	65.803	65.803	1.602	17.433	17.433	- 30.671
400	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
500	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
600	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
700	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
800	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
900	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1000	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1100	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1200	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1300	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1400	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1500	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1600	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1700	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1800	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
1900	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2000	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2100	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2200	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2300	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2400	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2500	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2600	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2700	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2800	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
2900	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3000	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3100	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3200	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3300	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3400	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3500	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3600	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3700	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3800	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
3900	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4000	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4100	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4200	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4300	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4400	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4500	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4600	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4700	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4800	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
4900	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5000	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5100	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5200	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5300	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5400	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5500	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5600	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5700	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5800	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
5900	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590
6000	22.588	65.941	65.941	1.602	17.458	17.458	- 30.590

Dec. 31, 1960; Mar. 31, 1965

Point Group C_{4v}

$\Delta H_f^o = 24.4 \pm 1.6$ kcal. mole⁻¹
 $\Delta H_f^o = 85.803$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^o = 298.15 = 17.5 \pm 1.6$ kcal. mole⁻¹

S_{298.15} = 65.803 cal. deg.⁻¹ mole⁻¹
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
2600 (1)	[1450](1)	[1500](1)	1449 (2)
2600 (1)	[500](1)	[1100](1)	1034 (2)
1844 (1)	1870 (1)	738 (1)	882 (2)
1413 (1)	1387 (1)	470 (1)	700 (2)
1126 (1)	[900](1)	2598 (2)	605 (2)
985 (1)	782 (1)	1802 (2)	568 (2)
799 (1)	2600 (1)	1621 (2)	

Bond Distance: B-B = 1.800 ± 0.003 Å B-B_{apex} = 1.687 ± 0.005 Å
 B-H = B_{apex}-H = 1.22 Å B-H_{bridge} = 1.35 ± 0.02 Å

Bond Angle: B_{apex}-B-H = 136° 10' ± 30' H-B_{apex}-B = 131° Å
 B-H_{bridge}-B = 83° 37' B-B-B = 90°

Angle between B_{apex}-B plane and B-H_{bridge} plane = 196 ± 2°
 Product of the Moments of Inertia: I_AI_BI_C = 2.3693 × 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

The enthalpy change (ΔH_f^o) of the reaction $B_5H_9(g) \rightarrow 5B(am.) + 9/2 H_2(g)$ was reported to be -12.99 ± 0.39 and -9.9 ± 1 kcal. mole⁻¹ by E. J. Prosen, W. H. Johnson and P. Y. Pergiel, J. Res. Natl. Bur. Std. 61, 247 (1958) and S. R. Dunn and L. O. Green, J. Phys. Chem. 65, 2173 (1961), respectively. Using ΔH_f^o 298.15 = 1.2 ± 0.4 kcal. mole⁻¹ for the reaction B(c) → B(am.), the corresponding ΔH_f^o 298.15 values for $B_5H_9(g)$ were derived as 18.99 and 15.9 kcal. mole⁻¹. The adopted value is the average of these two.

Heat Capacity and Entropy.

The molecular structure, a tetragonal pyramid of boron atoms, and constants were obtained from H. J. Krostowski and R. J. Myers, J. Chem. Phys. 22, 262 (1954). The vibrational frequencies were reported by H. J. Krostowski and O. C. Finelant, J. Am. Chem. Soc. 76, 998 (1954). The earlier models of pentaborane were assumed to have a hydrocarbon-like structure of low symmetry by S. H. Bauer and L. Pauling, J. Am. Chem. Soc. 59, 2403 (1936) and K. S. Pitzer, J. Am. Chem. Soc. 57, 1126 (1935). However, the electron diffraction and X-ray data by K. Hedberg, M. E. Jones and V. Schomaker, Proc. Natl. Acad. Sci., U. S. 39, 679 (1952) and W. J. Dulmage and W. N. Lipscomb, Acta Cryst. 5, 260 (1952) revealed an unusual pyramidal structure of C_{4v} symmetry. The Raman spectrum of liquid B_5H_9 and the infrared spectrum of the gas B_5H_9 from 3 to 25 microns have been obtained by W. J. Taylor, C. W. Beckett, J. Y. Kung, R. B. Holden and H. L. Johnston, Phys. Rev. 73, 234 (1950). The near infrared spectrum of $B_5H_9(l)$ have been examined at high resolution by P. R. Fondy and H. C. Bechtell, J. Chem. Phys. 25, 238 (1956). Ten bands were observed. The three principal moments of inertia are: I_A = I_B = 1.18344 × 10⁻³⁸ and I_C = 1.69172 × 10⁻³⁸ g.² cm.²



Dipotassium Hexaborate ($K_2B_6O_{10}$)

(Crystal)	Mol. Wt.	=	303.12
1	100		
2	100		
3	100		
4	100		
5	100		
6	100		
7	100		
8	100		
9	100		
10	100		
11	100		
12	100		
13	100		
14	100		
15	100		
16	100		
17	100		
18	100		
19	100		
20	100		
21	100		
22	100		
23	100		
24	100		
25	100		
26	100		
27	100		
28	100		
29	100		
30	100		
31	100		
32	100		
33	100		
34	100		
35	100		
36	100		
37	100		
38	100		
39	100		
40	100		
41	100		
42	100		
43	100		
44	100		
45	100		
46	100		
47	100		
48	100		
49	100		
50	100		
51	100		
52	100		
53	100		
54	100		
55	100		
56	100		
57	100		
58	100		
59	100		
60	100		
61	100		
62	100		
63	100		
64	100		
65	100		
66	100		
67	100		
68	100		
69	100		
70	100		
71	100		
72	100		
73	100		
74	100		
75	100		
76	100		
77	100		
78	100		
79	100		
80	100		
81	100		
82	100		
83	100		
84	100		
85	100		
86	100		
87	100		
88	100		
89	100		
90	100		
91	100		
92	100		
93	100		
94	100		
95	100		
96	100		
97	100		
98	100		
99	100		
100	100		

T, °K.	C _p ^a	S ^b -(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH_f° -kcal. mole ⁻¹	ΔF_f°	Log K _p
n						
100	84.000	121.651	79.257	-110.257	-971.142	351.820
200	84.000	121.651	59.363	-110.257	-971.142	296.056
298	62.600	60.000	6.668	-110.257	-971.142	757.707
300	42.700	60.398	60.001	-110.7445	-1040.349	785.706
400	68.300	79.197	62.528	-110.608	-1010.126	755.806
500	73.680	95.019	67.683	-110.9.57	-998.470	434.662
600	76.900	108.916	73.252	-110.9.57	-971.142	351.820
700	84.000	121.651	79.257	-110.257	-971.142	296.056
800	90.400	133.962	91.774	-110.9.57	-978.945	219.031
900	96.670	153.792	96.949	-110.9.57	-802.082	122.084
1000	101.170	163.480	102.571	-116.6.532	-943.887	160.644
1200	102.790	172.356	106.021	-115.2.780	-877.533	150.671
1400	105.120	180.997	111.383	-114.7.269	-820.542	130.608
1600	106.450	185.712	123.208	-115.1.465	-768.294	109.021
1800	107.520	128.042	119.320	-114.0.183	-722.116	99.632
1900	108.250	209.142	132.623	-113.7.472	-695.010	89.470
2000	108.250	209.142	132.623	-113.7.472	-695.010	89.470
2100	108.250	211.356	141.471	-113.6.276	-644.079	74.082
2200	110.620	227.035	145.731	-113.6.276	-618.209	67.551

DIPOTASSIUM HEXABORATE ($K_2B_6O_{10}$)

(CRYSTAL)

B₆K2010
MOL. WT. = 303.12

ΔH° = Unknown

$$\Delta H_{\text{cal}}^{\circ} = [60 + 3] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$\Delta H_{\text{comb}}^{\circ} = -1,107.44 + 2.4 \text{ kcal. mole}^{-1}$$
 $T_1 = 1098^\circ\text{K}$

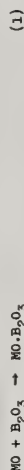
Heat of Formation.

The heat of reaction $K_2O(c) + 3B_2O_3(l) \rightarrow K_2B_6O_{10}(c)$ was reported by L. Shartais and W. Cappa, *J. Am. Ceram. Soc.*, **37**, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $B_2O_3(l)$ (Dec. 31, 1964) and for $K_2O(c)$ (June 30, 1963). The above $\Delta H_f^\circ = -122.8$ kcal. mole⁻¹. The above $\Delta H_f^\circ = -122.8$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-29346 in the range 298 to 973°K were graphically smoothed and used to determine C_p . Above this range C_p was extrapolated.

The entropy at 298°K was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by K. K. Kelley and E. G. King, Bureau of Mines Bull. 592 (1961). These indicate that for the reactions



The simple addition of entropies will give values at least 2.7 e.u. too low for reaction (1) and at least 2.7 e.u. too high for reaction (2). The reason for this is probably structural, the $\text{B}_2\text{O}_4^{--}$ ion being a flexible chain while the $\text{B}_2\text{O}_7^{--}$ ion probably is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the entropy difference for reaction (2) was assumed to hold for each additional mole of B_2O_3 added. Thus a value for $\text{Na}_2\text{B}_2\text{O}_7$ was estimated to be 55.5 ± 1.5 and then using an average value of 4.5 ± 1.5 e.u. for the difference between K_2 and Na_2 gave 60 ± 3 e.u. for the entropy of $\text{K}_2\text{B}_2\text{O}_7$.

Decomposition Temperature.

The incongruent melting point was given by A.-P. Rollé, *Comp. rend.* **200**, 1763 (1935), the decomposition products being $K_2B_2O_7(1)$ and $K_2B_8O_{13}(c)$.

B₆K2010

Dilithium Hexaborate ($\text{Li}_2\text{B}_6\text{O}_{10}$)
(Crystal) Mol. Wt. = 238.80

$\text{B}_6\text{Li}_2\text{O}_{10}$

T, °K.	C_p	$\text{cal. mole}^{-1}\text{deg}^{-1}$	$S^\circ - (F^\circ - H^\circ_{398})/T$	cal. mole^{-1}	$H^\circ - H^\circ_{398}$	ΔH°_f	ΔF°_f	Log K_p
0								
100								
200								
298	70.080	45.000	45.000	.000	-1113.740	-1047.448	767.763	
300	70.180	45.434	45.001	.430	-1113.727	-1047.039	762.731	
400	75.590	66.378	47.820	7.423	-1113.163	-1024.899	556.952	
500	80.440	83.779	53.319	15.230	-1114.325	-1002.773	438.269	
600	84.610	98.824	59.677	23.489	-1114.117	-980.419	357.100	
700	88.050	112.132	66.238	32.126	-1113.866	-958.156	299.135	
800	90.940	124.083	72.734	41.079	-1113.557	-935.939	255.674	
900	93.390	134.939	79.052	50.299	-1113.185	-913.759	221.880	
1000	95.500	144.890	85.145	59.745	-1112.764	-891.614	194.853	
1100	97.145	154.069	90.989	69.377	-1112.327	-869.526	172.751	
1200	98.777	162.591	96.614	78.177	-1111.862	-847.470	154.338	
1300	100.305	170.597	101.999	86.125	-1111.370	-825.461	138.766	
1400	101.819	178.046	107.166	93.232	-1110.835	-803.483	125.423	
1500	103.280	185.121	112.129	100.488	-1110.266	-781.538	113.867	
1600	104.717	191.833	116.903	115.888	-1109.651	-759.625	103.759	
1700	106.101	198.223	121.500	130.430	-1179.083	-735.145	94.505	
1800	107.441	204.326	125.933	141.107	-1178.015	-709.063	86.088	
1900	108.737	210.170	130.214	151.916	-1176.893	-683.039	78.564	
2000	109.990	215.760	134.353	162.853	-1175.706	-657.082	71.799	

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

DILITHIUM HEXABORATE ($\text{Li}_2\text{B}_6\text{O}_{10}$)

(CRYSTAL)

MOL. WT. = 238.80

$\Delta H^\circ_f 0$ = Unknown

$\Delta H^\circ_f 298.15$ = -1,113.74 \pm 2.40 kcal. mole⁻¹

$S^\circ_{298.15}$ = [45.0 \pm 1.0] cal. deg.⁻¹ mole⁻¹

T_d = 1107 \pm 4°K.

Heat of Formation.

The heat of reaction $\text{Li}_2\text{O}(c) + 3\text{B}_2\text{O}_3(l) \rightarrow \text{Li}_2\text{B}_6\text{O}_{10}(c)$ was reported by L. Shartsis and W. Capps, *J. Am. Ceram. Soc.* **37**, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and $\text{Li}_2\text{O}(c)$ (March 31, 1964). The above ΔH°_f = -72.80 kcal. mole⁻¹.

Heat Capacity and Entropy.

The enthalpy measurement of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 823°K. were used to determine C_p . Above this range C_p is extrapolated. Entropy at 298°K. is estimated from that of the component oxides and the difference from the oxides observed for twice $\text{LiBO}_2(c)$.

Temperature of Decomposition.

The incongruent melting point reported by B. S. R. Sastry and P. A. Hummel, *J. Am. Ceram. Soc.* **42**, 216-8 (1959) is used here.

$\text{B}_6\text{Li}_2\text{O}_{10}$

Disodium Hexaborate ($\text{Na}_2\text{B}_6\text{O}_{10}$)
(Crystal) Mol. Wt. = 270.902

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K_p
0					
100	112.680	164.745	-1094.760	-1076.411	753.810
200	112.680	164.745	-1094.760	-1076.411	753.810
298	58.200	55.500	-1094.760	-1076.411	753.810
300	58.200	55.501	-1094.771	-1076.401	748.862
400	67.680	73.944	-1086.638	-1065.551	549.381
500	76.480	90.005	-1097.039	-982.725	428.528
600	84.550	104.673	-1097.049	-959.852	349.409
700	94.560	130.590	-1095.733	-934.278	285.255
800	98.250	142.937	-1094.431	-861.667	216.516
900	104.250	154.176	-1092.784	-869.214	189.958
1000	109.000	164.745	-1090.904	-865.937	168.267
1100	112.680	164.745	-1090.904	-865.937	168.267
1200	112.680	164.745	-1090.904	-865.937	168.267
1300	112.680	164.745	-1090.904	-865.937	168.267
1400	112.680	164.745	-1090.904	-865.937	168.267
1500	112.680	164.745	-1090.904	-865.937	168.267
1600	112.680	164.745	-1090.904	-865.937	168.267
1700	112.680	164.745	-1090.904	-865.937	168.267
1800	112.680	164.745	-1090.904	-865.937	168.267
1900	112.680	164.745	-1090.904	-865.937	168.267
2000	112.680	164.745	-1090.904	-865.937	168.267

B_6Na_{20}
MOL. WT. = 270.902

(CRYSTAL)

DISODIUM HEXABORATE ($\text{Na}_2\text{B}_6\text{O}_{10}$)

$\Delta H_f^\circ =$ Unknown
 $\Delta H_f^\circ 298.15 = -1094.76 \pm 2.2 \text{ kcal. mole}^{-1}$
 $S^\circ 298.15 = [55.5 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_d = 1039^\circ\text{K.}$

Heat of Formation.

The heat of reaction $\text{Na}_2\text{O}(c) + 3\text{B}_2\text{O}_3(l) \rightarrow \text{Na}_2\text{B}_6\text{O}_{10}(c)$ was reported by L. Shartsis and W. Cappa, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and for $\text{Na}_2\text{O}(c)$ (June 30, 1962). The above $\Delta H_f^\circ = -97.52 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. Mic 59-2916 in the range 298 to 1039°K were smoothed graphically and used to determine C_p . Above this range C_p was extrapolated. Entropy at 298°K was estimated as described in detail for $\text{K}_2\text{B}_6\text{O}_{10}(c)$.

Decomposition Temperature.

The incongruent melting point was reported by G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. 58, 2249 (1936), the products are $\text{Na}_2\text{B}_4\text{O}_7(l)$ and $\text{Na}_2\text{B}_6\text{O}_{13}(c)$.

B_6Na_{20}

LEAD HEXABORATE (PbB₆O₁₀) (CRYSTAL)

T, °K.	C _p	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	ΔH_f°	ΔF_f°	Log K _p
0					
100					
200					
298	55.200	48.600	0.000	-937.311	687.034
300	55.400	48.942	-1.02	-936.905	687.402
400	68.400	66.696	6.305	-934.864	696.836
500	78.880	83.221	13.732	-892.906	390.270
600	89.830	98.678	22.225	-871.122	317.291
700	100.230	112.632	31.924	-859.351	255.179
800	106.230	126.632	41.924	-850.258	205.564
900	111.630	139.770	52.851	-856.826	194.515
1000	115.590	151.746	64.222	-856.009	171.774
1100	118.420	162.904	75.931	-859.322	152.087
1200	121.370	172.960	88.050	-855.384	135.734
1300	124.400	182.060	99.969	-850.451	121.614
1400	126.590	191.090	111.693	-845.458	110.162
1500	128.320	200.409	124.339	-840.458	99.987
1600	129.640	208.310	136.582	-835.458	91.111
1700	130.680	215.765	148.460	-830.458	83.304
1800	131.500	222.765	159.127	-825.458	76.217
1900	132.090	229.411	168.138	-820.458	70.217
2000	132.080	235.722	175.724	-815.458	64.680

Mar. 31, 1962; Dec. 31, 1962; Mar. 31, 1965

$S_{298.15}^{\circ} = [48.6 \pm 3] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} = -1003 \pm 2.0 \text{ kcal mole}^{-1}$

$\Delta H_f^{\circ} = \text{Unknown}$

Heat of Formation.

See lead diborate table for the complete writeup. W. H. Evans in NBS Report 7192, July 1, 1961, analysed the heats of formation of the lead borate system based upon Shartsis and Newman's heats of solution and Mazzetti and De Carli's phase studies. From the Shartsis and Newman paper Evans obtained the following:



and estimated a ΔH_{298}° of 16.0 kcal. mole⁻¹ for the conversion to the $\text{PbO} \cdot 3\text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the ΔH_f° 298.15 was calculated to be -1003.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of heat capacities of the constituent oxides.

The entropy at 298.15 was obtained in the manner described in the $\text{PbB}_6\text{O}_{10}$ table from $S_{298.15}^{\circ}$ for $\text{PbB}_6\text{O}_{10}$ and B_2O_3 and the subtraction of 4.2 e.u.

Dipotassium Octaborate (K₂B₈O₁₃)

(Liquid) Mol. Wt. = 372.76

DIPOTASSIUM OCTABORATE (K₂B₈O₁₃)

(LIQUID)

MOL. WT. = 372.76

T, °K.	C _p	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S^{\circ}}$	$\frac{-(F^{\circ}-H_{298}^{\circ})/T}{H^{\circ}-H_{298}^{\circ}}$	ΔH_f°	ΔF_f°	Log K _p
100						
200						
298	77.220	71.295	71.295	0.00	-1317.295	965.557
300	77.560	71.774	71.206	0.143	-1316.762	959.214
400	95.120	96.428	74.546	8.453	-1287.755	905.658
500	107.600	116.017	81.215	16.901	-1250.330	849.889
600	119.600	136.279	89.240	30.024	-1209.245	787.731
700	158.100	196.560	97.707	42.997	-1160.267	714.744
800	198.100	176.571	106.662	58.407	-1106.428	620.154
900	198.100	168.592	115.829	64.131	-1051.866	514.865
1000	198.100	174.650	124.823	66.037	-1007.359	414.087
1100	198.100	230.018	133.803	109.937	-942.1298	216.154
1200	198.100	243.775	142.403	121.647	-876.946	102.657
1300	198.100	256.450	150.694	132.457	-812.773	172.837
1400	198.100	268.066	158.670	142.266	-748.600	182.595
1500	198.100	279.054	166.336	160.077	-684.427	141.256
1600	198.100	289.257	173.703	184.867	-620.254	128.479
1700	198.100	298.842	180.789	200.697	-556.081	117.236
1800	198.100	307.822	187.597	216.507	-491.908	106.993
1900	198.100	316.231	194.131	232.317	-427.735	96.749
2000	198.100	324.536	200.473	248.127	-363.562	86.502
2100	198.100	332.250	206.566	263.937	-299.389	76.255
2200	198.100	339.604	212.447	279.747	-235.216	66.008
2300	198.100	346.633	218.150	295.557	-171.043	55.761
2400	198.100	353.383	223.683	311.367	-106.870	45.514
2500	198.100	359.815	228.943	327.177	-42.697	35.267
2600	198.100	366.016	234.098	342.987	11.477	25.020
2700	198.100	371.983	239.095	358.797	55.662	14.773
2800	198.100	377.733	243.645	374.607	99.847	4.526
2900	198.100	383.266	247.841	390.417	144.022	-6.721
3000	198.100	388.640	251.733	406.227	188.197	-16.974

Mar. 31, 1963; Mar. 31, 1965

$$S_{298.15}^{\circ} = [71.295] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} = -1,403.57 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^{\circ} = -1,403.57 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$T_m = 1130^{\circ}\text{K.}$$

Heat of Formation.

The heat of reaction $\text{K}_2\text{O}(\text{c}) + 4\text{B}_2\text{O}_3(\text{l}) \rightarrow \text{K}_2\text{B}_8\text{O}_{13}(\text{l})$ was reported by L. Shartais and W. Cappa, J. Am. Ceram. Soc. 37, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAF values for $\text{B}_2\text{O}_3(\text{l})$ (Dec. 31, 1964) and for $\text{K}_2\text{O}(\text{c})$ (June 30, 1963). The above $\Delta H_f^{\circ} = -119.65 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The enthalpy measurements of O. J. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. MC 59-2916 in the range 298 to 1373°K on the glass and liquid were smoothed graphically and used to determine C_p . There is a discontinuity in the C_p curve, a glass transition at about 675°K. Above 675°K the C_p values were estimated to be constant.

The entropy was obtained from that of the crystal by adding ΔS_m° and the difference between $S_{1130-298}$ for crystal and liquid.

Melting Data.

See the crystal table.

Lithium Octaborate ($\text{Li}_2\text{B}_8\text{O}_{13}$)
(Crystal) Mol. Wt. = 308.44

T, °K	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°	Log K _p
0							
100							
200							
298	77.800	63.400	63.400	0.000	-1413.570	-1330.011	974.876
300	78.100	63.682	63.401	.144	-1413.572	-1329.496	968.480
400	89.300	88.577	66.465	8.765	-1413.591	-1301.481	711.062
500	102.430	110.437	73.281	18.578	-1414.469	-1273.398	556.575
600	108.320	129.656	81.189	20.128	-1414.053	-1245.019	453.549
700	112.720	146.692	89.280	42.166	-1413.580	-1215.117	370.589
800	116.320	161.986	97.432	51.643	-1413.054	-1189.095	324.830
900	119.200	175.856	105.387	63.623	-1412.475	-1161.135	281.040
1000	121.570	188.542	113.078	75.664	-1411.869	-1131.279	237.655
1100	123.400	200.225	120.424	87.724	-1411.271	-1105.402	219.619
1200	125.388	211.057	127.426	100.724	-1410.682	-1079.452	198.452
1300	127.131	221.162	134.393	112.800	-1410.040	-1054.693	176.456
1400	128.628	230.646	140.993	125.598	-1409.413	-1029.207	155.456
1500	130.480	239.591	147.215	138.564	-1408.763	-1004.584	144.904
1600	132.087	248.063	153.235	151.693	-1408.081	-980.983	132.077
1700	133.648	256.118	159.071	165.080	-1407.382	-958.301	119.456
1800	135.164	263.800	164.678	178.421	-1406.652	-936.510	109.478
1900	136.635	271.148	170.089	192.011	-1405.897	-915.299	100.447
2000	138.060	278.193	175.320	205.746	-1405.080	-894.656	91.947

$\text{B}_8\text{Li}_{20}^{13}$

MOL. WT. = 308.44

(CRYSTAL)

LITHIUM OCTABORATE ($\text{Li}_2\text{B}_8\text{O}_{13}$)

ΔH°_f = Unknown

$\Delta F^\circ_{298.15} = -1413.57 \pm 2.50$ kcal. mole⁻¹

$S^\circ_{298.15} = [65.4 \pm 1.0]$ cal. deg.⁻¹ mole⁻¹

$T_d = 908 \pm 10^\circ\text{K}$.

Heat of Formation.

The heat of the reaction $\text{Li}_2\text{O}(c) + 4\text{B}_2\text{O}_3(l) \rightarrow \text{Li}_2\text{B}_8\text{O}_{13}(c)$ was reported by L. Scharis and V. Ceppe, J. Am. Ceram. Soc. 31, 27-32 (1954) from their heats of solution measurements. Their values for the heat of reaction of the oxides have been converted to the heats of formation using JANAP values for $\text{B}_2\text{O}_3(l)$ (Dec. 31, 1964) and for $\text{Li}_2\text{O}(c)$ (March 31, 1964). The above $\Delta H^\circ_f = -73.35$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The enthalpy measurements of G. S. Smith, Ph.D. Thesis, Penn. State Univ., Jan. 1959, L. C. Card No. MC 59-2316 in the range of 298 to 823°K. were used to determine C_p . Above this range C_p is extrapolated. Entropy at 298°K. is estimated from that of the component oxides and the difference from the oxides observed for twice $\text{LiB}_2\text{O}_4(c)$.

Temperature of Decomposition. The incongruent melting point reported by B. S. R. Sastry and P. A. Hummel, J. Am. Ceram. Soc. 42, 216-8 (1959) is used here.

$\text{B}_8\text{Li}_{20}^{13}$

T, °K.	C _p ^o	S ^o	-(H ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	Log K _p
0	-0.00	-0.00	INFINITE	-	3.426	INFINITE
100	13.294	12.718	71.126	-	14.656	- 32.025
200	20.490	26.229	46.230	-	31.652	- 34.566
298	52.092	42.200	42.200	-	49.634	- 36.527
300	52.431	42.524	42.201	-	50.183	- 36.556
400	72.900	62.500	62.500	-	68.686	- 38.078
500	78.600	77.259	49.513	14.023	89.207	- 38.991
600	87.200	92.614	55.456	22.204	109.211	- 39.778
700	95.000	106.680	61.779	31.416	129.416	- 40.403
800	100.750	119.759	68.215	41.210	149.720	- 40.900
900	105.750	131.420	74.827	51.531	169.481	- 41.304
1000	110.000	134.200	80.925	62.393	189.481	- 41.628
1100	113.500	133.914	87.081	73.516	210.667	- 41.893
1200	116.250	133.913	93.072	85.010	231.256	- 42.115
1300	118.250	133.102	98.686	96.741	251.611	- 42.298
1400	120.000	131.688	104.000	108.688	271.611	- 42.448
1500	120.000	130.332	109.671	120.616	292.510	- 42.568

$$\Delta H_f^o = 5.4 \pm 4.5 \text{ kcal. mole}^{-1}$$
$$\Delta H_f^o = -6.9 \pm 4.5 \text{ kcal. mole}^{-1}$$
$$\Delta H_m^o = 5.25 \pm 0.01 \text{ kcal. mole}^{-1}$$
$$\Delta H_g^o = 19.2 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 42.20 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 371.93^\circ \text{K}$$

Heat of Formation.

The enthalpy change (ΔH_f^o , 298.15) of the reaction $B_{10}H_{14}(c) \rightarrow 10B(am) + 7H_2(g)$ was reported to be 19.8 ± 1.4 and 18.0 ± 1.0 kcal. mole⁻¹ by W. H. Johnson, M. V. Kilday and E. J. Prosen, J. Res. Natl. Bur. Std. 64A, 521 (1960) and G. L. Gal'chenko, B. I. Timofeev and S. M. Skuratov, Doklady Akademii Nauk, USSR, 142, 1077 (1962), respectively. Using ΔH_f^o , 298.15 = 1.2 ± 0.4 kcal. mole⁻¹ for the reaction $B(c) \rightarrow B(am)$, the corresponding ΔH_f^o , 298.15, values for $B_{10}H_{14}(c)$ were calculated to be -7.8 and -6.0 kcal. mole⁻¹. The adopted value of ΔH_f^o , 298.15 for $B_{10}H_{14}(c)$ is the average of these two.

Heat Capacity and Entropy.

C_p (60° to 371.93°K.) was given by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955). The heat capacity above 371.93° was estimated by comparison with that of the liquid decaborane. Heat capacity (14° to 205°K.) was also reported by E. C. Kerr, N. C. Hallett and H. L. Johnston, J. Am. Chem. Soc., 73, 1117 (1951). The value of $S_{298.15}^o$ was taken from G. T. Furukawa and R. P. Park, loc. cit.

Melting Data.

T_m and ΔH_m^o were obtained from G. T. Furukawa and R. P. Park, loc. cit.

Heat of Sublimation.

ΔH_g^o , 298.15 was calculated from free energy functions and vapor pressure reported by G. T. Furukawa and R. P. Park, loc. cit. See $B_{10}H_{14}(g)$ table for details.

Decaborane ($B_{10}H_{14}$)
(Liquid) Mol. Wt. = 122.312

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0						
100						
200						
298	52.870	56.299	56.299	0.000	1.700	50.630 - 37.258
300	53.280	56.627	56.627	0.098	1.743	51.153 - 37.263
400	77.200	75.365	58.079	6.082	3.237	65.057 - 37.720
500	83.000	93.215	63.848	16.684	4.258	81.240 - 38.131
600	93.200	109.271	70.095	23.505	5.087	105.627 - 38.473
700	102.000	124.316	76.778	33.277	5.389	124.117 - 38.749
800	109.000	138.405	83.611	43.835	5.223	142.604 - 38.956
900	115.000	151.589	90.440	55.044	4.658	161.052 - 39.107
1000	120.000	163.983	97.161	66.802	3.776	179.425 - 39.211
1100	124.000	175.616	103.789	78.010	2.690	197.486 - 39.275
1200	127.000	186.541	110.234	91.569	1.459	215.861 - 39.312
1300	129.000	196.792	116.502	104.377	1.199	233.910 - 39.322
1400	130.000	206.395	122.564	117.335	1.011	251.883 - 39.319
1500	130.000	215.370	128.474	130.344	2.048	269.756 - 39.301

$B_{10}H_{14}$
MOL. WT. = 122.312

(LIQUID)

DECABORANE ($B_{10}H_{14}$)

$S_{298.15}^\circ = 56.299$ cal. deg.⁻¹ mole⁻¹
 $T_m = 371.93^\circ K.$
 $T_b = [492]^\circ K.$

Heat of Formation.

ΔH_f° 298.15 was calculated from ΔH_f° 298.15 for $B_{10}H_{14}(c)$ and ΔH_m° reported by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955) and the difference $H_m^\circ - H_{298.15}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

C_p (371.93° to 380°K) was measured by G. T. Furukawa and R. P. Park, J. Res. Natl. Bur. Standards, 55, 255 (1955). Heat capacities below 371.93° and above 380°K. were estimated by comparison with that of the gaseous decaborane. $S_{298.15}^\circ$ was calculated from that of crystal in a manner analogous to that of the heat of formation.

Melting and Vaporization Data.

T_m and ΔH_m° were obtained from G. T. Furukawa and R. P. Park, loc. cit. T_b and ΔH_v° were calculated from functions for $B_{10}H_{14}(l)$ and $B_{10}H_{14}(g)$, respectively.

$B_{10}H_{14}$

Dilead Decaborate ($\text{Pb}_2\text{B}_{10}\text{O}_{17}$)
(Crystal) Mol. Wt. = 794.62

DILEAD DECARBORATE ($\text{Pb}_2\text{B}_{10}\text{O}_{17}$) (CRYSTAL) $\text{B}_{10}\text{O}_{17}\text{Pb}_2$
MOL. WT. = 794.62

T, K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0							
100							
200							
298	97.200	84.300	84.300	0.00	-1694.000	-1581.528	1159.236
300	97.600	84.902	84.302	0.180	-1694.004	-1580.834	1151.581
400	120.200	116.823	86.412	11.411	-1693.641	-1543.134	843.089
500	137.500	144.897	96.886	24.034	-1692.407	-1505.634	636.081
600	153.400	171.511	107.140	38.623	-1690.366	-1468.453	534.858
700	166.100	196.135	118.117	54.613	-1689.889	-1431.296	446.849
800	176.700	219.316	127.316	71.983	-1688.884	-1394.396	380.967
900	186.100	240.435	135.035	89.983	-1687.453	-1357.853	326.043
1000	193.400	260.436	151.405	108.921	-1677.534	-1322.612	289.043
1100	199.100	279.149	162.259	128.579	-1672.466	-1287.375	255.766
1200	203.200	296.060	172.737	148.707	-1667.118	-1252.592	228.117
1300	206.000	311.456	181.856	168.456	-1661.486	-1218.370	204.860
1400	207.400	326.349	192.755	189.832	-1655.176	-1184.870	184.860
1500	208.200	342.683	202.277	210.612	-1650.775	-1150.869	167.673
1600	209.000	356.148	211.478	231.472	-1645.474	-1117.706	152.664
1700	209.800	368.842	220.365	252.412	-1640.259	-1084.878	139.464
1800	210.400	380.850	228.960	272.510	-1635.150	-1052.456	127.956
1900	211.400	392.267	237.278	292.532	-1630.067	-1022.130	117.936
2000	212.200	403.128	245.272	315.712	-1625.033	-988.159	107.676

Heat of Formation.

See lead diborate for the complete writeup. W. H. Evans in NBS. Report 7192, July 1, 1961, analyzed the heats of formation of the lead borate system based upon Sharvits and Newman's heats of solution and Mazzetti and DeCarli's phase studies. From the Sharvits and Newman paper Evans obtained the following:

$2\text{PbO}(c) + 5\text{B}_2\text{O}_3(c) \rightarrow 2\text{PbO} \cdot 5\text{B}_2\text{O}_3(\text{glass})$ $\Delta H_f^\circ = -45.2 \text{ kcal./mole}$
and estimated a ΔH_{298} of 26.8 kcal. mole⁻¹ for the conversion to the $2\text{PbO} \cdot 5\text{B}_2\text{O}_3(\text{crystal})$. With auxiliary JANAF values the ΔH_f° 298.15 was calculated to be -1694.00 kcal./mole.

Heat Capacity and Entropy.

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 was obtained in the manner described in the PbB_2O_7 table from $S_{298.15}^\circ$'s of $\text{Pb} \cdot 2\text{B}_2\text{O}_3$ and $\text{Pb} \cdot 3\text{B}_2\text{O}_3$ and the subtraction of 4.2 e.u.

$\text{B}_{10}\text{O}_{17}\text{Pb}_2$

Solid state to the melting point 1556°K.
Liquid state from 1556°K. to the boiling point 2757°K.
Ideal monatomic gas state above 2757°K.

See Crystal, Liquid, Ideal Monatomic Gas for details.

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0	.000	.000	IMFINITE	=	.468	.000	.000	.000	.000
100	2.437	1.130	.000	.000	.000	.000	.000	.000	.000
200	2.877	2.112	.000	.000	.000	.000	.000	.000	.000
298	3.032	2.280	.000	.000	.000	.000	.000	.000	.000
300	3.050	2.304	.000	.007	.000	.000	.000	.000	.000
400	3.770	3.561	.000	.446	.000	.000	.000	.000	.000
500	5.254	4.684	.000	.950	.000	.000	.000	.000	.000
600	5.379	5.671	3.188	1.492	.000	.000	.000	.000	.000
700	5.636	6.552	3.604	2.044	.000	.000	.000	.000	.000
800	6.065	7.346	4.022	2.659	.000	.000	.000	.000	.000
900	6.287	8.073	4.433	3.276	.000	.000	.000	.000	.000
1000	6.517	8.747	4.831	3.916	.000	.000	.000	.000	.000
1100	6.745	9.380	5.216	4.580	.000	.000	.000	.000	.000
1200	7.003	9.979	5.568	5.269	.000	.000	.000	.000	.000
1300	7.242	10.549	5.981	5.981	.000	.000	.000	.000	.000
1400	7.461	11.094	6.717	6.717	.000	.000	.000	.000	.000
1500	7.719	11.618	6.534	7.477	.000	.000	.000	.000	.000
1600	6.901	13.095	7.010	11.016	.000	.000	.000	.000	.000
1700	6.952	14.315	7.428	11.709	.000	.000	.000	.000	.000
1800	7.004	14.714	7.821	12.407	.000	.000	.000	.000	.000
1900	7.055	15.094	8.194	13.110	.000	.000	.000	.000	.000
2000	7.106	15.457	8.548	13.816	.000	.000	.000	.000	.000
2100	7.156	15.805	8.884	14.531	.000	.000	.000	.000	.000
2200	7.209	16.139	9.208	15.249	.000	.000	.000	.000	.000
2300	7.250	16.461	9.518	15.972	.000	.000	.000	.000	.000
2400	7.280	16.771	9.812	16.700	.000	.000	.000	.000	.000
2500	7.360	17.070	10.096	17.434	.000	.000	.000	.000	.000
2600	7.400	17.360	10.370	18.172	.000	.000	.000	.000	.000
2700	7.440	17.640	10.634	18.914	.000	.000	.000	.000	.000
2800	4.997	43.675	11.285	90.691	.000	.000	.000	.000	.000
2900	5.007	43.851	12.405	91.191	.000	.000	.000	.000	.000
3000	5.021	44.021	13.456	91.693	.000	.000	.000	.000	.000
3100	5.037	44.185	14.445	92.196	.000	.000	.000	.000	.000
3200	5.057	44.346	15.377	92.700	.000	.000	.000	.000	.000
3300	5.081	44.502	16.257	93.207	.000	.000	.000	.000	.000
3400	5.109	44.654	17.090	93.717	.000	.000	.000	.000	.000
3500	5.142	44.802	17.889	94.229	.000	.000	.000	.000	.000
3600	5.179	44.948	18.630	94.745	.000	.000	.000	.000	.000
3700	5.221	45.090	19.343	95.265	.000	.000	.000	.000	.000
3800	5.268	45.230	20.022	95.790	.000	.000	.000	.000	.000
3900	5.320	45.366	20.681	96.319	.000	.000	.000	.000	.000
4000	5.376	45.503	21.329	96.854	.000	.000	.000	.000	.000
4100	5.440	45.636	21.962	97.395	.000	.000	.000	.000	.000
4200	5.508	45.768	22.649	97.942	.000	.000	.000	.000	.000
4300	5.581	45.899	23.393	98.496	.000	.000	.000	.000	.000
4400	5.656	46.026	24.113	99.058	.000	.000	.000	.000	.000
4500	5.741	46.156	24.816	99.628	.000	.000	.000	.000	.000
4600	5.826	46.283	25.499	100.207	.000	.000	.000	.000	.000
4700	5.919	46.409	26.164	100.794	.000	.000	.000	.000	.000
4800	6.014	46.535	26.812	101.391	.000	.000	.000	.000	.000
4900	6.113	46.660	27.444	101.997	.000	.000	.000	.000	.000
5000	6.215	46.785	28.062	102.613	.000	.000	.000	.000	.000
5100	6.320	46.909	28.666	103.240	.000	.000	.000	.000	.000
5200	6.428	47.032	29.256	103.877	.000	.000	.000	.000	.000
5300	6.538	47.156	29.834	104.526	.000	.000	.000	.000	.000
5400	6.653	47.281	30.401	105.185	.000	.000	.000	.000	.000
5500	6.783	47.402	30.958	105.858	.000	.000	.000	.000	.000
5600	6.977	47.525	31.501	106.538	.000	.000	.000	.000	.000
5700	6.993	47.648	32.035	107.231	.000	.000	.000	.000	.000
5800	7.109	47.771	32.561	107.936	.000	.000	.000	.000	.000
5900	7.244	47.894	33.080	108.654	.000	.000	.000	.000	.000
6000	7.340	48.015	33.581	109.381	.000	.000	.000	.000	.000

Beryllium (Be)

(Crystal) Mol. Wt. = 9.013

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	.000	INFINITE	.468	.000	.000	INFINITE
100	.437	.130	4.712	.456	.000	.000	.000
200	2.400	1.010	2.610	.320	.000	.000	.000
298	3.932	2.280	2.280	.000	.000	.000	.000
300	3.950	2.304	2.280	.007	.000	.000	.000
400	4.770	3.561	2.446	.446	.000	.000	.000
500	5.254	4.684	2.764	.950	.000	.000	.000
600	5.379	5.671	3.184	1.492	.000	.000	.000
700	5.311	6.541	3.604	2.042	.000	.000	.000
800	4.965	7.346	4.022	2.659	.000	.000	.000
900	4.287	8.073	4.433	3.276	.000	.000	.000
1000	6.517	8.747	4.831	3.916	.000	.000	.000
1100	6.745	9.380	5.216	4.580	.000	.000	.000
1200	7.005	9.979	5.586	5.269	.000	.000	.000
1300	7.242	10.549	5.948	5.981	.000	.000	.000
1400	7.461	11.094	6.296	6.717	.000	.000	.000
1500	7.719	11.618	6.634	7.477	.000	.000	.000
1600	7.950	12.124	6.961	8.261	.078	.078	.011
1700	8.145	12.609	7.278	9.078	.242	.242	.032
1800	8.315	13.089	7.589	9.900	.507	.507	.052
1900	8.474	13.551	7.891	10.756	.766	.766	.066
2000	8.613	14.002	8.185	11.635	.979	.979	.079
2100	8.732	14.443	8.472	12.538	1.193	.867	.090
2200	8.829	14.868	8.741	13.465	1.406	.966	.102
2300	8.909	15.297	9.029	14.417	1.555	1.122	.107
2400	9.068	15.712	9.299	15.391	1.709	1.233	.112
2500	10.106	16.120	9.564	16.390	1.844	1.332	.116
2600	10.245	16.521	9.823	17.413	.759	1.423	.120
2700	10.322	16.905	10.070	18.459	.759	1.514	.124
2800	10.382	17.283	10.310	19.529	.711	1.605	.126
2900	11.060	17.669	10.537	20.623	.530	1.695	.130
3000	11.299	18.060	10.820	21.741	.695	1.790	.134

BERYLLIUM (Be)

(CRYSTAL)

MOL. WT. = 9.013

Be

$$\Delta H_f^0 = 0$$

$$\Delta H_f^0 = 298.15 = 0$$

$$\Delta H_g^0 = 76.25 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^0 = 2800 \pm 500 \text{ cal. mole}^{-1}$$

$$T_m = 1556^\circ\text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Extrapolation.

Heat capacity measurements have been reported by F. Simon and M. Ruheman, (71° to 79°K.), Z. physik. Chem. 129, 321 (1935); S. Cristescu and F. Simon, (10° to 300°K.), Z. physik. Chem. 259, 273 (1934); E. J. Lewis, (97° to 463°K.), Phys. Rev. 34, 1575 (1925); D. C. Ginnings, T. B. Douglas and A. F. Ball, (0° to 900°K.), J. Am. Chem. Soc. 73, 1236 (1951), and R. W. Hill and P. L. Smith, (4° to 300°K.), Phil. Mag. 44, 636 (1953).

A five constant equation was fit to both sets of data adopted from Ginnings and co-workers by the method of least squares, standard deviation ± 0.017 , and joined smoothly with the C_p values of Hill and Smith. C_p from 1200°K. to the melting point was extrapolated.

P. B. Kantor, R. M. Krasovitskaya and A. N. Kisel, Fiz. Metal. i Metalloved., Akad. Nauk. S.S.S.R. 10, 835 (1960), report enthalpy data for pure beryllium, purity not given, from 600° to 1560°K. (crystal) and from 1560° to 2200°K. (liquid). Their values for the crystal are too high.

Entropy.

Third law entropy calculated from C_p .

Melting.

Data from O. Kubaschewski, P. Brizys, O. Ruchler, R. Jauch, and K. Reinartz, Z. Elektrochem. 54, 275 (1950).

Heat of Sublimation.

ΔH_g^0 298.15 was derived from a third law analysis of the vapor pressure data of E. A. Gulbransen and K. P. Andrews, J. Electrochem. Soc. 97, 393 (1952), and of R. B. Holden, R. Speiser, and H. L. Johnston, J. Am. Chem. Soc. 70, 3697 (1948) which are in good agreement. The results of R. Schuman and A. B. Garrett, J. Am. Chem. Soc. 66, 442 (1944), are too low, and the values given by E. Baur and R. Brunner, Helv. Chim. Acta 17, 958 (1934), have a wrong temperature dependence.

MOL. WT. = 9.013

(LIQUID)

BERYLLIUM (Be)

Log K_p

$$S_{298.15}^{\circ} = [3.954] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^{\circ} = 2800 \pm 500 \text{ cal. mole}^{-1}$$

$$\Delta H_v^{\circ} = 71.137 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = [2.881] \text{ kcal. mole}^{-1}$$

$$T_m = 1556^{\circ}\text{K.}$$

$$T_b = 2757^{\circ}\text{K.}$$

Heat of Formation.

Obtained from ΔH_m 1556°K.

Heat Capacity and Extrapolation.

Heat capacity from T_m to 2200°K. taken from P. B. Kantor, R. M. Krasovitskaya and A. N. Kisil, *Viz. Metal.* 1 Metalloved., Akad. Nauk S.S.S.R. 10, 635 (1960). C_p values below T_m and above 2200°K. were extrapolated.

Entropy.

Third law entropies between T_m and T_b extrapolated in both directions by means of extrapolated heat capacities.

Vaporization Phenomena.

T_b and ΔH_v derived from a third law analysis of the vapor pressure data of E. A. Gulbransen and K. P. Andrew, *J. Electrochem. Soc.* 37, 383 (1952), and of R. B. Holden, R. Speiser, and H. L. Johnston, *J. Am. Chem. Soc.* 70, 3897 (1948).

A mass spectrometric study and review undertaken by O. T. Mikitin and L. N. Gorokhov, *Zhur. Neorg. Khim.* 6, 224 (1961), on the composition of beryllium vapor reveals that beryllium vaporizing both below and above the melting point, 1556°K., consists only of monatomic Be.

Beryllium (Be) (Ideal Gas) Mol. Wt. = 9.013

BERYLLIUM (Be) (IDEAL GAS) MOL. WT. = 9.013

Be

Ground State Configuration $1s^2 2s^2$

$\Delta H_{f0}^\circ = 77.241 \text{ kcal. mole}^{-1}$

$\Delta H_{f0}^\circ = 78.25 \pm 0.5 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = 32.545 \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Electronic Levels and Multiplicities

Heat of Formation

Derived from a third law analysis of the vapor pressure data. See Be crystal for references.

Heat Capacity and Entropy

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949).

T, °K.	C_p°	S°	ΔH_{f0}°	ΔF_{f0}°	Log K _p
100	4.000	27.000	77.241	75.881	1.00000
200	4.968	30.561	78.067	76.177	1.00000
298	4.968	32.545	78.255	76.231	1.00000
300	4.968	32.576	78.257	76.175	1.00000
400	4.968	35.114	78.307	76.093	1.00000
600	4.968	36.019	78.262	76.053	1.00000
700	4.968	36.785	78.187	76.024	1.00000
800	4.968	37.449	78.089	76.007	1.00000
900	4.968	38.037	77.969	75.994	1.00000
1000	4.968	38.557	77.825	75.983	1.00000
1100	4.968	39.031	77.658	75.972	1.00000
1200	4.968	39.463	77.466	75.961	1.00000
1300	4.968	39.861	77.251	75.950	1.00000
1400	4.968	40.224	77.018	75.939	1.00000
1500	4.968	40.572	76.768	75.928	1.00000
1600	4.968	40.892	76.506	75.917	1.00000
1700	4.968	41.193	76.237	75.906	1.00000
1800	4.968	41.477	75.965	75.895	1.00000
1900	4.968	41.745	75.695	75.884	1.00000
2000	4.968	42.001	75.428	75.873	1.00000
2100	4.969	42.243	75.165	75.862	1.00000
2200	4.970	42.474	74.906	75.851	1.00000
2300	4.972	42.695	74.651	75.840	1.00000
2400	4.975	42.907	74.400	75.829	1.00000
2500	4.977	43.110	74.154	75.818	1.00000
2600	4.982	43.306	73.913	75.807	1.00000
2700	4.986	43.494	73.677	75.796	1.00000
2800	4.997	43.675	73.446	75.785	1.00000
2900	5.007	43.851	73.220	75.774	1.00000
3000	5.021	44.021	73.000	75.763	1.00000
3100	5.037	44.186	72.785	75.752	1.00000
3200	5.057	44.346	72.575	75.741	1.00000
3300	5.081	44.502	72.370	75.730	1.00000
3400	5.109	44.654	72.170	75.719	1.00000
3500	5.142	44.802	71.975	75.708	1.00000
3600	5.179	44.948	71.785	75.697	1.00000
3700	5.221	45.090	71.600	75.686	1.00000
3800	5.268	45.230	71.420	75.675	1.00000
3900	5.319	45.368	71.245	75.664	1.00000
4000	5.376	45.503	71.075	75.653	1.00000
4100	5.440	45.637	70.910	75.642	1.00000
4200	5.508	45.768	70.750	75.631	1.00000
4300	5.581	45.899	70.595	75.620	1.00000
4400	5.659	46.028	70.445	75.609	1.00000
4500	5.741	46.156	70.300	75.598	1.00000
4600	5.828	46.283	70.160	75.587	1.00000
4700	5.919	46.410	70.025	75.576	1.00000
4800	6.014	46.535	69.895	75.565	1.00000
4900	6.113	46.660	69.770	75.554	1.00000
5000	6.215	46.785	69.650	75.543	1.00000
5100	6.320	46.909	69.535	75.532	1.00000
5200	6.428	47.033	69.425	75.521	1.00000
5300	6.538	47.156	69.320	75.510	1.00000
5400	6.650	47.278	69.220	75.499	1.00000
5500	6.763	47.402	69.125	75.488	1.00000
5600	6.877	47.525	69.035	75.477	1.00000
5700	6.993	47.648	68.950	75.466	1.00000
5800	7.109	47.771	68.870	75.455	1.00000
5900	7.226	47.894	68.795	75.444	1.00000
6000	7.340	48.015	68.725	75.433	1.00000

Beryllium Unipositive Ion (Be⁺)
(Ideal Gas) Mol. Wt. = 9.0165

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0					
100	33.922	33.922	+0.00	283.779	- 208.005
200	4.968	33.922	+0.09	284.711	- 206.673
300	4.968	33.922	+0.09	284.711	- 206.673
400	4.968	33.922	+0.09	284.711	- 206.673
500	4.968	33.922	+0.09	284.711	- 206.673
600	4.968	33.922	+0.09	284.711	- 206.673
700	4.968	33.922	+0.09	284.711	- 206.673
800	4.968	33.922	+0.09	284.711	- 206.673
900	4.968	33.922	+0.09	284.711	- 206.673
1000	4.968	33.922	+0.09	284.711	- 206.673
1100	4.968	33.922	+0.09	284.711	- 206.673
1200	4.968	33.922	+0.09	284.711	- 206.673
1300	4.968	33.922	+0.09	284.711	- 206.673
1400	4.968	33.922	+0.09	284.711	- 206.673
1500	4.968	33.922	+0.09	284.711	- 206.673
1600	4.968	33.922	+0.09	284.711	- 206.673
1700	4.968	33.922	+0.09	284.711	- 206.673
1800	4.968	33.922	+0.09	284.711	- 206.673
1900	4.968	33.922	+0.09	284.711	- 206.673
2000	4.968	33.922	+0.09	284.711	- 206.673
2100	4.968	33.922	+0.09	284.711	- 206.673
2200	4.968	33.922	+0.09	284.711	- 206.673
2300	4.968	33.922	+0.09	284.711	- 206.673
2400	4.968	33.922	+0.09	284.711	- 206.673
2500	4.968	33.922	+0.09	284.711	- 206.673
2600	4.968	33.922	+0.09	284.711	- 206.673
2700	4.968	33.922	+0.09	284.711	- 206.673
2800	4.968	33.922	+0.09	284.711	- 206.673
2900	4.968	33.922	+0.09	284.711	- 206.673
3000	4.968	33.922	+0.09	284.711	- 206.673
3100	4.968	33.922	+0.09	284.711	- 206.673
3200	4.968	33.922	+0.09	284.711	- 206.673
3300	4.968	33.922	+0.09	284.711	- 206.673
3400	4.968	33.922	+0.09	284.711	- 206.673
3500	4.968	33.922	+0.09	284.711	- 206.673
3600	4.968	33.922	+0.09	284.711	- 206.673
3700	4.968	33.922	+0.09	284.711	- 206.673
3800	4.968	33.922	+0.09	284.711	- 206.673
3900	4.968	33.922	+0.09	284.711	- 206.673
4000	4.968	33.922	+0.09	284.711	- 206.673
4100	4.968	33.922	+0.09	284.711	- 206.673
4200	4.968	33.922	+0.09	284.711	- 206.673
4300	4.968	33.922	+0.09	284.711	- 206.673
4400	4.968	33.922	+0.09	284.711	- 206.673
4500	4.968	33.922	+0.09	284.711	- 206.673
4600	4.968	33.922	+0.09	284.711	- 206.673
4700	4.968	33.922	+0.09	284.711	- 206.673
4800	4.968	33.922	+0.09	284.711	- 206.673
4900	4.968	33.922	+0.09	284.711	- 206.673
5000	4.968	33.922	+0.09	284.711	- 206.673
5100	4.968	33.922	+0.09	284.711	- 206.673
5200	4.968	33.922	+0.09	284.711	- 206.673
5300	4.968	33.922	+0.09	284.711	- 206.673
5400	4.968	33.922	+0.09	284.711	- 206.673
5500	4.968	33.922	+0.09	284.711	- 206.673
5600	4.968	33.922	+0.09	284.711	- 206.673
5700	4.968	33.922	+0.09	284.711	- 206.673
5800	4.968	33.922	+0.09	284.711	- 206.673
5900	4.968	33.922	+0.09	284.711	- 206.673
6000	4.968	33.922	+0.09	284.711	- 206.673

June 30, 1965

BERYLLIUM UNIPosITIVE ION (Be⁺) (IDEAL GAS)

MOL. WT. = 9.0165

Ground State Configuration 2s^{1/2}

ΔH_f⁰ = 292.2 ± .5 kcal/mole

ΔH_f⁰ 298.15 = 294.7 ± .5 kcal/mole

Electronic Levels and Quantum Weight

E, cm ⁻¹	g _i
0.0	2
31928.8	2
31935.4	4
88231.2	2
96495.4	2
96498.2	4
98053.2	10

Heat of Formation

The heat of formation was calculated from the equation: Be(g) + e⁻ → Be⁺(g) with the JANAP auxiliary value for Be(g) using an I.P. = 7.519225 X 10⁴ cm⁻¹ (215.001 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy

The electronic levels and quantum weights were obtained from C. E. Moore loc. cit. The electronic levels above 1 X 10⁵ cm⁻¹ were omitted because their contribution is negligible below 6000°K. The H⁺-H⁺ value at 0°K. is -1.481 kcal./mole.

Be⁺

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (R°-H ₂₉₈ °)/T cal. mole ⁻¹	H° - H ₂₉₈ kcal. mole ⁻¹	ΔH _f kcal. mole ⁻¹	ΔF _f kcal. mole ⁻¹	Log K _p
0	6.080	46.090	INFINITE	10.082	10.082	INFINITE
100	6.080	46.090	1.377	10.082	10.082	1.169
200	7.235	51.856	35.526	10.082	10.082	1.169
298	7.719	54.639	54.639	10.082	10.082	1.060
300	7.727	54.687	54.687	10.082	10.082	1.060
400	8.110	57.165	57.165	10.082	10.082	1.060
500	8.365	59.005	59.005	10.082	10.082	1.060
600	8.534	60.546	60.546	10.082	10.082	1.060
700	8.650	61.870	61.870	10.082	10.082	1.060
800	8.733	63.021	63.021	10.082	10.082	1.060
900	8.793	64.031	64.031	10.082	10.082	1.060
1000	8.843	64.993	64.993	10.082	10.082	1.060
1100	8.882	65.838	65.838	10.082	10.082	1.060
1200	8.913	66.572	66.572	10.082	10.082	1.060
1300	8.936	67.205	67.205	10.082	10.082	1.060
1400	8.953	67.738	67.738	10.082	10.082	1.060
1500	8.963	68.168	68.168	10.082	10.082	1.060
1600	8.967	68.500	68.500	10.082	10.082	1.060
1700	8.967	68.735	68.735	10.082	10.082	1.060
1800	8.963	68.881	68.881	10.082	10.082	1.060
1900	8.955	68.943	68.943	10.082	10.082	1.060
2000	8.943	68.920	68.920	10.082	10.082	1.060
2100	8.927	68.811	68.811	10.082	10.082	1.060
2200	8.908	68.619	68.619	10.082	10.082	1.060
2300	8.885	68.354	68.354	10.082	10.082	1.060
2400	8.859	68.028	68.028	10.082	10.082	1.060
2500	8.832	67.649	67.649	10.082	10.082	1.060
2600	8.800	67.224	67.224	10.082	10.082	1.060
2700	8.763	66.760	66.760	10.082	10.082	1.060
2800	8.722	66.260	66.260	10.082	10.082	1.060
2900	8.678	65.728	65.728	10.082	10.082	1.060
3000	8.631	65.168	65.168	10.082	10.082	1.060
3100	8.581	64.584	64.584	10.082	10.082	1.060
3200	8.528	63.980	63.980	10.082	10.082	1.060
3300	8.473	63.359	63.359	10.082	10.082	1.060
3400	8.416	62.725	62.725	10.082	10.082	1.060
3500	8.357	62.080	62.080	10.082	10.082	1.060
3600	8.295	61.427	61.427	10.082	10.082	1.060
3700	8.231	60.768	60.768	10.082	10.082	1.060
3800	8.165	60.106	60.106	10.082	10.082	1.060
3900	8.098	59.443	59.443	10.082	10.082	1.060
4000	8.030	58.780	58.780	10.082	10.082	1.060
4100	7.960	58.117	58.117	10.082	10.082	1.060
4200	7.889	57.454	57.454	10.082	10.082	1.060
4300	7.817	56.791	56.791	10.082	10.082	1.060
4400	7.744	56.128	56.128	10.082	10.082	1.060
4500	7.670	55.465	55.465	10.082	10.082	1.060
4600	7.595	54.802	54.802	10.082	10.082	1.060
4700	7.519	54.139	54.139	10.082	10.082	1.060
4800	7.442	53.476	53.476	10.082	10.082	1.060
4900	7.364	52.813	52.813	10.082	10.082	1.060
5000	7.285	52.150	52.150	10.082	10.082	1.060
5100	7.205	51.487	51.487	10.082	10.082	1.060
5200	7.124	50.824	50.824	10.082	10.082	1.060
5300	7.042	50.161	50.161	10.082	10.082	1.060
5400	6.959	49.498	49.498	10.082	10.082	1.060
5500	6.875	48.835	48.835	10.082	10.082	1.060
5600	6.790	48.172	48.172	10.082	10.082	1.060
5700	6.704	47.509	47.509	10.082	10.082	1.060
5800	6.617	46.846	46.846	10.082	10.082	1.060
5900	6.529	46.183	46.183	10.082	10.082	1.060
6000	6.440	45.520	45.520	10.082	10.082	1.060

Ground State Configuration $2s^2 +$

$$\Delta H_f^0 = [10.1 \pm 5.0] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = [54.64] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 298.15 = [6.6 \pm 5.0] \text{ kcal. mole}^{-1}$$

Electronic Levels and Multiplicities

$$\frac{E_i}{\bar{h} \nu} = \frac{E_i}{\bar{h} \nu}$$

$$\omega_e = [743] \text{ cm.}^{-1}$$

$$\omega_e x_e = [4.06] \text{ cm.}^{-1}$$

$$\omega_e = [1.97] \text{ Å}$$

$$B_e = [0.53780] \text{ cm.}^{-1}$$

$$r_e = [1.97] \text{ Å}$$

Heat of Formation.

The dissociation energy was estimated from the experimental energies for BeF(g), BeCl(g), and the gaseous lithium halides. The resulting value, 97.1 kcal. mole⁻¹, was combined with JANAF heats of formation for Be(g) and Br(g) in arriving at $\Delta H_f^0 298.15$.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of BeF(g), BeCl(g), and the gaseous lithium halides. The ground term was assumed to be similar to that of BeCl(g) and BeF(g), tabulated by G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950. A correlation of the internuclear distances for the alkali halides, BeF(g), and BeCl(g) was employed in deriving r_e .

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0						
100						
200						
298	16.500	25.400	25.400	4.000	- 88.400	61.897
300	16.562	25.502	25.500	4.031	- 88.409	61.897
400	18.100	30.506	26.072	1.774	- 95.345	44.605
500	18.850	34.630	27.464	3.623	- 94.883	34.210
600	19.350	38.114	28.889	5.535	- 94.401	27.315
700	19.656	41.120	30.427	7.485	- 93.916	22.415
800	19.900	43.762	31.932	9.464	- 93.428	18.756
900	20.063	46.115	33.380	11.462	- 92.945	15.930
1000	20.200	48.236	34.761	13.475	- 92.472	13.678
1100	20.311	50.167	36.075	15.501	- 92.012	11.846
1200	20.397	51.938	37.324	17.537	- 91.568	10.326
1300	20.457	53.573	38.512	19.580	- 91.142	9.046
1400	20.491	55.091	39.643	21.627	- 90.737	7.954
1500	20.500	56.505	40.720	23.677	- 90.355	7.012

Dec. 31, 1961; June 30, 1965

BERYLLIUM DIBROMIDE (BeBr₂)

(CRYSTAL)

MOL. WT. = 168.8302

$\Delta H_f^\circ =$ Unknown
 $\Delta H_f^\circ 298.15 = [-88.4 \pm 8] \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = [4.5] \text{ kcal. mole}^{-1}$
 $\Delta H_g^\circ 298.15 = 29.8 \pm 1.5 \text{ kcal. mole}^{-1}$

$S^\circ_{298.15} = [25.4 \pm 2.0] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $T_m = 761^\circ \text{K.}$

Heat of Formation.

The heat of formation was estimated from the work of W. Blitz and C. Messermecht, Z. Anorg. Chem. 148, 157 (1925) and Blitz, Klatte and Rahlfs, Z. Anorg. Chem. 166, 339 (1927) as reported in N. B. S. Circular 500, Washington, 1952. They measured the heat of solution of BeBr₂ in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be⁺⁺ and 2Br⁻ to obtain ΔH_f° of the crystal. However Be⁺⁺ was estimated by N. B. S. An uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with BeCl₂ and BeF₂. The entropy was also estimated by comparing with BeCl₂ and BeF₂ and using additive entropy values for the halide ions.

Melting Data.

The melting point has been reported by O. Rahlfs and W. Fischer, Z. Anorg. Chem. 211, 351 (1933) and by Lebean, Ann. Chim. Phys. 15, 472 (1899) as reported in N. B. S. Circular 500, Washington, 1952. The heat of melting was estimated by comparison with the sum of the heat of transition and melting for BeF₂ and BeCl₂.

Sublimation Data.

The heat of sublimation was obtained from an analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 624-695°K. The 3rd law analysis gave $\Delta H_{\text{sub}}^\circ 298 = 29.78$ with a drift of $-2.1 \pm 0.8 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$. A 2nd law analysis gave $\Delta H_{\text{sub}}^\circ 298 = 31.1 \pm 0.5 \text{ kcal. mole}^{-1}$. The 2nd law result was adopted in order to yield a real liquid region, no attempt was made to eliminate the drift since this would have caused the liquid region to become unreal.

Beryllium Dibromide (BeBr₂)
(Liquid) Mol. Wt. = 168.8302

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0							
100							
298	16.500	28.070	28.070	0.000	- 85.880	- 82.721	60.634
300	16.542	28.172	28.070	0.031	- 85.889	- 82.701	60.245
400	18.100	33.176	28.742	1.774	- 92.825	- 80.190	43.612
500	27.000	37.307	30.054	5.626	- 92.360	- 77.085	33.692
600	27.000	42.230	31.486	6.326	- 91.090	- 74.150	27.008
700	27.000	46.392	33.497	9.402	- 89.855	- 71.426	22.299
800	27.000	48.897	35.339	11.726	- 88.646	- 68.876	18.615
900	27.000	53.177	37.148	14.426	- 87.461	- 66.475	16.142
1000	27.000	56.022	38.896	17.126	- 86.301	- 64.206	14.031
1100	27.000	58.596	40.472	19.826	- 85.167	- 62.032	12.328
1200	27.000	60.945	42.173	22.526	- 84.059	- 60.000	10.927
1300	27.000	63.106	43.701	25.226	- 82.976	- 58.038	9.757
1400	27.000	65.107	45.160	27.926	- 81.918	- 56.160	8.767
1500	27.000	66.970	46.552	30.626	- 80.886	- 54.356	7.920
1600	27.000	68.712	47.883	33.326	- 82.634	- 52.542	7.177
1700	27.000	70.349	49.157	36.026	- 81.537	- 50.695	6.517
1800	27.000	71.892	50.378	38.726	- 80.446	- 48.913	5.939
1900	27.000	73.352	51.549	41.426	- 79.361	- 47.190	5.428
2000	27.000	74.737	52.674	44.126	- 78.283	- 45.527	4.975

BeBr₂

MOL. WT. = 168.8302

(LIQUID)

BERYLLIUM DIBROMIDE (BeBr₂)

S°_{298.15} = [28.07] cal. mole⁻¹ deg.⁻¹

T_m = 761°K.

T_b = [794]°K.

ΔH_f^o 298.15 = [-85.68 ± 3] kcal. mole⁻¹

ΔH_m^o = [4.5] kcal. mole⁻¹

ΔH_v^o = [23.9] kcal. mole⁻¹

Heat of Formation.

The heat of formation was obtained from that of BeBr₂(c) by adding ΔH_m^o and the difference between H₂₉₈ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for BeCl₂. A glass transition was assumed at 500°K. below which the heat capacity is that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeBr₂(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over between BeBr₂(l) and (g).

BERYLLIUM DIBROMIDE: (BeBr₂) (IDEAL GAS) MOL. WT. = 168.8302

Point Group D_{∞h}
S_{298.15} = [56.4 ± 2] cal. mole⁻¹ deg.⁻¹
Ground State Quantum Weight = 1
ΔH_f⁰ = [-54.2 ± 9.5] kcal. mole⁻¹
ΔH_f⁰ 298.15 = [-57.3 ± 9.5] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹
[205] (1)
[180] (2)
[890] (1)

Bond Distances: Be-Br = 1.90 Å

Bond Angle: Br-Be-Br = [180°]

Rotational Constant: B₀ = 0.02922 cm.⁻¹

Heat of Formation.

The heat of formation was obtained from that of the crystal plus ΔH_g⁰ 298.15, see BeBr₂(c) for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with BeCl₂. The bond length was reported by F. A. Alkshin, V. P. Spirodinov and O. A. Sobolev, Dokl. Akad. Nauk. SSSR 118, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k₁ for the BeF₂, BeCl₂, BeBr₂, BeI₂ series and also assuming k₁/k₂^{1/2} = 50 as for BeF₂. The principal moment of inertia is 95.7984 x 10⁻³⁹ g. cm.²

T, °K.	C _p ⁰	S ⁰ - (F ⁰ - H ₂₉₈ ⁰)/T	H ⁰ - H ₂₉₈ ⁰	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	3.200	-54.173	-54.173	INFINITE
100	10.302	53.488	77.372	-54.039	-54.088	176.046
200	14.473	66.400	100.000	-53.740	-53.769	246.001
300	16.194	75.057	109.068	-53.416	-53.460	294.675
400	17.359	80.083	114.314	-53.076	-53.137	324.763
500	18.048	83.259	117.771	-52.728	-52.806	346.001
600	18.473	85.359	120.156	-52.369	-52.457	359.599
700	18.753	86.821	121.821	-51.999	-52.099	366.001
800	18.921	87.771	122.821	-51.621	-51.721	369.599
900	19.000	88.359	123.359	-51.236	-51.336	371.001
1000	19.048	88.682	123.682	-50.844	-50.944	371.599
1100	19.073	88.771	123.771	-50.444	-50.544	371.721
1200	19.083	88.821	123.821	-50.036	-50.136	371.771
1300	19.088	88.859	123.859	-49.621	-49.721	371.799
1400	19.090	88.877	123.877	-49.200	-49.300	371.806
1500	19.091	88.883	123.883	-48.773	-48.873	371.811
1600	19.091	88.886	123.886	-48.344	-48.444	371.814
1700	19.091	88.887	123.887	-47.911	-48.011	371.816
1800	19.091	88.887	123.887	-47.473	-47.573	371.817
1900	19.091	88.887	123.887	-47.036	-47.136	371.818
2000	19.091	88.887	123.887	-46.600	-46.700	371.819
2100	19.091	88.887	123.887	-46.164	-46.264	371.820
2200	19.091	88.887	123.887	-45.729	-45.829	371.821
2300	19.091	88.887	123.887	-45.294	-45.394	371.822
2400	19.091	88.887	123.887	-44.859	-44.959	371.823
2500	19.091	88.887	123.887	-44.424	-44.524	371.824
2600	19.091	88.887	123.887	-43.989	-44.089	371.825
2700	19.091	88.887	123.887	-43.554	-43.654	371.826
2800	19.091	88.887	123.887	-43.119	-43.219	371.827
2900	19.091	88.887	123.887	-42.684	-42.784	371.828
3000	19.091	88.887	123.887	-42.249	-42.349	371.829
3100	19.091	88.887	123.887	-41.814	-41.914	371.830
3200	19.091	88.887	123.887	-41.379	-41.479	371.831
3300	19.091	88.887	123.887	-40.944	-41.044	371.832
3400	19.091	88.887	123.887	-40.509	-40.609	371.833
3500	19.091	88.887	123.887	-40.074	-40.174	371.834
3600	19.091	88.887	123.887	-39.639	-39.739	371.835
3700	19.091	88.887	123.887	-39.204	-39.304	371.836
3800	19.091	88.887	123.887	-38.769	-38.869	371.837
3900	19.091	88.887	123.887	-38.334	-38.434	371.838
4000	19.091	88.887	123.887	-37.899	-37.999	371.839
4100	19.091	88.887	123.887	-37.464	-37.564	371.840
4200	19.091	88.887	123.887	-37.029	-37.129	371.841
4300	19.091	88.887	123.887	-36.594	-36.694	371.842
4400	19.091	88.887	123.887	-36.159	-36.259	371.843
4500	19.091	88.887	123.887	-35.724	-35.824	371.844
4600	19.091	88.887	123.887	-35.289	-35.389	371.845
4700	19.091	88.887	123.887	-34.854	-34.954	371.846
4800	19.091	88.887	123.887	-34.419	-34.519	371.847
4900	19.091	88.887	123.887	-33.984	-34.084	371.848
5000	19.091	88.887	123.887	-33.549	-33.649	371.849
5100	19.091	88.887	123.887	-33.114	-33.214	371.850
5200	19.091	88.887	123.887	-32.679	-32.779	371.851
5300	19.091	88.887	123.887	-32.244	-32.344	371.852
5400	19.091	88.887	123.887	-31.809	-31.909	371.853
5500	19.091	88.887	123.887	-31.374	-31.474	371.854
5600	19.091	88.887	123.887	-30.939	-31.039	371.855
5700	19.091	88.887	123.887	-30.504	-30.604	371.856
5800	19.091	88.887	123.887	-30.069	-30.169	371.857
5900	19.091	88.887	123.887	-29.634	-29.734	371.858
6000	19.091	88.887	123.887	-29.199	-29.299	371.859

Beryllium Monochloride (BeCl)
(Ideal Gas) GFW = 44.4652

BERYLLIUM MONOCHLORIDE (BeCl)

(IDEAL GAS)

OPW = 44.4652

T, K	Cp ^a	gibbs/mol S ^b - (G ^c - H ^c)/T	H ^c - H ^c ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log Kp
0	-0.000	INFINITE	-2.118	13.947	13.947	INFINITE
100	6.959	44.200	58.426	-14.284	-26.531	-12.135
200	7.118	49.057	52.662	-14.721	-26.531	-10.809
298	7.563	51.984	-	0.000	14.500	7.625
300	7.571	52.031	0.014	14.499	7.582	5.524
400	8.243	56.074	3.932	14.423	3.016	-2.868
500	8.437	57.595	5.353	14.304	-1.318	-5.589
600	8.437	57.595	5.353	14.162	-4.771	-8.281
700	8.437	57.595	5.353	14.002	-8.449	-10.809
800	8.437	57.595	5.353	13.826	-12.402	-13.135
900	8.437	57.595	5.353	13.635	-16.645	-15.135
1000	8.437	57.595	5.353	13.426	-21.171	-16.816
1100	8.437	57.595	5.353	13.196	-26.006	-18.171
1200	8.437	57.595	5.353	12.944	-31.154	-19.131
1300	8.437	57.595	5.353	12.672	-36.639	-19.709
1400	8.437	57.595	5.353	12.377	-42.465	-20.006
1500	8.437	57.595	5.353	12.060	-48.639	-20.931
1600	8.437	57.595	5.353	11.727	-55.154	-21.431
1700	8.437	57.595	5.353	11.378	-62.006	-21.554
1800	8.437	57.595	5.353	10.995	-69.206	-21.291
1900	8.437	57.595	5.353	10.582	-76.751	-20.635
2000	8.437	57.595	5.353	10.143	-84.639	-19.581
2100	8.437	57.595	5.353	9.682	-92.865	-18.131
2200	8.437	57.595	5.353	9.204	-101.431	-16.281
2300	8.437	57.595	5.353	8.714	-110.343	-14.031
2400	8.437	57.595	5.353	8.214	-119.606	-11.381
2500	8.437	57.595	5.353	7.704	-129.221	-8.331
2600	8.437	57.595	5.353	7.184	-139.191	-4.781
2700	8.437	57.595	5.353	6.654	-149.516	-0.731
2800	8.437	57.595	5.353	6.114	-160.196	3.819
2900	8.437	57.595	5.353	5.564	-171.231	8.869
3000	8.437	57.595	5.353	5.004	-182.621	14.419
3100	8.437	57.595	5.353	4.434	-194.366	20.469
3200	8.437	57.595	5.353	3.854	-206.466	27.019
3300	8.437	57.595	5.353	3.264	-218.921	34.069
3400	8.437	57.595	5.353	2.664	-231.731	41.619
3500	8.437	57.595	5.353	2.054	-244.901	49.669
3600	8.437	57.595	5.353	1.434	-258.431	58.219
3700	8.437	57.595	5.353	0.804	-272.331	67.269
3800	8.437	57.595	5.353	0.164	-286.601	76.819
3900	8.437	57.595	5.353	-0.486	-301.241	86.869
4000	8.437	57.595	5.353	-1.126	-316.251	97.419
4100	8.437	57.595	5.353	-1.756	-331.631	108.469
4200	8.437	57.595	5.353	-2.376	-347.381	119.919
4300	8.437	57.595	5.353	-2.986	-363.501	131.769
4400	8.437	57.595	5.353	-3.586	-379.991	144.019
4500	8.437	57.595	5.353	-4.176	-396.841	156.669
4600	8.437	57.595	5.353	-4.756	-414.051	169.719
4700	8.437	57.595	5.353	-5.326	-431.621	183.169
4800	8.437	57.595	5.353	-5.886	-449.551	197.019
4900	8.437	57.595	5.353	-6.436	-467.841	211.269
5000	8.437	57.595	5.353	-6.976	-486.481	225.919
5100	8.437	57.595	5.353	-7.506	-505.471	240.969
5200	8.437	57.595	5.353	-8.026	-524.811	256.419
5300	8.437	57.595	5.353	-8.536	-544.501	272.269
5400	8.437	57.595	5.353	-9.036	-564.541	288.519
5500	8.437	57.595	5.353	-9.526	-584.931	305.169
5600	8.437	57.595	5.353	-10.006	-605.671	322.219
5700	8.437	57.595	5.353	-10.476	-626.761	339.669
5800	8.437	57.595	5.353	-10.936	-648.201	357.519
5900	8.437	57.595	5.353	-11.386	-669.991	375.769
6000	8.437	57.595	5.353	-11.826	-692.131	394.419

Dec. 31, 1960; Sept. 30, 1961; Mar. 31, 1962; Mar. 31, 1964; Sept. 30, 1966

Ground State Configuration $2\Sigma^+$
 $S_{298.15}^\circ = 51.984$ gibbs/mol
 $\Delta H_{298.15}^\circ = 13.9 \pm 3.0$ kcal/mol
 $\Delta H_{298.15}^\circ = 14.5 \pm 3.0$ kcal/mol

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	g_i
0	2
27970	4

$\omega_e = 845.29$ cm⁻¹
 $\omega_e x_e = 4.831$ cm⁻¹
 $\sigma = 1$

$B_0 = [0.769]$ cm⁻¹
 $\alpha_e = [0.0063]$
 $x_e = [1.75]$ Å

Heat of Formation.

Novikov¹ measured 39 bands in the ultraviolet spectrum of BeCl(g). A linear extrapolation leads to a ground state dissociation energy of 36,555 cm⁻¹. The authors assumed that the non-crossing rule applied and that the ground and first excited states had a common dissociation limit. However, in the analogous case of BeF, treated in the same way by the above authors, it was shown by Mann² that these assumptions were not correct. If it is assumed that the excited state dissociates $A''\pi \rightarrow Be(^3P) + P(^2P)$ and the ground state $X^2\Sigma \rightarrow Be(^1S_0) + P(^2P)$, then $V_{00} + D'$ should equal D'' + excitation energy of Be atom. We find $V_{00} + D' = 27,960 + 30,390 = 58,350$ and $D'' + E_e = 36,555 + 21,981 = 58,536$ which is in excellent agreement. Thus the dissociation energy to ground state atoms is taken as 104.5 kcal/mol, which leads to a heat of formation of 3 kcal/mol using reaction a.

Greenbaum et al.³ report equilibrium constants for reaction b in the temperature range 1575 - 1724°K using the molecular flow effusion method. Also Hildenbrand et al.⁴ report equilibrium constants for reactions c and d which were calculated from mass spectrometric ion intensities. The $\Delta H_{298.15}^\circ$ values by second and third law analysis for these data and the corresponding $\Delta H_{298.15}^\circ$ values are listed below.

Author	Method	Reaction	T°K	Second Law $\Delta H_{298.15}^\circ$ kcal/mol	Third Law $\Delta H_{298.15}^\circ$ kcal/mol	Drift eu
--------	--------	----------	-----	--------------------------------------------------	-------------------------------------------------	-------------

1. Novikov Spectroscopic (a) $BeCl(g) \rightarrow Be(g) + Cl(g)$ 1575-1724 93.56 ± 7 85.87 -4.521 1.3

3. Greenbaum Kp (b) $BeCl_2(g) + Be(l) \rightarrow 2 BeCl(g)$ 1382-1554 27.5 ± 2 28.25 - .779 15.3 ± 2

4. Hildenbrand Kp from Mass Spectroscopy (c) $Be(g) + AlCl(g) \rightarrow BeCl(g) + Al(g)$ 1382-1556 33.41 ± 8 36.08 2.198 14.1 ± 2.5

(d) $Be(g) + BeCl_2(g) \rightarrow 2 BeCl(g)$ 1382-1556 33.41 ± 8 36.08 2.198 14.1 ± 2.5

The equilibrium data of Greenbaum et al.³ was not weighted, since calculations indicated the possibility of reaction of BeCl(g) with the Al_2O_3 tube at the temperatures and pressures used. The data of Hildenbrand et al.⁴, which reflect the true gas phase equilibria and appear consistent with each other, were adopted, yielding $\Delta H_{298.15}^\circ = 14.5$ kcal/mol.

Heat Capacity and Entropy.

The vibrational constants used to calculate the functions were derived by Novikov¹ from a two constant equation $(\omega_0 - (2\nu'' + 1)\omega_0 x_0'' = 0)$. The electronic levels were obtained from Herzberg⁵. B_e was obtained from the estimated bond length, which was taken to be slightly less than that in $BeCl_2(g)$, and α_e was estimated from the Morse potential function.

References

1. M. M. Novikov and L. N. Tunitskii, Optics and Spectroscopy **9**, 396 (1960).

2. D. E. Mann, Natl. Bureau Standards Report 7587, July 1, 1962.

3. M. A. Greenbaum, M. L. Arin, M. Vong and M. Farber, J. Phys. Chem. **68**, 791-5 (1964).

4. D. L. Hildenbrand, E. Murad, L. F. Theard and F. Ju, Philco Report U-5197, Contract AF 04(611) - 10743, July 30, 1965.

5. G. Herzberg, "Molecular Spectra and Molecular Structure of Diatomic Molecules", 2nd Edition, D. Van Nostrand Company, Inc., New York, 1950.

T, °K	Cp°	S° -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0				234.000	225.970	-165.640
100	7.826	50.870	50.870	234.009	225.920	-164.562
200	7.834	50.919	50.871	234.009	225.920	-164.562
300	7.834	50.919	50.871	234.009	225.920	-164.562
400	7.834	50.919	50.871	234.009	225.920	-164.562
500	7.834	50.919	50.871	234.009	225.920	-164.562
600	7.834	50.919	50.871	234.009	225.920	-164.562
700	7.834	50.919	50.871	234.009	225.920	-164.562
800	7.834	50.919	50.871	234.009	225.920	-164.562
900	7.834	50.919	50.871	234.009	225.920	-164.562
1000	7.834	50.919	50.871	234.009	225.920	-164.562
1100	7.834	50.919	50.871	234.009	225.920	-164.562
1200	7.834	50.919	50.871	234.009	225.920	-164.562
1300	7.834	50.919	50.871	234.009	225.920	-164.562
1400	7.834	50.919	50.871	234.009	225.920	-164.562
1500	7.834	50.919	50.871	234.009	225.920	-164.562
1600	7.834	50.919	50.871	234.009	225.920	-164.562
1700	7.834	50.919	50.871	234.009	225.920	-164.562
1800	7.834	50.919	50.871	234.009	225.920	-164.562
1900	7.834	50.919	50.871	234.009	225.920	-164.562
2000	7.834	50.919	50.871	234.009	225.920	-164.562
2100	7.834	50.919	50.871	234.009	225.920	-164.562
2200	7.834	50.919	50.871	234.009	225.920	-164.562
2300	7.834	50.919	50.871	234.009	225.920	-164.562
2400	7.834	50.919	50.871	234.009	225.920	-164.562
2500	7.834	50.919	50.871	234.009	225.920	-164.562
2600	7.834	50.919	50.871	234.009	225.920	-164.562
2700	7.834	50.919	50.871	234.009	225.920	-164.562
2800	7.834	50.919	50.871	234.009	225.920	-164.562
2900	7.834	50.919	50.871	234.009	225.920	-164.562
3000	7.834	50.919	50.871	234.009	225.920	-164.562
3100	7.834	50.919	50.871	234.009	225.920	-164.562
3200	7.834	50.919	50.871	234.009	225.920	-164.562
3300	7.834	50.919	50.871	234.009	225.920	-164.562
3400	7.834	50.919	50.871	234.009	225.920	-164.562
3500	7.834	50.919	50.871	234.009	225.920	-164.562
3600	7.834	50.919	50.871	234.009	225.920	-164.562
3700	7.834	50.919	50.871	234.009	225.920	-164.562
3800	7.834	50.919	50.871	234.009	225.920	-164.562
3900	7.834	50.919	50.871	234.009	225.920	-164.562
4000	7.834	50.919	50.871	234.009	225.920	-164.562
4100	7.834	50.919	50.871	234.009	225.920	-164.562
4200	7.834	50.919	50.871	234.009	225.920	-164.562
4300	7.834	50.919	50.871	234.009	225.920	-164.562
4400	7.834	50.919	50.871	234.009	225.920	-164.562
4500	7.834	50.919	50.871	234.009	225.920	-164.562
4600	7.834	50.919	50.871	234.009	225.920	-164.562
4700	7.834	50.919	50.871	234.009	225.920	-164.562
4800	7.834	50.919	50.871	234.009	225.920	-164.562
4900	7.834	50.919	50.871	234.009	225.920	-164.562
5000	7.834	50.919	50.871	234.009	225.920	-164.562
5100	7.834	50.919	50.871	234.009	225.920	-164.562
5200	7.834	50.919	50.871	234.009	225.920	-164.562
5300	7.834	50.919	50.871	234.009	225.920	-164.562
5400	7.834	50.919	50.871	234.009	225.920	-164.562
5500	7.834	50.919	50.871	234.009	225.920	-164.562
5600	7.834	50.919	50.871	234.009	225.920	-164.562
5700	7.834	50.919	50.871	234.009	225.920	-164.562
5800	7.834	50.919	50.871	234.009	225.920	-164.562
5900	7.834	50.919	50.871	234.009	225.920	-164.562
6000	7.834	50.919	50.871	234.009	225.920	-164.562

June 30, 1968

Ground State Configuration $[1s^2 2s^1]$
 $S_{298.15}^\circ = [50.9 \pm 2]$ gibbs/mol

$\Delta H_f^\circ = [233 \pm 20]$ kcal/mol
 $\Delta H_f^\circ = [234 \pm 20]$ kcal/mol

State	$\epsilon_i, \text{cm}^{-1}$	Quantum Weights g_i
$1s^+$	0	1
$2s^+$	[10000]	6
$3s^+$	[15000]	2
$4s^+$	[30000]	3
$1d$	[35000]	2
$2d$	[40000]	1

$\omega_8 \times g_8 = [4.8] \text{ cm}^{-1}$
 $\sigma = 1$
 $\tau_0 = [1.8] \text{ Å}$

Heat of Formation

Krasnov (1) has reported calculations of the ionization potentials(IP) for the monohalides (MX, where X = F, Cl, Br, and I) of Group IIA elements (M = Mg, Ca, Sr, and Ba). Based on his data we obtain graphically the value IP(BeCl, g) = 8.9 ± 0.5 eV. The value of $\Delta H_{f298}^\circ(\text{BeCl}^+, \text{g})$ is derived as 219 ± 15 kcal/mol, using $\Delta H_{f298}^\circ(\text{BeCl}, \text{g}) = 13.9$ kcal/mol. Beckett (2) reported the ionization potential of BeCl(g) to be approximately 9 ± 1 eV, yielding $\Delta H_{f298}^\circ(\text{BeCl}^+, \text{g}) = 222 \pm 23$ kcal/mol. Hildenbrand (3) measured the appearance potential (AP) of BeCl⁺(g) to be 9.5 ± 0.7 eV which is on the same order of the above IP values, and assumed that IP(BeCl⁺, g) = AP(BeCl⁺, g) = 9.5 ± 0.7 eV. Using this IP value, we obtain $\Delta H_{f298}^\circ(\text{BeCl}^+, \text{g}) = 234 \pm 20$ kcal/mol which is adopted.

Heat Capacity and Entropy

The six electronic states are obtained from Fougere (3). The electronic levels are estimated by comparison with those of isoelectronic molecules, BeS (4), BeO (5, 6), and MgO (5, 7). The values of $\omega_e, \omega_e x_e$ are estimated by comparison with those for BeCl(g) and LiCl(g). B_e and a_e are calculated using the method suggested by Herzberg (8). The bond distance is estimated (8). The moment of inertia is $3.865 \times 10^{-39} \text{ gm}^2$. The enthalpy at 0°K is -2.15 kcal/mol.

References

1. K. S. Krasnov, Teplotiz. Vysokikh Temperatur, Akad. Nauk SSSR, 3, 927 (1965).
2. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
3. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. 44, 285 (1965).
4. G. Verhaegen and W. G. Richards, Proc. Phys. Soc. 90, 579 (1967).
5. G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950.
6. G. Verhaegen and W. G. Richards, J. Chem. Phys. 45, 1828 (1966).
7. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).
8. K. S. Krasnov, Zh. Strukt. Khim. 3, 209 (1960).
9. D. L. Hildenbrand, E. Murad, L. P. Theard, and F. Ju, Aeronutronic, Philco Corporation, Report No. U-3187, July 30, 1965.

(Ideal Gas)	Mol. Wt. = 63.4636
-------------	--------------------

(Ideal Gas)	Mol. Wt.	=	63.4636
-------------	----------	---	---------

BeCIF

(IDEAL GAS)

BERYLLIUM CHLORIDE FLUORIDE (BeClF)

$$\Delta H^\circ_c = [-137.2 + 10] \text{ kcal. mole}^{-1}$$
$$\Delta H_{\text{f}}^{\circ} \text{ kcal. mole}^{-1} = [-137 + 10] \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$$\text{Be-F} = [1.43] \text{\AA}$$

$\tau = \phi$

Rotational Constant: $B_0 = 0.12970 \text{ cm}^{-1}$

Heat of Formation.

The heat of formation was estimated by assuming $\Delta H_f = 0$ for the reaction $\text{BeF}_2 + \text{BeCl}_2 \rightarrow 2\text{BeClF}$

Heat Capacity and Entropy.

The structure, bond lengths and frequencies were all estimated from the properties of BaCl_2 and BeF_2 . The principal moment of inertia is $21.579 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.318	67.830	68.514	-2.797	-137.177	INFINITE
200	13.218	67.830	68.514	-2.068	-137.156	300.761
300	18.118	67.830	68.514	-1.400	-137.136	150.957
400	22.988	67.830	68.514	-0.867	-137.116	101.675
500	27.830	67.830	68.514	-0.422	-137.096	76.103
600	32.650	67.830	68.514	-0.222	-137.085	61.129
700	37.450	67.830	68.514	-0.122	-137.074	51.162
800	42.230	67.830	68.514	-0.068	-137.063	44.005
900	46.990	67.830	68.514	-0.033	-137.052	38.445
1000	51.740	67.830	68.514	-0.018	-137.041	33.145
1100	56.480	67.830	68.514	-0.008	-137.030	28.132
1200	61.210	67.830	68.514	-0.003	-137.020	24.202
1300	65.940	67.830	68.514	-0.001	-137.010	22.545
1400	70.670	67.830	68.514	-0.000	-137.000	21.107
1500	75.400	67.830	68.514	-0.000	-137.000	19.836
1600	80.130	67.830	68.514	-0.000	-137.000	18.700
1700	84.860	67.830	68.514	-0.000	-137.000	17.680
1800	89.590	67.830	68.514	-0.000	-137.000	16.780
1900	94.320	67.830	68.514	-0.000	-137.000	15.980
2000	99.050	67.830	68.514	-0.000	-137.000	15.250
2100	103.780	67.830	68.514	-0.000	-137.000	14.570
2200	108.510	67.830	68.514	-0.000	-137.000	13.940
2300	113.240	67.830	68.514	-0.000	-137.000	13.360
2400	117.970	67.830	68.514	-0.000	-137.000	12.850
2500	122.700	67.830	68.514	-0.000	-137.000	12.400
2600	127.430	67.830	68.514	-0.000	-137.000	12.000
2700	132.160	67.830	68.514	-0.000	-137.000	11.650
2800	136.890	67.830	68.514	-0.000	-137.000	11.350
2900	141.620	67.830	68.514	-0.000	-137.000	11.090
3000	146.350	67.830	68.514	-0.000	-137.000	10.850
3100	151.080	67.830	68.514	-0.000	-137.000	10.650
3200	155.810	67.830	68.514	-0.000	-137.000	10.480
3300	160.540	67.830	68.514	-0.000	-137.000	10.340
3400	165.270	67.830	68.514	-0.000	-137.000	10.220
3500	170.000	67.830	68.514	-0.000	-137.000	10.120
3600	174.730	67.830	68.514	-0.000	-137.000	10.040
3700	179.460	67.830	68.514	-0.000	-137.000	9.980
3800	184.190	67.830	68.514	-0.000	-137.000	9.940
3900	188.920	67.830	68.514	-0.000	-137.000	9.910
4000	193.650	67.830	68.514	-0.000	-137.000	9.890
4100	198.380	67.830	68.514	-0.000	-137.000	9.880
4200	203.110	67.830	68.514	-0.000	-137.000	9.880
4300	207.840	67.830	68.514	-0.000	-137.000	9.890
4400	212.570	67.830	68.514	-0.000	-137.000	9.910
4500	217.300	67.830	68.514	-0.000	-137.000	9.940
4600	222.030	67.830	68.514	-0.000	-137.000	9.980
4700	226.760	67.830	68.514	-0.000	-137.000	10.040
4800	231.490	67.830	68.514	-0.000	-137.000	10.120
4900	236.220	67.830	68.514	-0.000	-137.000	10.22

Dec. 31, 1960; June 30, 1965

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	8.045	6.825	31.435	-2.461	-117.536	-117.536	INFINITE
200	12.800	18.110	21.095	-1.397	-117.845	-114.006	249.147
298	15.360	19.760	18.760	∞	-117.845	-110.239	120.446
300	15.340	19.856	18.760	∞	-117.845	-108.659	76.176
400	17.390	24.598	20.394	1.662	-117.328	-106.592	77.649
500	18.530	28.612	21.647	3.482	-116.944	-103.070	56.312
600	19.140	32.049	23.101	5.360	-116.501	-99.651	43.555
700	19.445	35.024	24.597	7.290	-116.024	-96.325	32.085
800	19.660	37.635	26.067	9.245	-115.508	-93.000	22.559
900	19.843	39.962	27.484	11.230	-115.070	-89.694	15.073
1000	20.000	42.061	28.838	13.222	-114.602	-86.786	9.721
1100	20.131	43.973	30.129	15.220	-114.144	-83.721	5.032
1200	20.237	45.730	31.357	17.248	-113.698	-80.400	1.033
1300	20.317	47.353	32.525	19.276	-113.268	-77.779	14.754
1400	20.371	48.861	33.639	21.310	-112.854	-74.773	12.570
1500	20.400	50.267	34.701	23.349	-112.460	-71.860	11.217
					-112.087	-68.972	10.049

Heat of Formation.

W. H. Johnson and A. A. Gilliland, J. Res. Nat'l. Bur. Stand. 65A, 59 (1961) have directly reacted beryllium and chlorine and obtained $\Delta H_f^\circ = -118.03 \pm 0.56$ though the crystal form of the product was unknown. P. Gross, C. Haymen, P. D. Greene and J. T. Bingham, Fulmer Research Institute, Report R. 163/SR.1/Sept. 1964 under Contract AF61(052)-447 also by direct combustion of the elements obtain $\Delta H_f^\circ = -117.1 \pm 0.4$ kcal. mole⁻¹. The crystal form of the sample was deduced to be α' by a comparison experiment, the assumption is made here that α and α' are identical. C. J. Thompson, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 380 (1962) by solution calorimetry report a $\Delta H_f^\circ = -118.25 \pm 0.5$ kcal. mole⁻¹. Initially this sample was reported to be of unknown crystal form. However, G. C. Sinke, private communication February 1965, reports that an x-ray of the sample used has been reinterpreted, in the light of more recent data, as being approximately 50% α' and 50% β . Using the heats of transition adopted for these tables heats of formation of -117.3 ± 0.8 kcal. mole⁻¹ for α and -118.6 ± 0.8 kcal. mole⁻¹ for β have been adopted as being the most consistent with all measurements.

Heat Capacity and Entropy.

R. A. McDonald and F. L. Oetting, J. Phys. Chem. scheduled for publication in the Nov. 1965 issue have measured the heat capacity of the α' form from 13° to 304°K. and the enthalpy (relative to the α' form) from 676° to 688°K. The assumption has been made that the α and α' forms are identical and the heat capacity curve between 304° and 676°K. has been estimated graphically. The entropy was obtained by integration of the heat capacity curve assuming $S_{13} = 0.16$ cal. mole⁻¹ deg.⁻¹. The sample was identified as α' by x-ray diffraction both before and after the experiments.

Melting Data.

The temperature and heat of melting were reported by McDonald and Oetting, loc. cit. Several investigations of the melting point are in disagreement mainly due to the uncertainty of the crystal form of the material and a solid state transition just below the pure α -liquid melting point.

Sublimation Data.

The adopted heat of sublimation was derived from that of the β form and heat of the α - β transition at 298°K.

Beryllium Dichloride, Beta (β -BeCl₂)

(Crystal) Mol. Wt. = 79.9182

BERYLLIUM DICHLORIDE, BETA (β -BeCl₂) (CRYSTAL)

MOL. WT. = 79.9182

BeCl₂

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞	∞
100	7.595	5.761	12.650	19.410	2.474	-118.667	-118.667	-118.667	INFINITE
200	12.380	12.650	19.410	1.352	-118.860	-111.157	-111.157	-111.157	251.686
298	14.920	18.120	18.120	∞	∞	-107.435	-107.435	-107.435	121.460
300	14.960	18.212	18.120	1.028	-118.594	-107.435	-107.435	-107.435	78.748
400	16.420	22.729	18.726	1.000	-117.290	-100.050	-100.050	-100.050	78.212
500	17.400	26.506	19.915	3.295	-117.953	-100.050	-100.050	-100.050	54.212
600	18.120	29.744	21.200	5.073	-117.956	-96.503	-96.503	-96.503	43.730
800	18.660	32.583	22.704	6.915	-117.194	-93.020	-93.020	-93.020	35.149
900	19.450	37.377	25.191	12.79	-115.185	-84.595	-84.595	-84.595	29.041
1000	19.730	39.442	26.748	12.693	-115.938	-82.866	-82.866	-82.866	24.675
1100	19.930	41.332	27.900	14.677	-115.515	-79.611	-79.611	-79.611	19.116
1200	20.060	43.073	29.175	16.678	-115.103	-76.366	-76.366	-76.366	15.817
1300	20.160	44.685	30.475	18.685	-114.703	-73.121	-73.121	-73.121	13.907
1400	20.263	46.184	31.798	20.712	-114.323	-69.876	-69.876	-69.876	12.298
1500	20.300	47.583	32.421	22.743	-113.958	-66.631	-66.631	-66.631	10.795

Heat of Formation.

See table for α -BeCl₂ for details.

Heat Capacity and Entropy.

R. A. McDonald and P. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the heat capacity of the β -form from 13 to 304°K. and the enthalpy of the β -form from 298° to 678°K. The entropy was obtained by integration of the heat capacity curve based on S₁₃ = 0.06 cal. mole⁻¹ deg.⁻¹. The sample was identified as β -BeCl₂ both before and after the low temperature experiments.

Melting Data.

The temperature and heat of melting were obtained from cross over point of the tables for β -BeCl₂ and liquid BeCl₂.

Transition Data.

The temperature of the β to α transition was obtained from McDonald and Oetting, loc. cit. The heat of the transition is a function of the heat capacity curve chosen for α -BeCl₂ between 298 and 678°K. A straight line interpolation was used by McDonald and Oetting, which gives a different result (1.49 kcal. mole⁻¹) than the curve employed here. It should also be noted that the transitional heat is not included in this table, which is for β -BeCl₂ only.

Sublimation Data.

The heat of sublimation was determined by 2nd and 3rd law analysis of vapor pressure data as described fully on the table for BeCl₂ (g).

T, °K. C_p $\left[\frac{\text{cal. mole}^{-1} \text{ deg.}^{-1}}{S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T} \right] \left[\frac{\text{kcal. mole}^{-1}}{H^{\circ} - H_{298}^{\circ}} \right] \Delta H_f^{\circ} \Delta F_f^{\circ} \log K_p$

0									
100									
200									
298	14.920	19.095	19.095	0.000	-117.425	-106.541			76.063
300	14.960	19.137	19.095	0.028	-117.410	-106.476			77.483
400	16.420	23.674	19.671	1.603	-117.113	-102.870			96.203
500	29.020	26.432	20.000	3.766	-116.307	-98.357			43.431
600	29.020	33.723	22.609	6.668	-114.816	-96.120			35.010
700	29.020	42.021	24.495	12.270	-113.864	-93.119			29.072
800	29.020	45.489	26.407	15.376	-110.568	-87.706			21.207
1000	29.020	48.547	30.271	18.276	-109.180	-85.243			18.629
1100	29.020	51.313	32.060	21.178	-107.830	-82.914			16.473
1200	29.020	53.822	33.701	24.080	-106.526	-80.707			14.698
1300	29.020	56.121	35.105	26.982	-105.264	-78.634			13.144
1400	29.020	58.311	36.066	29.986	-104.076	-76.608			11.948
1500	29.020	60.313	36.456	32.786	-102.740	-74.699			10.882
1600	29.020	62.166	36.861	35.688	-101.285	-72.786			9.942
1700	29.020	63.806	37.286	38.688	-99.709	-70.957			9.109
1800	29.020	65.604	42.102	41.602	-97.983	-69.057			8.388
1900	29.020	67.173	43.808	44.394	-96.405	-67.222			7.732
2000	29.020	68.662	45.014	47.206	-94.126	-65.510			7.158

$S_{298.15}^{\circ} = 19.065 \pm 1 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $T_m = 688^{\circ}\text{K.}$
 $T_b = 805^{\circ}\text{K.}$
 $\Delta H_f^{\circ} = 2.07 \pm 0.06 \text{ kcal. mole}^{-1}$
 $\Delta H_v^{\circ} = 25.0 \pm 2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} = -117.4 \pm 1.5 \text{ kcal. mole}^{-1}$

Heat of Formation.

The heat of formation was obtained from that of the α -BeCl₂ plus ΔH_m° plus the difference of $H_{808}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

R. A. McDonald and P. L. Oetting, J. Phys. Chem. scheduled for publication in the November 1965 issue have measured the enthalpy of the liquid, relative to α -BeCl₂, from 688° to 713°K. The heat capacity was assumed constant above this point and also below the melting point to 480°K, where a glass transition was assumed. Below 416°K, the heat capacity was assumed to be that of β -BeCl₂. The entropy was calculated in a manner analogous to the heat of formation.

Melting Data.

See the table for α -BeCl₂ (c) for details.

Vaporization Data.

The boiling point and heat of vaporization were obtained from the cross over point of the BeCl₂ (l) and (g) tables. The analysis of the liquid vapor pressure data is given on the table for BeCl₂ (g).

Mol. wt. = 79.9182

(Ideal Gas)

Mol. wt. = 79.9182

BERYLLIUM DICHLORIDE (BeCl_2) (IDEAL GAS)

MOL. WT. = 79.9182

 BeCl_2 Point Group D_{∞h}
$$\Delta H^\circ = -86.4 + 2.5 \text{ kcal. mole}^{-1}$$

∞ h

$$\Delta H_f^\circ \text{ (kcal. mole}^{-1}\text{)} = -86.1 + 2.5 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$$\omega, \text{ cm.}^{-1}$$

Bond Distance: Be-Cl = 1.77 Å

Bond Angle: Cl-Be-Cl = 180°
Rotational Constant: $B = 0.0759 \text{ cm}^{-1}$

Heat of Formation.

The vapor pressure data over the crystal was assumed to be for the β -form. The 2nd and 3rd law analyses of the data are summarized below after conversion to a common process. The data were also analyzed using gaseous free energy data¹⁰ but no significant improvement of the results was noted.

Ref.	Temperature Range	ΔH°_{298} sub β -BeCl ₂ kcal. mole ⁻¹	Drift in 3rd law cal. mole ⁻¹ deg. ⁻¹
1	20-250°C.	1.0	0.0
2	20-250°C.	1.0	0.0
3	20-250°C.	1.0	0.0
4	20-250°C.	1.0	0.0
5	20-250°C.	1.0	0.0
6	20-250°C.	1.0	0.0
7	20-250°C.	1.0	0.0
8	20-250°C.	1.0	0.0
9	20-250°C.	1.0	0.0
10	20-250°C.	1.0	0.0
11	20-250°C.	1.0	0.0
12	20-250°C.	1.0	0.0
13	20-250°C.	1.0	0.0
14	20-250°C.	1.0	0.0
15	20-250°C.	1.0	0.0
16	20-250°C.	1.0	0.0
17	20-250°C.	1.0	0.0
18	20-250°C.	1.0	0.0
19	20-250°C.	1.0	0.0
20	20-250°C.	1.0	0.0
21	20-250°C.	1.0	0.0
22	20-250°C.	1.0	0.0
23	20-250°C.	1.0	0.0
24	20-250°C.	1.0	0.0
25	20-250°C.	1.0	0.0
26	20-250°C.	1.0	0.0
27	20-250°C.	1.0	0.0
28	20-250°C.	1.0	0.0
29	20-250°C.	1.0	0.0
30	20-250°C.	1.0	0.0
31	20-250°C.	1.0	0.0
32	20-250°C.	1.0	0.0
33	20-250°C.	1.0	0.0
34	20-250°C.	1.0	0.0
35	20-250°C.	1.0	0.0
36	20-250°C.	1.0	0.0
37	20-250°C.	1.0	0.0
38	20-250°C.	1.0	0.0
39	20-250°C.	1.0	0.0
40	20-250°C.	1.0	0.0
41	20-250°C.	1.0	0.0
42	20-250°C.	1.0	0.0
43	20-250°C.	1.0	0.0
44	20-250°C.	1.0	0.0
45	20-250°C.	1.0	0.0
46	20-250°C.	1.0	0.0
47	20-250°C.	1.0	0.0
48	20-250°C.	1.0	0.0
49	20-250°C.	1.0	0.0
50	20-250°C.	1.0	0.0
51	20-250°C.	1.0	0.0
52	20-250°C.	1.0	0.0
53	20-250°C.	1.0	0.0
54	20-250°C.	1.0	0.0
55	20-250°C.	1.0	0.0
56	20-250°C.	1.0	0.0
57	20-250°C.	1.0	0.0
58	20-250°C.	1.0	0.0
59	20-250°C.	1.0	0.0
60	20-250°C.	1.0	0.0
61	20-250°C.	1.0	0.0
62	20-250°C.	1.0	0.0
63	20-250°C.	1.0	0.0
64	20-250°C.	1.0	0.0
65	20-250°C.	1.0	0.0
66	20-250°C.	1.0	0.0
67	20-250°C.	1.0	0.0
68	20-250°C.	1.0	0.0
69	20-250°C.	1.0	0.0
70	20-250°C.	1.0	0.0
71	20-250°C.	1.0	0.0
72	20-250°C.	1.0	0.0
73	20-250°C.	1.0	0.0
74	20-250°C.	1.0	0.0
75	20-250°C.	1.0	0.0
76	20-250°C.	1.0	0.0
77	20-250°C.	1.0	0.0
78	20-250°C.	1.0	0.0
79	20-250°C.	1.0	0.0
80	20-250°C.	1.0	0.0
81	20-250°C.	1.0	0.0
82	20-250°C.	1.0	0.0
83	20-250°C.	1.0	0.0
84	20-250°C.	1.0	0.0
85	20-250°C.	1.0	0.0
86	20-250°C.	1.0	0.0
87	20-250°C.	1.0	0

Ref.	Temperature Range T_D	ΔH_{298}° sub 2nd law	β -BaCl ₂ 3rd law	ΔH_{298}° cal. mole ⁻¹	Drift in 3rd law cal. mole ⁻¹ deg. ⁻¹
1	680 - 740*	33.5 \pm 0.6	31.98	-3.4 \pm 0.7	
2	680 - 740	34.3	31.22	-4.7	
1	613 - 663	31.6 \pm 1.6	30.91	-1.3 \pm 2.6	
2	638 - 668	35.6	31.07	-7.0	
3	441 - 518	31.4 \pm 0.8	32.45	2.5 \pm 1.7	
3	510 - 600*	31.8 \pm 0.3	32.07	0.40 \pm 0.5	
4	460 - 504*	32.45 \pm 0.4	32.40	0.14 \pm 0.8	

experiments rejected due to failure of a statistical test.

References:

1. O. Röhlfes and W. Fischer, *Z. Anorg. Allgem. Chem.* **211**, 349 (1953).
2. W. Fischer, T. Petzel and S. Lauter, *Z. Anorg. Allgem. Chem.* **335**, 226 (1964).
3. M. A. Greenbaum et al., Rocket Power, Inc., 7th Quarterly Report March 31, 1963 under Contract AF 04(611)-7414.
4. D. L. Hildenbrand, L. P. Theard, G. Murad and F. Ju, Ford Motor Co., Aeronutronic Div., Report U-3068 April 1965.

It is obvious that there is no real agreement between the data sets, and some of this is undoubtedly due to the difficulty of keeping a single crystal form throughout a series of measurements. It is also doubtful that water vapor was adequately excluded in some experiments. We have adopted the only piece of work which shows adequate 2nd and 3rd law agreement, and no third law trend, that is $\Delta H_{\text{fus}} = 32.5 \pm 1$ kcal. mole⁻¹ from ref. 4. It is interesting to note that all the other data can be made much more precise and its drift removed if a constant pressure is added to all points. The addition which varied from 20-30% of the lowest pressure in each data set serves to indicate the magnitude of the possible systematic errors.

Heat Capacity and Entropy.

The linear structure of $\text{BeCl}_2(\text{g})$ has been confirmed by the electric deflection experiments of A. Büchler, A. D. Little, Inc. Progress Report No. 6, 31st Dec. 1963 under Contract No. DA-19-020-ORD-5584. The bond length was obtained from the electron diffraction data of P. A. Akishin, V. P. Spiridonov and G. A. Sobel'ev, Dokl. Akad. Nauk SSSR 118, 1134 (1958). A Büchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958) have reported the infra-red spectrum and assigned 1113 as the asymmetric stretch ν_3 and 482 as the bending frequency ν_2 . However, A. Snelson, IIT Research Institute, Report No. IIRI-C6013-4 May 1964 under Contract No. DA-31-124-ARO(D)-111 using matrix isolation experiments has shown this second band to be due to beryllium chloride solid. The unobserved frequencies were estimated from a valence force field treatment by assuming that the ratio of stretching to bending force constant was 50:1 the same as for $\text{BeF}_2(\text{g})$. This gives 230 cm^{-1} for ν_2 and 375 cm^{-1} for the asymmetric stretch. The principal moment of inertia is 36.864×10^{-40} gm^2 .

 BeCl_2 2.

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1961; June 30, 1965

Electronic Levels and Multiplicities

E , cm. ⁻¹	g_i
0	2

$$\omega_e = 1265.62 \text{ cm.}^{-1}$$

$$\omega_e x_e = 9.12 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$B_e = 1.4877 \text{ cm.}^{-1}$$

$$\alpha_e = 0.01685 \text{ cm.}^{-1}$$

$$r_e = 1.361 \text{ \AA}$$

Heat of Formation.

The selected ΔH_f° 298.15 was calculated from the experimental data of M. A. Greenbaum, R. E. Yates, M. L. Arlin, M. Areshadi, J. Heher, and M. Farber, *J. Phys. Chem.* **67**, 703 (1963). A molecular flow effusion method was employed by Farber, et al., for the reaction: $\text{BeF}_2(\text{g}) + \text{Be}(\text{c}, 1) = 2\text{BeF}(\text{g})$ from 1425°-1675°K. Using the data reported by Farber, et al. partial pressures, and equilibrium constants were calculated and used to obtain a third law heat for this reaction. From this third law heat the selected ΔH_f° 298.15 was calculated. The following auxiliary data was used: ΔH_f° 298.15 = -168 ± 3 kcal. mole and free energy functions from the JANAP Table for $\text{BeF}_2(\text{g})$, dated June 30, 1963.

The vapor pressure of an equal mixture of Be powder and $\text{BeF}_2(\text{c})$ was measured in a graphite cell by a torsion-effusion method over the temperature range 800°-900°K by D. L. Hildenbrand, L. P. Theard, and N. D. Potter, *Aeronautic Technical Report U-1606*, March 15, 1962. No vapor pressure increase over pure BeF_2 was detected. Assuming a detection limit of 20% of the BeF_2 vapor pressure they calculated that $D_0^\circ < 6.8 \text{ e.v.}$ for BeF . In a similar manner mass spectrometric and effusion pressure measurements on a BeF_2 -Al system by D. L. Hildenbrand, L. P. Theard, and P. Ju, *Aeronautic Technical Report U-1988*, Jan. 31, 1963, and D. L. Hildenbrand, *Aeronautic*, spectrometrically measured the species formed when a reducing agent (Al) was added to BeF_2 , SrF_2 , CaF_2 , and MgF_2 . The D_0° values found for the species, BeF , SrF , CaF , and MgF , suggested to Margrave that the D_0° of BeF was likely to be in the range 5 ± 1 e.v.

J. L. Margrave and co-workers, University of Wisconsin, private communication, Dec. 13, 1962, have mass spectrometrically measured the species formed when a reducing agent (Al) was added to BeF_2 , SrF_2 , CaF_2 , and MgF_2 . The D_0° values found for the species, BeF , SrF , CaF , and MgF , suggested to Margrave that the D_0° of BeF was likely to be in the range 5 ± 1 e.v.

V. M. Tatevskii, L. N. Tuntakii, and M. M. Navikov, *Optics and Spectroscopy* **5**, 521 (1958), measured the emission spectra of BeF . On the basis of their analysis of the vibrational structure they gave a rather high value (6.0 ± 0.5 e.v.) for the D_0° of BeF . In a recent report on the dissociation energy of BeF , D. E. Mann, National Bureau of Standards Preliminary Report No. 7587, July 1, 1962, has analyzed the spectral data in the literature including the Russian work and concludes that a $D_0^\circ \approx 6.2 \text{ e.v.}$ is probable.

A. G. Ouydon, Imperial College, London, private communication, Sept. 5, 1962, and W. C. Price, Kings College, London, private communication, March 1, 1963, suggested the Russians have chosen the wrong dissociation products. Therefore, the D_0° value they reported was about 2.5 e.v. too high.

Heats of formation and D_0° values for $\text{BeF}(\text{g})$ are summarized as follows:

D_0°	Remarks
$5 \pm 1 \text{ e.v.}$	J. L. Margrave (loc. cit.)
5.5 e.v.	A. G. Ouydon (loc. cit.) and W. C. Price (loc. cit.)
$-19.2 \text{ kcal. mole}^{-1}$	D. E. Mann (loc. cit.)
$-30.7 \text{ kcal. mole}^{-1}$	Calculated from the 2nd law ΔH_f° of Farber, et al.
$-46.8 \text{ kcal. mole}^{-1}$	The selected value.
$-48.3 \pm 2.5 \text{ kcal. mole}^{-1}$	Vapor Pressure of a BeF_2 -Al system. Hildenbrand, et al.
$-49.7 \pm 2.0 \text{ kcal. mole}^{-1}$	Vapor pressure of a BeF_2 -Be system. Hildenbrand, et al.
$> -58 \text{ kcal. mole}^{-1}$	V. M. Tatevskii et al., (loc. cit.)
$< 6.7 \text{ e.v.}$	
$< 6.8 \text{ e.v.}$	
$> -60 \text{ kcal. mole}^{-1}$	
$-86.3 \text{ kcal. mole}^{-1}$	
$8.0 \pm 0.5 \text{ e.v.}$	

Heat Capacity and Entropy.

The molecular constants used for this table were taken from O. Herzberg, "Molecular Spectra and Structure I. Spectra of Diatomic Molecules," D. van Nostrand Co., Inc., New York, 1950. To facilitate a comparison with Herzberg's constants, the molecular constants reported by Tatevskii, et al., were changed to the equilibrium state. The two sets of constants showed very slight differences.

T, °K.	C _p ^o	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-2.082	50.237	50.237	50.237	INFINITE
100	6.958	41.515	-1.388	49.900	52.004	52.004	113.649
200	9.980	46.741	-0.692	49.692	54.226	54.226	59.226
298	7.140	48.132	0.000	49.678	56.451	56.451	41.263
300	7.144	48.196	0.013	49.679	56.473	56.473	41.138
400	7.431	51.280	0.436	49.775	58.724	58.724	32.084
500	7.726	52.980	0.981	49.924	60.946	60.946	25.638
600	7.977	54.611	1.500	50.086	63.134	63.134	22.095
700	8.177	56.057	2.085	50.286	65.282	65.282	20.384
800	8.335	57.359	2.728	50.488	67.423	67.423	18.618
900	8.456	58.544	3.419	50.703	69.556	69.556	16.882
1000	8.554	59.644	4.152	50.935	71.686	71.686	15.169
1100	8.632	59.663	4.942	51.186	73.801	73.801	13.434
1200	8.696	60.217	5.785	51.457	75.902	75.902	11.685
1300	8.749	60.915	6.680	51.748	77.990	77.990	9.936
1400	8.794	61.566	7.625	52.060	79.665	79.665	8.185
1500	8.833	62.174	8.620	52.304	81.646	81.646	6.434
1600	8.866	62.745	9.665	52.569	83.597	83.597	4.683
1700	8.896	63.283	10.761	52.850	85.549	85.549	2.932
1800	8.922	63.792	11.907	53.138	87.476	87.476	1.181
1900	8.945	64.275	13.103	53.434	89.384	89.384	-0.570
2000	8.967	64.735	14.350	53.738	91.269	91.269	-2.279
2100	8.986	65.173	15.647	54.050	93.137	93.137	-3.938
2200	9.002	65.591	16.994	54.369	94.984	94.984	-5.547
2300	9.016	65.992	18.391	54.694	96.814	96.814	-7.106
2400	9.027	66.376	19.838	55.025	98.629	98.629	-8.615
2500	9.035	66.745	21.335	55.362	100.426	100.426	-10.074
2600	9.040	67.101	22.882	55.705	102.206	102.206	-11.483
2700	9.043	67.443	24.480	56.054	103.969	103.969	-12.842
2800	9.045	67.773	26.127	56.408	105.714	105.714	-14.151
2900	9.046	68.093	27.824	56.767	107.441	107.441	-15.410
3000	9.046	68.402	29.571	57.130	109.150	109.150	-16.619
3100	9.045	68.701	31.368	57.497	110.841	110.841	-17.778
3200	9.043	68.991	33.215	57.868	112.514	112.514	-18.887
3300	9.040	69.272	35.112	58.242	114.170	114.170	-19.946
3400	9.036	69.545	37.059	58.619	115.809	115.809	-20.955
3500	9.031	69.811	39.056	59.000	117.431	117.431	-21.914
3600	9.025	70.069	41.103	59.384	119.037	119.037	-22.823
3700	9.019	70.321	43.200	59.771	120.628	120.628	-23.682
3800	9.012	70.566	45.347	60.161	122.204	122.204	-24.491
3900	9.004	70.805	47.544	60.555	123.765	123.765	-25.250
4000	9.000	71.039	49.791	60.954	125.311	125.311	-25.959
4100	9.229	71.267	52.088	61.358	126.842	126.842	-26.618
4200	9.238	71.489	54.435	61.767	128.358	128.358	-27.227
4300	9.247	71.707	56.832	62.181	129.859	129.859	-27.786
4400	9.256	71.919	59.279	62.600	131.345	131.345	-28.295
4500	9.265	72.127	61.776	63.024	132.816	132.816	-28.754
4600	9.274	72.331	64.333	63.453	134.272	134.272	-29.163
4700	9.283	72.531	66.946	63.887	135.713	135.713	-29.522
4800	9.292	72.726	69.613	64.326	137.139	137.139	-29.831
4900	9.301	72.918	72.336	64.770	138.550	138.550	-30.090
5000	9.309	73.106	75.091	65.219	139.946	139.946	-30.300
5100	9.318	73.290	77.888	65.673	141.327	141.327	-30.461
5200	9.326	73.471	80.729	66.132	142.693	142.693	-30.572
5300	9.335	73.649	83.613	66.596	144.044	144.044	-30.643
5400	9.343	73.824	86.544	67.065	145.380	145.380	-30.674
5500	9.352	73.995	89.519	67.539	146.701	146.701	-30.674
5600	9.360	74.164	92.539	68.018	148.007	148.007	-30.645
5700	9.369	74.329	95.603	68.501	149.298	149.298	-30.586
5800	9.377	74.492	98.711	68.988	150.574	150.574	-30.497
5900	9.385	74.653	101.863	69.480	151.835	151.835	-30.378
6000	9.394	74.811	105.059	69.976	153.081	153.081	-30.229

GFW = 47.009

(CRYSTAL)

BERYLLIUM DIFLUORIDE (BeF₂)Beryllium Difluoride (BeF₂)

(Crystal)

GFW = 47.009

S_{298.15} = 12.752 ± 0.04 gibbs/mol

Tt = 500°K (low quartz + high quartz)

Tm = 825°K

 $\Delta H_f^\circ = -244.8 \pm 1.0$ kcal/mol $\Delta H_f^\circ_{298.15} = -245.4 \pm 1.0$ kcal/mol $\Delta H_t^\circ = 0.0526$ kcal/mol $\Delta H_m^\circ = 1.137$ kcal/mol $\Delta H_s^\circ_{298.15} = 55.15$ kcal/mol

Heat of Formation

ΔH_f° is the value selected by Parker (1), based on a thorough review of data for BeF₂(c, vitreous, aqueous) and BeO(c). Parker's analysis remains essentially unchanged for BeO(c) and BeF₂(c), even though the results for BeF₂(HF, aqueous) become more negative by 0.93 kcal/mol due to JANAF selections for HF(aqueous). Three values derived by Parker for BeF₂(c) from PbF₂(c) are changed due to JANAF auxiliary data; these values become -246.9, -246.0 and -247.2 for the three paths used by Parker.

The adopted ΔH_f° was derived by combination of calorimetric data for Be(c) + F₂(g) → BeF₂(vitreous) and BeF₂(c) → BeF₂(vitreous). Churney and Armstrong (2) obtained $\Delta H_f^\circ_{298.15} = -244.32 \pm 0.8$ kcal/mol for vitreous BeF₂ by combustion in fluorine of polytetrafluoroethylene and mixtures of Be(c) with polytetrafluoroethylene. $\Delta H_f^\circ_{298.15}(c + \text{vitreous}) = 1.125 \pm 0.016$ kcal/mol was measured via solution calorimetry by Taylor and Gardner (3).

Heat Capacity and Entropy

Cp° is based on JANAF curve fits of measurements by adiabatic calorimetry (8-300°K) and by ice calorimetry (354-776°K) as reported by Taylor and Gardner (3). The sample was estimated as approximately 99.5% BeF₂. Analyses indicated that the major impurity was about 0.3% oxygen, mainly in the form of absorbed water. Petrographic examination and X-ray diffraction showed the sample to be composed almost completely of quartz-type crystals. The entropy is derived from the smoothed Cp° based on the extrapolation S° = 0.0065 gibbs/mol. The adopted Cp° above 300°K agrees closely with the relative enthalpy data and shows a remarkable similarity to that of SiO₂ (low quartz, high quartz).

Transition Data

Tt is the value selected by Taylor and Gardner (3) from their relative enthalpy data. ΔH_t° is the corresponding difference in relative enthalpy from the JANAF curve fits for the two crystalline forms. Levina (4) studied the polymorphism of BeF₂ by observing the peaks in Cp near the transition temperatures. For low quartz + high quartz, Levina's peak began near 438°K, was complete near 503°K, and gave $\Delta H_t = 0.17$ kcal/mol. Levina found a second transition attributed to a form analogous to tridymite; this began above 670°K, was complete by 740°K, and gave $\Delta H_t = 0.24$ kcal/mol. There is no evidence for this transition in the relative enthalpy data, so we suspect that its occurrence may be due to impurities in Levina's sample. Levina also found that the cristobalite-like phase transformed in the region 380 to 420°K with $\Delta H_t = 1.27$ kcal/mol.

Melting Data

See the table for BeF₂(t).

Heat of Sublimation

See the table for BeF₂(g).

References

1. V. B. Parker, Natl. Bur. Std. Report 10004, chapter 3, p. 58, issued Jan. 1, 1969.
2. K. L. Churney and G. T. Armstrong, J. Res. Natl. Bur. Std. 73A, 281 (1969).
3. A. R. Taylor and T. Estelle Gardner, U. S. Bur. Mines RI-665H, 1965.
4. M. E. Levina, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 8 (2), 177 (1965).

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	-2.024	-244.846	-244.846	INFINITE
100	5.020	3.526	21.571	-1.605	-245.132	-241.602	528.020
200	9.341	6.430	13.791	-1.072	-245.437	-237.612	259.669
298	12.385	12.752	12.752	.000	-245.400	-234.078	171.564
300	12.435	12.829	12.752	.023	-245.398	-234.008	170.674
400	14.943	16.749	13.270	1.392	-245.238	-230.231	125.792
500	15.370	20.514	14.333	3.090	-244.851	-226.513	99.009
600	16.170	23.378	15.607	4.662	-244.653	-222.864	81.174
700	17.120	25.275	16.772	6.314	-244.453	-219.250	68.453
800	18.220	26.235	17.772	8.058	-244.253	-215.617	58.117
900	19.520	26.368	18.814	9.858	-243.834	-212.100	50.117
1000	19.370	32.361	20.610	11.750	-243.467	-208.627	45.595
1100	20.120	34.240	21.765	13.722	-243.051	-205.163	40.762
1200	20.720	35.725	22.674	15.604	-242.565	-201.739	36.742
1300	21.720	37.731	23.957	17.604	-242.008	-198.355	33.346

Beryllium Difluoride (BeF₂)

GFW = 47.009

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGr°	Log Kp
0							
100							
200							
298	11.927	14.321	14.321	0.000	-244.275	-233.421	171.102
300	11.977	14.395	14.321	.022	-244.274	-233.353	169.998
400	14.151	18.159	14.820	1.316	-244.169	-229.726	125.516
500	15.669	21.488	15.827	2.830	-243.986	-226.135	98.844
600	16.862	24.054	17.022	4.459	-243.731	-222.588	81.077
700	17.680	26.131	18.258	6.148	-243.502	-219.066	66.402
800	18.797	28.379	19.540	8.032	-243.287	-215.568	53.510
900	19.653	31.643	20.783	9.956	-242.613	-212.237	43.016
1000	20.469	33.956	21.996	11.961	-242.131	-208.688	45.652
1100	21.058	35.946	23.174	14.047	-241.601	-205.588	40.847
1200	22.028	38.427	24.317	16.214	-240.987	-202.761	36.671
1300	22.785	39.620	25.426	18.452	-240.397	-199.140	33.071
1400	23.532	41.336	26.502	20.768	-239.724	-195.992	30.596
1500	24.271	42.985	27.546	23.156	-239.005	-192.683	28.104
1600	25.005	44.575	28.561	25.622	-240.995	-189.766	25.221
1700	25.734	46.113	29.548	28.166	-240.995	-187.475	23.279
1800	26.460	47.604	30.510	30.769	-239.079	-184.475	21.279
1900	27.183	49.054	31.448	33.451	-238.024	-180.414	20.752
2000	27.904	50.467	32.364	36.205	-236.905	-177.410	19.386

Sept. 30, 1961; June 30, 1963; Dec. 31, 1963; June 30, 1964

Heat of Formation

ΔHf° is obtained from that of the crystal by means of ΔHr° = 1.125 ± 0.016 kcal/mol for BeF₂(c) + BeF₂(vitreous) at 298.15°K. Further details are given in the section on Melting Data. ΔHf°(l) actually is based on the direct determination of ΔHf°(vitreous) by Churney and Armstrong (2) as discussed on the crystal table.

Heat Capacity and Entropy

Cp° is based on a JANAF curve fit of relative enthalpies of Taylor and Gardner (2) for the liquid (828-1183°K) and vitreous (320-473°K) forms of BeF₂. The combined data yield a normal Cp° curve and reveal no need for a glass transition. Scatter in the data is somewhat larger than for the crystal, presumably due to minor variations in the vitreous state at the conclusion of each drop. S°_{298.15}(l) is calculated from that of the crystal by addition of ΔSm° and the difference for crystal and liquid of (S°₈₂₈-S°_{298.15}).

Melting Data

Tm is the value selected by Taylor and Gardner (2) from their relative enthalpy data. These showed premelting starting near 804°K and complete melting above 828°K. Cooling of the liquid produced the vitreous state. Tm has also been reported as 815 (3), 821 (4), 818 (5) and 816 ± 5°K (6).

Solution calorimetry (2) gave ΔHr° = 1.125 ± 0.016 kcal/mol for BeF₂(low quartz) + BeF₂(vitreous) at 298.15°K. Confirmation of this result came from transposed temperature-drop calorimetry (1) and calorimetric conversion (3). These gave 1.1 ± 0.2 and 1.1 ± 0.5 kcal/mol, respectively. Combination of ΔHr° = 1.125 with JANAF enthalpies yields ΔHm° = 1.137 kcal/mol.

Vaporization Data

Tb is the calculated temperature at which ΔGr° = 0 for BeF₂(l) + BeF₂(g). ΔHv° is the corresponding value of ΔHr°. These calculations neglect the presence of dimer, which is assumed to be negligible based on extrapolation of the equations of Belousov (3). Cantor (10) obtained Tb = 1442°K by extrapolation of his vapor pressures (1146-1372°K).

References

1. K. L. Churney and G. T. Armstrong, J. Res. Natl. Bur. Std. 73A, 281 (1969).
2. A. R. Taylor and T. E. Gardner, U. S. Bur. Mines RI-6664, 1965.
3. M. A. Greenbaum, J. N. Foster, M. L. Arin and M. Farber, J. Phys. Chem. 67, 36 (1963).
4. R. E. Thoma, H. Insley, H. A. Friedman and C. F. Weaver, J. Phys. Chem. 64, 865 (1960).
5. K. A. Sene and R. W. Stone, J. Phys. Chem. 62, 453 (1958).
6. D. M. Roy, R. Roy and E. F. Osborn, J. Amer. Ceram. Soc. 36, 185 (1953).
7. M. E. Melnichak, unpublished result quoted by J. L. Holm and O. J. Kleppa, Inorg. Chem. 8, 207 (1969).
8. P. Gross, Fulmer Res. Inst. Report R.163/19/April 1965, Stokes Porges, England.
9. V. I. Belousov, L. N. Sidorov, S. A. Komarov and P. A. Akishin, Zh. Fiz. Khim. 41, 2969 (1967); Russ. J. Phys. Chem. 41, 1598 (1967).
10. S. Cantor, J. Chem. Eng. Data 10, 237 (1965).

Point Group D_{∞h}

$$\Delta H_f^\circ = -190.3 \pm 1.0 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 54.36 \pm 0.3 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = -190.25 \pm 1.0 \text{ kcal/mol}$$

Ground State Quantum Weight = 1

Beryllium Difluoride (BeF₂)

$$GFW = 47.009$$

(Ideal Gas)

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	-0.00	INF INITE		2.615	-190.287	INF INITE
100	7.088	46.287		1.000	-190.287	190.287
200	9.774	50.192		1.029	-190.284	206.694
298	11.061	54.360		1.000	-190.250	196.251
300	11.100	54.429		1.021	-190.250	196.391
400	11.955	57.767		1.176	-190.304	194.738
500	12.573	60.404		2.404	-190.387	63.938
600	13.038	62.819		3.685	-190.480	
700	13.392	64.857		5.008	-190.580	
800	13.663	66.664		6.361	-190.680	
900	13.873	68.266		7.738	-190.804	
1000	14.036	69.756		9.134	-190.933	
1100	14.166	71.100		10.544	-191.079	
1200	14.269	72.337		11.966	-191.243	
1300	14.353	73.483		13.398	-191.426	
1400	14.422	74.548		14.853	-191.627	
1500	14.479	75.536		16.332	-191.847	
1600	14.527	76.482		17.832	-192.080	
1700	14.567	77.384		19.351	-192.326	
1800	14.602	78.198		20.895	-192.584	
1900	14.631	78.956		22.461	-192.854	
2000	14.656	79.673		24.044	-193.134	
2100	14.678	80.359		25.648	-193.424	
2200	14.698	81.018		27.276	-193.724	
2300	14.715	81.672		28.931	-194.034	
2400	14.729	82.319		30.606	-194.354	
2500	14.743	82.960		32.303	-194.684	
2600	14.755	83.599		34.021	-195.024	
2700	14.765	84.236		35.760	-195.374	
2800	14.775	84.873		37.519	-195.734	
2900	14.783	85.511		39.298	-196.104	
3000	14.791	86.151		41.097	-196.484	
3100	14.798	86.796		42.916	-196.874	
3200	14.804	87.443		44.755	-197.274	
3300	14.810	88.091		46.614	-197.684	
3400	14.815	88.739		48.493	-198.104	
3500	14.820	89.387		50.392	-198.534	
3600	14.825	89.995		52.311	-198.974	
3700	14.829	90.603		54.250	-199.424	
3800	14.833	91.211		56.209	-199.884	
3900	14.838	91.819		58.188	-200.354	
4000	14.843	92.427		60.187	-200.834	
4100	14.848	93.035		62.206	-201.324	
4200	14.853	93.643		64.245	-201.824	
4300	14.858	94.251		66.304	-202.334	
4400	14.863	94.859		68.383	-202.854	
4500	14.868	95.467		70.482	-203.384	
4600	14.873	96.075		72.601	-203.924	
4700	14.878	96.683		74.740	-204.474	
4800	14.883	97.291		76.900	-205.034	
4900	14.888	97.899		79.079	-205.604	
5000	14.893	98.507		81.278	-206.184	
5100	14.898	99.115		83.507	-206.774	
5200	14.903	99.723		85.756	-207.374	
5300	14.908	100.331		88.035	-207.984	
5400	14.913	100.939		90.344	-208.604	
5500	14.918	101.547		92.683	-209.234	
5600	14.923	102.155		95.052	-209.874	
5700	14.928	102.763		97.461	-210.524	
5800	14.933	103.371		99.900	-211.184	
5900	14.938	103.979		102.369	-211.854	
6000	14.943	104.587		104.868	-212.534	

Dec. 31, 1960; Sept. 30, 1961; June 30, 1963; Dec. 31, 1963; June 30, 1964; June 30, 1970

Vibrational Frequencies and Degeneracies

$$\sigma = 2$$

$$\text{Bond Distance: Be-F} = 1.40 \pm 0.03 \text{ \AA}$$

$$\text{Bond Angle: F-Be-F} = 180^\circ$$

$$\text{Rotational Constant: } B_0 = 0.22635 \text{ cm}^{-1}$$

$$\text{Heat of Formation}$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

$$\Delta H_f^\circ$$

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	22.140	21.300	21.300	0.000	-390.240	-372.171	272.008
300	22.200	21.437	21.300	0.041	-390.238	-372.059	271.045
400	25.200	28.244	22.208	2.414	-390.080	-366.019	199.083
500	27.800	34.154	24.019	5.068	-390.559	-359.958	157.337
600	30.000	39.426	26.155	7.862	-390.187	-353.871	128.897
700	32.500	43.760	28.352	11.276	-389.629	-347.863	108.808
800	34.770	48.480	30.642	14.271	-388.093	-341.940	93.414
900	35.620	52.392	32.845	17.592	-388.294	-336.099	81.616
1000	34.330	55.971	34.981	20.960	-387.554	-330.339	72.196
1100	35.000	59.275	37.041	24.457	-386.776	-324.654	64.503
1200	35.500	62.544	39.072	27.986	-385.970	-319.042	58.106
1300	36.100	65.214	40.939	31.570	-385.138	-313.498	52.704
1400	36.550	67.906	42.761	35.203	-384.287	-308.020	48.084
1500	37.000	70.443	44.523	38.860	-383.419	-302.602	44.089

GFW = 72.9464

(CRYSTAL)

LITHIUM TRIFLUOROBERYLLATE (LiBeF₃)

ΔHf° = Unknown

ΔHf°_{298.15} = -390.2 ± 0.7 kcal/mol

ΔHm° = Unknown

S°_{298.15} = [21.3 ± 2] gibbs/mol

Tm = 633°K

Heat of Formation.

The ΔHf°_{298.15} = -390.2 ± 0.7 kcal/mol was calculated from the ΔHr°_{298.15} = -2.24 ± 0.08 kcal/mol of the reaction $\text{LiF}(c) + \text{LiBeF}_3(c) = \text{Li}_2\text{BeF}_4(c)$ measured (calorimetrically) by P. Gross, Fulmer Research Institute, Administrative Report No. 4, January 1966.

Heat Capacity and Entropy.

The heat capacity (298 - 1100°K) was estimated from the difference of the Cp° values for $\text{Li}_2\text{BeF}_4(c)$ and $\text{LiF}(c)$. Above 1100°K the values were extrapolated graphically. The entropy was estimated by addition of S°₂₉₈ for $\text{BeF}_2(c)$ and $\text{LiF}(c)$.

Melting Data.

Tm was obtained from the phase diagram of a mixture of $\text{LiF}(c)$ and $\text{BeF}_2(c)$ reported by A. L. Mathews and C. F. Bass, Jr., ORNL-TM 1129, May 1965.

Lithium Trifluoroberyllate (LiBeF₃)
(Ideal Gas) Mol. Wt. = 72.953 INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	-2.978	-210.240	-210.240	INFINITE
100	8.450	52.222	-2.180	-210.614	-209.573	457.999
200	10.450	55.106	-1.825	-211.314	-208.269	227.575
298	14.691	60.889	-1.009	-212.000	-206.629	131.436
300	14.665	63.979	-0.889	-212.012	-206.596	150.498
400	17.636	68.629	-0.651	-212.603	-204.697	111.836
500	19.704	72.891	-0.573	-213.862	-202.585	88.545
600	21.137	76.428	-0.570	-214.319	-200.284	72.050
700	22.148	79.487	-0.591	-214.701	-197.614	61.789
800	22.879	82.074	-0.602	-215.033	-195.495	53.404
900	23.420	85.002	-0.607	-215.339	-193.033	46.873
1000	23.830	88.091	-0.611	-215.633	-190.539	41.640
1100	24.146	90.378	-0.610	-215.924	-188.015	37.353
1200	24.395	92.490	-0.609	-216.219	-185.465	33.776
1300	24.593	94.451	-0.607	-216.522	-182.890	30.745
1400	24.754	96.280	-0.605	-216.835	-180.291	28.143
1500	24.886	97.992	-0.603	-217.163	-177.659	25.885
1600	24.996	99.602	-0.601	-217.501	-174.947	23.895
1700	25.088	101.120	-0.599	-217.844	-172.179	22.195
1800	25.165	102.556	-0.597	-218.191	-169.364	20.729
1900	25.232	103.919	-0.595	-218.541	-166.507	19.463
2000	25.289	105.214	-0.593	-218.894	-163.608	18.363
2100	25.338	106.449	-0.591	-219.251	-160.665	17.404
2200	25.381	107.629	-0.589	-219.611	-157.680	16.569
2300	25.419	108.758	-0.587	-220.000	-154.654	15.843
2400	25.452	109.841	-0.585	-220.399	-151.597	15.213
2500	25.481	110.880	-0.583	-220.800	-148.509	14.673
2600	25.507	111.880	-0.581	-221.211	-145.390	14.217
2700	25.531	112.843	-0.579	-221.634	-142.242	13.833
2800	25.552	113.772	-0.577	-222.069	-139.065	13.513
2900	25.571	114.669	-0.575	-222.516	-135.868	13.253
3000	25.588	115.536	-0.573	-222.974	-132.650	13.049
3100	25.603	116.376	-0.571	-223.443	-129.411	12.897
3200	25.617	117.189	-0.569	-223.924	-126.152	12.793
3300	25.630	117.977	-0.567	-224.416	-122.874	12.733
3400	25.642	118.743	-0.565	-224.919	-119.577	12.713
3500	25.652	119.486	-0.563	-225.434	-116.261	12.733
3600	25.662	120.209	-0.561	-225.960	-112.926	12.793
3700	25.671	120.912	-0.559	-226.497	-109.572	12.893
3800	25.680	121.597	-0.557	-227.044	-106.200	13.033
3900	25.688	122.264	-0.555	-227.601	-102.809	13.213
4000	25.695	122.914	-0.553	-228.168	-99.399	13.433
4100	25.701	123.549	-0.551	-228.744	-95.972	13.693
4200	25.708	124.168	-0.549	-229.330	-92.529	14.003
4300	25.713	124.773	-0.547	-229.926	-89.069	14.363
4400	25.719	125.365	-0.545	-230.532	-85.592	14.773
4500	25.724	125.943	-0.543	-231.148	-82.099	15.233
4600	25.729	126.508	-0.541	-231.774	-78.592	15.743
4700	25.733	127.061	-0.539	-232.409	-75.069	16.303
4800	25.737	127.603	-0.537	-233.054	-71.532	16.913
4900	25.741	128.134	-0.535	-233.708	-67.980	17.573
5000	25.745	128.654	-0.533	-234.371	-64.413	18.283
5100	25.748	129.164	-0.531	-235.043	-60.830	19.043
5200	25.752	129.664	-0.529	-235.724	-57.233	19.853
5300	25.755	130.154	-0.527	-236.414	-53.620	20.713
5400	25.758	130.636	-0.525	-237.113	-49.992	21.623
5500	25.760	131.108	-0.523	-237.820	-46.349	22.583
5600	25.763	131.573	-0.521	-238.534	-42.696	23.593
5700	25.765	132.029	-0.519	-239.254	-39.033	24.653
5800	25.768	132.477	-0.517	-239.980	-35.360	25.763
5900	25.770	132.917	-0.515	-240.711	-31.677	26.923
6000	25.772	133.350	-0.513	-241.446	-27.984	28.133

December 31, 1962

BeF₃Li

BeF₃Li

LITHIUM TRIFLUORBERYLLATE (LiBeF₃) (Ideal Gas)

Mol. Wt. = 72.953
ΔH°_f 298.15 = -212 kcal. mole⁻¹
S°_{298.15} = [64] cal. deg.⁻¹ mole⁻¹
Point Group [C_{3v}]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[1530] (1)	[485] (2)
[800] (2)	[800] (5)
[700] (1)	

Bond distances: Be-F = [1.40] Å Li-Be = [1.209] Å
Li-F = [1.85] Å
Bond angle: F-Be-F = [120]° Li-Be-F = [90]°
Moment of inertia: I_{ABC} = 2.1604 X 10⁻¹⁴ g. cm.² σ = [3]
72, 1073 (1960).

Heat of Formation. ΔH°_f 298.15 was calculated from ΔH°_f 298 = 53 kcal. mole for the reaction: LiF(g) + BeF₂(g) = LiBeF₃(g) reported by J. Berkowitz and W. A. Chupka, Ann. N. Y. Acad. Sci., 72, 1073 (1960).

Heat Capacity and Entropy. The molecular structure was assumed to be pyramidal with Li atom at the top and BeF₃ located at the bottom. Beryllium atom was taken at the center of the equilateral triangle formed by the three F atoms. The Be-F distance was estimated from that of BeF₂(g). The bond distance of Li-F was taken from R. P. Porter and E. Zeller, J. Chem. Phys., 33, 858 (1960). Vibrational frequencies were estimated by comparison with related fluorides.

T, °K	Cp	$\frac{\text{gibbs/mol}}{S}$	$\frac{-(G^\circ - H^\circ_{298})}{T}$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	32.290	29.800	29.800	+0.00	- 539.000	- 514.169	376.896
300	32.300	30.000	29.801	+0.60	- 538.997	- 514.016	376.660
400	35.960	38.794	31.111	3.473	- 538.805	- 505.713	276.309
500	38.590	48.210	33.707	7.251	- 539.981	- 497.324	217.380
600	43.140	55.742	36.762	11.388	- 539.476	- 488.823	178.057
700	46.680	62.661	39.076	15.681	- 538.657	- 480.444	150.005
800	49.760	68.105	43.217	20.711	- 537.538	- 472.214	128.003
900	52.235	75.113	46.431	25.813	- 536.187	- 464.127	112.706
1000	54.360	80.729	49.883	31.146	- 534.644	- 456.202	98.703
1100	56.053	85.092	52.456	35.660	- 532.948	- 448.439	80.007
1200	57.560	90.035	55.042	42.392	- 531.121	- 440.836	80.287
1300	58.800	95.592	58.518	48.170	- 529.193	- 433.389	72.659
1400	59.940	99.092	61.843	54.108	- 527.175	- 426.095	66.516
1500	60.965	104.163	64.060	60.154	- 525.077	- 418.947	61.041
1600	61.820	108.128	66.492	66.209	- 525.663	- 411.863	56.258
1700	62.810	111.409	69.241	72.536	- 523.409	- 402.166	51.702
1800	63.620	115.523	71.713	78.858	- 520.623	- 390.997	47.474
1900	64.350	118.983	74.110	85.257	- 517.769	- 379.983	43.708
2000	65.000	122.300	76.437	91.776	- 514.858	- 369.120	40.336

June 30, 1966

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (CRYSTAL)

ΔH°_f = Unknown

$\Delta H^\circ_{298.15} = -539.0 \pm 1.3$ kcal/mol

$\Delta H^\circ = 10.806$ kcal/mol

$S^\circ_{298.15} = [29.8 \pm 2]$ gibbs/mol

$T_m = 745^\circ\text{K}$

Heat of Formation.

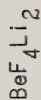
The $\Delta H^\circ_{298.15} = -539.0 \pm 1.3$ kcal/mol was calculated from the $\Delta H^\circ_{298.15} = -5.05 \pm 0.06$ kcal/mol of the reaction $2\text{LiF}(c) + \text{BeF}_2(g) = \text{Li}_2\text{BeF}_4(c)$ measured (calorimetrically) by F. Gross, Pulver Research Institute, R.163/23/May 1966. A value of $\Delta H^\circ_{298} = 1.17$ kcal/mol was used for $\text{BeF}_2(c) \rightarrow \text{BeF}_2(g)$.

Heat Capacity and Entropy.

The heat capacity is based on the enthalpy data ($323\text{--}723^\circ\text{K}$) of T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report 8186, January, 1964. The entropy was estimated by addition of values for the component fluorides.

Melting Data.

T_m and ΔH_m° were obtained from Douglas et al., loc. cit., who measured the high temperature enthalpies.



Dilithium Tetrafluoroberyllate (Li_2BeF_4)

(Liquid) GFW = 98.8838

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	32.290	39.304	39.304	0.000	- 531.217	- 509.220	373.268
300	32.300	39.304	39.305	0.060	- 531.214	- 509.084	370.868
400	35.960	49.298	40.615	3.473	- 531.022	- 501.732	274.134
500	55.500	57.713	43.211	7.251	- 532.198	- 494.293	216.055
600	55.500	67.832	46.497	12.801	- 530.280	- 486.891	177.350
700	55.500	76.387	53.171	18.951	- 526.200	- 465.810	149.459
800	55.500	83.788	53.922	23.961	- 526.565	- 472.590	129.216
900	55.500	90.335	57.612	29.451	- 524.764	- 468.407	113.259
1000	55.500	96.182	61.182	35.001	- 523.006	- 460.017	100.537
1100	55.500	101.472	64.668	40.551	- 521.280	- 453.802	90.162
1200	55.500	106.301	67.464	46.101	- 518.580	- 443.945	81.200
1300	55.500	110.744	71.012	51.651	- 517.929	- 441.823	74.277
1400	55.500	114.857	73.999	57.201	- 516.299	- 436.030	68.067
1500	55.500	118.686	76.652	62.751	- 514.697	- 430.352	62.702
1600	55.500	122.268	79.480	68.301	- 513.076	- 424.702	58.012
1700	55.500	125.692	82.151	73.851	- 511.430	- 419.080	53.821
1800	55.500	128.804	84.693	79.401	- 509.767	- 413.492	49.934
1900	55.500	131.804	87.094	84.951	- 508.092	- 407.946	46.350
2000	55.500	134.652	89.402	90.501	- 506.400	- 402.446	42.918

DILITHIUM TETRAFLUOROBERYLLATE (Li_2BeF_4) (LIQUID)

GFW = 98.8838

$$\Delta H^\circ_{298.15} = -531.2 \pm 1.3 \text{ kcal/mol}$$

$$\Delta H^\circ = -10.606 \text{ kcal/mol}$$

$$S^\circ_{298.15} = [39.3 \pm 2] \text{ gibbs/mol}$$

$$T_m = 745^\circ\text{K}$$

Heat of Formation.

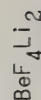
The $\Delta H^\circ_{298.15}$ was obtained from $\Delta H^\circ_{298.15}(c)$ by adding ΔH°_f and the difference between $H^\circ_m - H^\circ_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 500°K . The heat capacity below 500°K was obtained from the heat capacity of the crystal. Above 500°K the heat capacity was assumed constant at 55.5 gibbs/mol calculated from the liquid enthalpy equation given by T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report No. 6186, Washington, 1964. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{Li}_2\text{BeF}_4(c)$ table.



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f kcal. mole ⁻¹	ΔF° _f kcal. mole ⁻¹	Log K _p
0	∞.000	INFINITE	-2.066	76.181	INFINITE	INFINITE
100	6.962	34.025	48.434	76.478	-162.260	-
200	6.967	39.452	42.874	76.735	-78.563	-
298	6.985	42.236	42.236	76.768	69.507	-50.948
300	6.986	42.279	42.236	76.767	69.462	-50.401
400	7.050	44.298	42.511	76.683	67.038	-36.656
500	7.205	45.887	43.033	76.542	64.642	-28.254
600	7.393	47.217	43.522	76.380	62.277	-22.083
700	7.593	48.372	43.965	76.207	60.042	-17.481
800	7.785	49.398	44.364	76.029	57.928	-13.743
900	7.958	50.326	44.737	75.842	55.940	-10.438
1000	8.111	51.172	45.006	75.646	53.072	-7.1598
1100	8.245	51.952	45.221	75.437	50.325	-4.0098
1200	8.361	52.674	45.412	75.212	47.697	-0.950
1300	8.462	53.347	45.581	74.969	45.189	7.798
1400	8.550	53.978	45.730	74.707	42.800	6.900
1500	8.628	54.570	45.860	74.423	40.531	6.124
1600	8.697	55.130	45.972	74.121	38.389	5.458
1700	8.758	55.659	46.068	73.807	36.360	4.885
1800	8.813	56.161	46.148	73.481	34.449	4.378
1900	8.862	56.639	46.217	73.147	32.657	3.926
2000	8.908	57.094	50.167	70.480	32.209	3.520
2100	8.949	57.530	50.507	70.248	30.302	3.153
2200	8.988	57.947	50.836	70.011	28.405	2.822
2300	9.023	58.346	51.154	69.769	26.521	2.520
2400	9.057	58.732	51.461	69.521	24.647	2.244
2500	9.088	59.103	51.760	69.267	22.779	1.991
2600	9.118	59.460	52.049	68.999	20.927	1.759
2700	9.146	59.804	52.330	68.747	19.083	1.545
2800	9.172	60.137	52.603	68.491	17.250	1.343
2900	9.198	60.460	52.868	68.231	15.435	1.140
3000	9.222	60.772	53.127	67.966	13.651	0.946
3100	9.246	61.075	53.378	67.696	11.906	0.762
3200	9.269	61.369	53.623	67.421	10.200	0.588
3300	9.291	61.654	53.862	67.143	8.533	0.424
3400	9.312	61.932	54.096	66.863	6.910	0.269
3500	9.333	62.202	54.323	66.579	5.330	0.124
3600	9.354	62.465	54.546	66.291	3.795	0.000
3700	9.374	62.722	54.763	65.998	2.306	-0.108
3800	9.393	62.972	54.976	65.700	0.863	-0.220
3900	9.412	63.216	55.184	65.398	-0.635	-0.336
4000	9.431	63.455	55.388	65.092	-2.077	-0.456
4100	9.450	63.688	55.588	64.781	-3.502	-0.580
4200	9.468	63.916	55.783	64.466	-4.914	-0.708
4300	9.486	64.139	55.975	64.146	-6.313	-0.840
4400	9.504	64.357	56.163	63.821	-7.699	-0.976
4500	9.521	64.571	56.348	63.492	-9.073	-1.116
4600	9.539	64.780	56.529	63.159	-10.437	-1.260
4700	9.556	64.986	56.706	62.822	-11.792	-1.408
4800	9.573	65.187	56.881	62.480	-13.137	-1.560
4900	9.590	65.385	57.052	62.134	-14.472	-1.716
5000	9.606	65.579	57.221	61.783	-15.798	-1.876
5100	9.623	65.769	57.387	61.428	-17.115	-2.040
5200	9.639	65.956	57.550	61.069	-18.424	-2.208
5300	9.656	66.140	57.710	60.706	-19.725	-2.380
5400	9.672	66.320	57.868	60.339	-21.019	-2.556
5500	9.688	66.498	58.023	59.968	-22.308	-2.736
5600	9.704	66.673	58.176	59.593	-23.592	-2.918
5700	9.720	66.845	58.327	59.214	-24.872	-3.104
5800	9.736	67.014	58.475	58.831	-26.147	-3.292
5900	9.752	67.180	58.621	58.445	-27.417	-3.484
6000	9.767	67.344	58.765	58.056	-28.682	-3.680

Dec. 31, 1960 Mar. 31, 1963

MOL. WT. = 10.021

BERYLLIUM MONOHYDRIDE (BeH)

(IDEAL GAS)

Ground State Configuration $2s^2 2p^1$
 $\Delta H_f^0 = 42.256 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = 76 \pm 7 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 77 \pm 7 \text{ kcal. mole}^{-1}$

Electronic Level and Multiplicity

$$\frac{E_1}{E_2}, \text{ cm.}^{-1}$$

$$\omega_e x_e = 35.5 \text{ cm.}^{-1}$$

$$\omega_e = 2058.6 \text{ cm.}^{-1}$$

$$B_e = 10.308 \text{ cm.}^{-1}$$

$$\sigma^+ = 1$$

$$r_e = 1.3431 \text{ \AA}$$

Heat of Formation

Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1953, selected a value of $2.3 \pm 0.3 \text{ e.v. (53} \pm 7 \text{ kcal. mole}^{-1})$ for D_0 . Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950, estimated D_0 as being $2.2 \text{ e.v. (50.7 kcal. mole}^{-1})$. Gaydon's value was used in this table.

Heat Capacity and Entropy

Molecular constants were found in Herzberg, op. cit.

BeH

BeH

BeH⁺

OPW = 10.01962

BERYLLIUM MONOHYDRIDE UNIPOSITIVE ION (BeH⁺) (IDEAL GAS)

Ground State Configuration 1 Σ
 $S_{298.15}^0 = 40.76$ gibbs/mol
 $\Delta H_f^0 = 274.3 \pm 10$ kcal/mol
 $\Delta H_f^0 = 276.4 \pm 10$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$ g_i
[20000] 1
[5] 3
 $\omega_e x_e = 39.79 \text{ cm}^{-1}$
 $\sigma = 1$
 $\nu_e = 1.31216 \text{ \AA}$
 $\omega_e = 10.7996 \text{ cm}^{-1}$
 $\omega_e^2 = 0.2835 \text{ cm}^{-1}$

Heat of Formation.

The heat of formation was calculated from the equation $\text{BeH}(g) \rightarrow \text{BeH}^+(g) + e^-$ with the JANAP auxiliary data for $\text{BeH}(g)$, using an ionization potential = 8.6 ± 0.4 eV (198.34 ± 9.25 kcal/mol) obtained from C. W. Beckett, NBS Report 8628, Jan. 1, 1965.

The dissociation energy, $D_0 (\text{Be}^+ - \text{H}) = 3.2 \pm 0.2$ eV (73.8 kcal/mol), has been reported by A. G. Oaydon, "Dissociation Energies," 2nd Ed., Chapman and Hall Ltd., London, 1953. This yields $\Delta H_f^0 (\text{BeH}^+, g) = 270.0$ kcal/mol, which is in agreement with the value adopted.

Heat Capacity and Entropy.

The molecular constants were obtained from the ultraviolet spectroscopic studies by W. W. Watson and R. P. Humphreys, Phys. Rev. 52, 318 (1937).

The ground state configuration was given by O. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, New York, 1950. The estimated electronic level and quantum weight were obtained by assuming that a 3Σ level lies below the first observed excited state ($1\Sigma^-$) at 40,000 cm^{-1} .

BeH⁺

Sept. 30, 1966

Beryllium Monohydride Unipositive Ion (BeH⁺)

(Ideal Gas) GFW = 10.01962

T, K	C_p^0	$\frac{\text{gibbs/mol}}{S^0}$	$-(G^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	$\frac{\text{kcal/mol}}{\Delta H_f^0}$	ΔG_f^0	Log Kp
0							
100							
200							
298	6.977	40.760	40.760	0.000	276.400	268.092	-196.517
300	6.978	40.803	40.760	0.013	276.408	268.041	-195.267
400	7.050	42.846	41.034	0.713	276.819	265.187	-184.892
500	7.144	44.936	41.554	1.421	277.171	262.236	-174.624
600	7.307	45.713	42.161	2.443	277.498	259.220	-164.421
700	7.490	46.853	42.734	2.983	277.811	256.148	-154.973
800	7.673	47.855	43.313	3.641	278.118	253.032	-145.125
900	7.856	48.727	43.871	4.317	278.418	249.879	-135.679
1000	8.000	49.613	44.404	5.110	278.709	246.693	-126.915
1100	8.137	50.382	44.913	6.017	278.986	243.479	-118.375
1200	8.258	51.096	45.399	6.936	279.246	240.239	-110.753
1300	8.364	51.761	45.863	7.868	279.490	236.977	-103.839
1400	8.454	52.384	46.306	8.808	279.715	233.699	-96.482
1500	8.539	52.971	46.731	9.759	279.919	230.404	-88.570
1600	8.612	53.524	47.139	10.716	277.345	227.175	-81.031
1700	8.677	54.048	47.530	11.681	277.620	224.032	-73.801
1800	8.735	54.546	47.906	12.651	277.890	220.870	-66.817
1900	8.786	55.017	48.269	13.628	278.158	217.698	-59.061
2000	8.836	55.471	48.617	14.609	278.420	214.508	-51.440
2100	8.880	55.904	48.954	15.595	278.678	211.304	-43.991
2200	8.921	56.318	49.279	16.585	278.931	208.090	-36.672
2300	8.960	56.715	49.594	17.579	279.179	204.866	-29.487
2400	9.000	57.097	49.900	18.577	279.422	201.632	-22.361
2500	9.031	57.465	50.194	19.578	279.659	198.383	-15.343
2600	9.065	57.820	50.480	20.583	279.893	195.129	-8.402
2700	9.099	58.163	50.759	21.591	280.123	191.865	-1.530
2800	9.131	58.494	51.039	22.603	280.318	188.600	14.807
2900	9.161	58.814	51.318	23.618	280.790	185.334	29.243
3000	9.198	59.127	51.592	24.636	210.261	182.063	33.715
3100	9.232	59.429	51.787	25.657	210.732	187.519	13.220
3200	9.267	59.722	52.041	26.682	211.203	186.771	12.756
3300	9.303	60.008	52.278	27.711	211.672	186.000	12.318
3400	9.339	60.286	52.509	28.743	212.139	185.214	11.905
3500	9.379	60.558	52.739	29.779	212.605	184.413	11.515
3600	9.419	60.822	52.956	30.819	213.070	183.605	11.146
3700	9.461	61.081	53.172	31.863	213.531	182.775	10.796
3800	9.505	61.334	53.384	32.911	213.990	181.939	10.464
3900	9.551	61.581	53.591	33.964	214.447	181.094	10.148
4000	9.597	61.824	53.794	35.021	214.899	180.227	9.847
4100	9.646	62.061	53.992	36.083	215.349	179.354	9.560
4200	9.696	62.294	54.187	37.150	215.796	178.475	9.287
4300	9.748	62.523	54.379	38.222	216.239	177.582	9.026
4400	9.801	62.748	54.566	39.300	216.677	176.676	8.776
4500	9.856	62.969	54.750	40.382	217.108	175.758	8.536
4600	9.912	63.186	54.931	41.469	217.536	174.837	8.307
4700	9.969	63.400	55.109	42.561	217.959	173.902	8.086
4800	10.027	63.610	55.284	43.658	218.377	172.961	7.875
4900	10.087	63.817	55.456	44.760	218.789	172.011	7.672
5000	10.147	64.022	55.626	45.867	219.194	171.057	7.477
5100	10.208	64.224	55.792	46.979	219.593	170.085	7.289
5200	10.269	64.422	55.956	48.094	219.987	169.113	7.108
5300	10.331	64.619	56.118	49.214	220.373	168.128	6.933
5400	10.394	64.813	56.277	50.339	220.753	167.139	6.764
5500	10.455	65.004	56.434	51.467	221.126	166.140	6.602
5600	10.517	65.192	56.589	52.599	221.491	165.138	6.445
5700	10.579	65.379	56.741	53.736	221.851	164.136	6.293
5800	10.641	65.564	56.892	54.877	222.203	163.116	6.146
5900	10.704	65.748	57.041	56.021	222.548	162.093	6.004
6000	10.763	65.926	57.187	57.167	222.886	161.068	5.867

Vibrational Frequencies and Multiplicities

 ω_e , cm. $^{-1}$

[1500] (1)

[1200] (1)

[3600] (1)

[1500] (1)

[1200] (1)

[3600] (1)

Bond Distance: Be-O = [1.4] Å

Bond Angle: Be-O-H = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [0.447] \times 10^{-117}$ g. 3 cm. 6

Heat of Formation.

D. L. Hildenbrand, L. P. Theard, and F. Ju, Ford Motor Co., Aeronutronic Division, Third Quarterly Report, U-2231, April-June, 1963, studied the equilibrium $BeO(g) + H_2O(g) \rightarrow 2BeOH(g)$ in a mass spectrometer. Using the JANAP values for the free energy functions and heats of formation yielded $\Delta H_f^\circ BeOH(g) = -24.8 \pm 10$ kcal. mole $^{-1}$, which was rounded to -25 ± 10 kcal. mole $^{-1}$. This value is a minimum one, that is, it is the most negative possible value.

Heat Capacity and Entropy.

The molecule was assumed to be nonlinear, the OH stretch was estimated as 3600 cm. $^{-1}$, the Be-O stretch as 1500 cm. $^{-1}$, from $BeO(g)$, and the bending frequency as 1200 cm. $^{-1}$. The Be-O bond length was taken as a little larger than in $BeO(g)$ while the O-H bond length is that in $H_2O(g)$. The bond angle was taken arbitrarily to be 120° and changes in this will have negligible effect on the functions unless it goes to 180°. The molecule contains one free electron and so was assumed to have a statistical weight of 2.

Dec. 31, 1960; Sept. 30, 1963

T, °K.

 C_p° S° $-(F^\circ - H_{298}^\circ)/T$ $H^\circ - H_{298}^\circ$ ΔH_f° ΔF_f° Log K_p

100

200

300

400

500

600

700

800

900

1000

1100

1200

1300

1400

1500

1600

1700

1800

1900

2000

2100

2200

2300

2400

2500

2600

2700

2800

2900

3000

3100

3200

3300

3400

3500

3600

3700

3800

3900

4000

4100

4200

4300

4400

4500

4600

4700

4800

4900

5000

5100

5200

5300

5400

5500

5600

5700

5800

5900

6000

6100

6200

6300

6400

6500

6600

6700

6800

6900

7000

7100

7200

7300

7400

7500

7600

7700

7800

7900

8000

8100

8200

8300

8400

8500

8600

8700

8800

8900

9000

9100

9200

9300

9400

9500

9600

9700

9800

9900

10000

10100

10200

10300

10400

10500

10600

10700

10800

10900

11000

11100

11200

11300

11400

11500

11600

11700

11800

11900

12000

12100

12200

12300

12400

12500

12600

12700

12800

12900

13000

13100

13200

13300

13400

13500

13600

13700

13800

13900

14000

14100

14200

14300

14400

14500

14600

14700

14800

14900

15000

15100

15200

15300

15400

15500

15600

15700

15800

15900

16000

16100

16200

16300

16400

16500

16600

16700

16800

16900

17000

17100

17200

17300

17400

17500

17600

17700

17800

17900

18000

18100

18200

18300

18400

18500

18600

18700

18800

18900

19000

19100

19200

19300

19400

19500

19600

19700

19800

19900

20000

20100

20200

20300

20400

20500

20600

20700

20800

20900

21000

21100

21200

21300

21400

21500

21600

21700

21800

21900

22000

22100

22200

22300

22400

22500

22600

22700

22800

22900

23000

23100

23200

23300

23400

23500

23600

23700

23800

23900

24000

24100

24200

24300

24400

24500

24600

24700

24800

24900

25000

25100

25200

25300

25400

25500

25600

25700

25800

25900

26000

26100

26200

26300

26400

26500

26600

26700

26800

26900

27000

27100

27200

27300

27400

27500

27600

27700

27800

27900

28000

28100

28200

28300

28400

28500

28600

28700

28800

28900

29000

29100

29200

29300

29400

29500

29600

29700

29800

29900

30000

30100

30200

30300

30400

30500

30600

Beryllium Monohydroxide Unipositive Ion (BeOH⁺)

(Ideal Gas) GFW = 26.01902

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	7.663	47.983	.000	194.000	190.844	- 139.893
300	7.679	48.030	.014	194.003	190.824	- 139.9015
400	8.605	50.364	.826	194.152	189.739	- 139.649
500	9.486	52.382	1.733	194.356	188.611	- 139.422
600	10.217	54.178	2.720	194.570	187.442	- 139.276
700	10.804	55.799	3.772	194.806	186.235	- 139.155
800	11.283	57.274	4.877	195.061	184.993	- 139.058
900	11.682	58.626	6.026	195.327	183.719	- 138.981
1000	12.023	59.875	7.212	195.597	182.415	- 138.927
1100	12.317	61.035	8.429	195.865	181.085	- 138.893
1200	12.572	62.118	9.674	196.127	179.730	- 138.873
1300	12.796	63.134	10.942	196.379	178.352	- 138.864
1400	12.993	64.099	12.232	196.621	176.956	- 138.864
1500	13.166	64.992	13.540	196.847	175.543	- 138.877
1600	13.320	65.846	14.865	197.056	174.114	- 138.894
1700	13.455	66.658	16.204	197.247	172.669	- 138.921
1800	13.576	67.431	17.555	197.417	171.215	- 138.958
1900	13.683	68.168	18.918	197.564	169.743	- 138.994
2000	13.779	68.872	20.291	197.688	168.255	- 139.029
2100	13.864	69.546	21.674	197.790	166.745	- 139.062
2200	13.941	70.193	23.064	197.870	165.215	- 139.092
2300	14.010	70.814	24.462	197.928	163.665	- 139.117
2400	14.072	71.412	25.866	197.966	162.095	- 139.137
2500	14.129	71.986	27.276	197.984	160.505	- 139.152
2600	14.180	72.543	28.691	197.989	158.895	- 139.162
2700	14.226	73.079	30.112	197.974	157.265	- 139.167
2800	14.268	73.597	31.536	197.940	155.615	- 139.167
2900	14.307	74.096	32.961	197.887	153.945	- 139.162
3000	14.342	74.584	34.396	197.816	152.255	- 139.152
3100	14.374	75.055	35.834	197.728	150.545	- 139.137
3200	14.404	75.512	37.272	197.624	148.815	- 139.117
3300	14.432	75.955	38.714	197.506	147.065	- 139.092
3400	14.457	76.386	40.159	197.374	145.295	- 139.062
3500	14.480	76.806	41.606	197.228	143.505	- 139.027
3600	14.502	77.214	43.055	197.070	141.695	- 138.987
3700	14.522	77.612	44.503	196.898	139.865	- 138.942
3800	14.540	77.999	45.959	196.714	137.995	- 138.892
3900	14.557	78.377	47.414	196.518	136.095	- 138.837
4000	14.574	78.746	48.870	196.310	134.165	- 138.777
4100	14.589	79.106	50.328	196.090	132.205	- 138.712
4200	14.603	79.458	51.788	195.858	130.215	- 138.642
4300	14.616	79.801	53.249	195.614	128.195	- 138.567
4400	14.626	80.137	54.711	195.358	126.145	- 138.487
4500	14.636	80.466	56.175	195.090	124.065	- 138.402
4600	14.651	80.788	57.639	194.810	121.955	- 138.312
4700	14.661	81.103	59.105	194.518	119.815	- 138.217
4800	14.670	81.412	60.571	194.214	117.645	- 138.117
4900	14.679	81.715	62.039	193.898	115.445	- 138.012
5000	14.688	82.011	63.507	193.570	113.215	- 137.902
5100	14.696	82.302	64.976	193.230	110.955	- 137.787
5200	14.704	82.588	66.446	192.878	108.665	- 137.667
5300	14.711	82.868	67.917	192.514	106.345	- 137.542
5400	14.718	83.143	69.386	192.138	103.995	- 137.412
5500	14.724	83.413	70.849	191.750	101.615	- 137.277
5600	14.730	83.678	72.313	191.350	99.205	- 137.137
5700	14.736	83.939	73.780	190.938	96.765	- 137.002
5800	14.742	84.196	75.240	190.514	94.295	- 136.862
5900	14.747	84.446	76.696	190.078	91.795	- 136.717
6000	14.752	84.696	78.150	189.630	89.265	- 136.567

June 30, 1968

BERYLLIUM MONOHYDROXIDE UNIPOSITIVE ION (BeOH⁺)

(IDEAL GAS)

Point Group [C_{∞v}]

S_{298.15}^o = [48.0] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_i, cm⁻¹

[1300] (1)

[1100] (2)

[3500] (1)

O-H = [10.96] Å

σ = 1

Bond Distance: Be-O = [1.4] Å

Bond Angle: Be-O-H = [180°]

Rotational Constant: B₀ = [1.2602] cm⁻¹

Heat of Formation

The ionization potential (IP) of BeOH(g) is estimated as 9.5 ± 1 eV by comparison with the values IP(BeF, g) = 9.1 ± 0.5, IP(NgF, g) = 7.8 ± 0.3 (1) and IP(MgOH, g) = 8.5 eV. (JANAF value). Based on IP(BeOH, g) = 9.5 eV or 219 kcal/mol and ΔH_f^o(BeOH, g) = -25 ± 10 kcal/mol, we derive the heat of formation at 298°K for BeOH⁺(g) as 194 ± 30 kcal/mol, which is tentatively adopted.

Heat Capacity and Entropy

The BeOH⁺(g) molecule has eight valence electrons. Based on the criterion given by Walsh (2) that ABH molecules (H = hydrogen atom) containing ten or less valence electrons will be linear in their ground state, we assume that the structure of BeOH⁺(g) is linear. The vibrational frequencies are estimated by comparison with those for BeOH(g) and LiOH(g). The Be-O and O-H bond distances are assumed to be the same as those in BeOH and H₂O molecules, respectively. The ground state quantum weight of BeOH⁺(g) is assumed to be the same as that of the isoelectronic molecule LiOH(g). The moment of inertia is 2.22 × 10⁻⁴⁰ g cm². The enthalpy at 0°K is -2.11 kcal/mol.

References

1. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).

GFW = 26.01902

ΔH_f^o = [194 ± 30] kcal/mol

ΔH_f^o_{298.15} = [194 ± 30] kcal/mol

BeHO⁺

BeHO⁺

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° _T	Log K _p
0	6.950	INFINITE	8.083	30.409	INFINITE
100	6.956	33.700	1.992	30.413	64.276
200	6.960	36.524	42.002	30.286	31.128
298	7.259	41.350	6.696	30.000	27.658 = 20.271
300	7.268	41.395	0.013	29.993	27.641 = 20.136
400	7.693	43.371	41.432	29.619	26.911 = 14.704
500	8.005	45.435	42.216	29.253	26.279 = 11.486
600	9.667	47.117	42.697	28.934	25.715 = 9.366
700	10.439	48.667	3.539	28.668	25.201 = 7.688
800	11.068	50.105	28.443	28.443	24.731 = 6.263
900	11.608	51.455	5.755	28.254	24.268 = 5.063
1000	12.102	52.696	45.754	28.083	23.834 = 5.209
1100	12.477	53.868	46.439	27.921	23.416 = 4.952
1200	12.789	54.982	47.106	27.769	23.015 = 4.801
1300	13.059	56.057	47.768	27.625	22.635 = 4.733
1400	13.294	56.977	48.374	27.493	22.250 = 4.673
1500	13.447	57.698	48.978	27.366	21.886 = 4.619
1600	13.603	58.771	49.563	24.244	21.615 = 2.952
1700	13.762	60.098	50.129	23.904	21.306 = 2.687
1800	13.839	60.596	50.678	23.740	21.068 = 2.435
1900	13.948	61.130	51.209	23.574	21.037 = 2.299
2000	14.034	61.686	51.723	23.408	20.913 = 2.176
2100	14.109	62.544	52.252	23.240	20.790 = 2.066
2200	14.213	63.653	52.777	23.070	20.662 = 1.966
2300	14.333	64.859	53.197	22.900	20.593 = 1.875
2400	14.425	64.440	53.634	22.726	20.498 = 1.792
2500	14.331	65.024	54.078	22.551	20.413 = 1.716
2600	14.372	65.587	54.509	22.381	20.341 = 1.640
2700	14.442	66.455	55.339	22.213	20.275 = 1.570
2800	14.482	66.455	55.339	22.048	20.215 = 1.500
2900	14.472	67.162	55.738	21.881	20.155 = 1.430
3000	14.500	67.653	56.127	21.714	20.093 = 1.360
3100	14.524	68.159	56.507	21.548	20.036 = 1.294
3200	14.546	68.687	56.887	21.383	19.980 = 1.228
3300	14.566	69.039	57.239	21.218	19.924 = 1.162
3400	14.587	69.474	57.593	21.053	19.868 = 1.096
3500	14.604	69.897	57.938	20.888	19.812 = 1.030
3600	14.620	70.109	58.274	20.723	19.756 = 0.964
3700	14.635	70.709	58.607	20.558	19.700 = 0.898
3800	14.650	71.100	58.930	20.393	19.644 = 0.832
3900	14.664	71.461	59.247	20.228	19.588 = 0.766
4000	14.673	71.652	59.558	20.063	19.532 = 0.700
4100	14.684	72.214	59.862	19.898	19.476 = 0.634
4200	14.694	72.914	60.453	19.733	19.420 = 0.568
4300	14.704	73.252	60.740	19.568	19.364 = 0.502
4400	14.713	73.252	60.740	19.403	19.308 = 0.436
4500	14.721	73.563	61.022	19.238	19.252 = 0.370
4600	14.729	73.097	61.298	19.073	19.196 = 0.304
4700	14.734	73.594	61.637	18.908	19.140 = 0.238
4800	14.738	74.254	62.099	18.743	19.084 = 0.172
4900	14.749	74.638	62.420	18.578	19.028 = 0.106
5000	14.755	75.136	62.357	18.413	18.972 = 0.040
5100	14.761	75.428	62.610	18.248	18.916 = -0.026
5200	14.766	75.725	62.860	18.083	18.860 = -0.092
5300	14.771	75.996	63.105	17.918	18.804 = -0.158
5400	14.776	76.272	63.346	17.753	18.748 = -0.224
5500	14.781	76.544	63.584	17.588	18.692 = -0.290
5600	14.785	76.810	63.817	17.423	18.636 = -0.356
5700	14.789	77.072	64.046	17.258	18.580 = -0.422
5800	14.793	77.329	64.274	17.093	18.524 = -0.488
5900	14.797	77.582	64.498	16.928	18.468 = -0.554
6000	14.800	77.830	64.718	16.763	18.412 = -0.620

December 31, 1960.

Beryllium Dihydride (BeH₂)

(Ideal Gas)

Mol. Wt. = 11.029

ΔH_f⁰ 298.15 = [30] kcal. mole⁻¹

S_{298.15}⁰ = 41.4 cal. deg.⁻¹ mole⁻¹

Point Group [D_{∞h}]

Ground State Multiplicity = 1

Vibrational Levels and Multiplicities

Q, cm. ⁻¹
[2200] (1)
[1500] (2)
[1300] (1)

Moment of Inertia: I = [6.01 X 10⁻⁴⁰] g. cm.² σ = 2.

Heat of Formation. Estimated by C. J. O'Brien and J. R. Perrin, Marquardt Corp., Van Nuys, Calif., and J. Perrine, Olin Mathieson Chemical Corp., New York 22, N. Y., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules", October, 1959.

Heat Capacities and Entropies. Molecular and spectroscopic parameters estimated.

Beryllium Dihydroxide, Alpha (α -Be(OH)₂)
(Crystal)

GFW = 43.02694

T, °K	Cp	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100						
200						
298	15.630	11.800	11.800	.000	- 215.750	- 194.673
300	15.704	11.897	11.800	.029	- 215.754	- 194.543
400	19.330	16.931	12.462	1.789	- 215.639	- 187.452
500	22.136	21.358	13.825	3.867	- 215.694	- 180.367
600	24.253	25.784	15.472	6.188	- 215.370	- 173.330
700	26.174	29.669	17.226	8.710	- 214.900	- 166.359
800	27.976	33.283	19.010	11.418	- 214.291	- 159.466



BERYLLIUM DIHYDROXIDE, ALPHA (α -Be(OH)₂)
(CRYSTAL)

GFW = 43.02694

ΔH°_f = Unknown

$\Delta H^\circ_{298.15} = -215.75 \pm 0.5$ kcal/mol

$S^\circ_{298.15} = [11.0 \pm 2]$ gibbs/mol

$T_d = [407]^\circ\text{K}$

Heat of Formation.

The heat of formation is based on $\Delta H^\circ_{298.15} = -79.16 \pm 0.5$ kcal/mol for the reaction $\text{Be}(c) + 2\text{H}_2\text{O}(l) = \text{Be}(\text{OH})_2(a,c) + \text{H}_2(g)$. The heat of this reaction is obtained by combination of the calorimetric heats of solution for pure beryllium metal and α -Be(OH)₂ in aqueous HF, measured by I. J. Bear and A. G. Turnbull, J. Phys. Chem. **69**, 2828-33 (1965).

Heat Capacity and Entropy.

The heat capacity was assumed the same as that of the beta phase. The entropy is calculated from the value of $\Delta G^\circ_{298.15} = -0.50$ kcal/mol for the change $\alpha\text{-Be}(\text{OH})_2 \rightarrow \beta\text{-Be}(\text{OH})_2$ which is obtained from the solubilities in concentrated alkali measured by R. Fricke and H. Hummel, Z. Anorg. Allgem. Chem. **178**, 400 (1929). This is combined with the $\Delta H^\circ_{298.15}$ difference and gives a change in entropy, $\Delta S^\circ_{298.15} = -0.8$ eu and an entropy of $\alpha\text{-Be}(\text{OH})_2$, $S^\circ_{298.15} = 11.8 \pm 2$ eu.

Decomposition Data.

T_d is calculated as the temperature at which ΔH°_f equals zero for $\text{Be}(\text{OH})_2(a,c) = \text{BeO}(c) + \text{H}_2\text{O}(g)$.



T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log K _p
100							
200							
298	15.430	11.000	11.000	.000	-216.500	-195.165	143.074
300	15.704	11.097	11.000	.029	-216.504	-195.053	142.096
400	19.330	16.131	11.662	1.788	-216.589	-187.862	102.654
500	22.130	20.758	13.025	3.667	-216.444	-180.717	78.992
600	24.253	24.984	14.672	6.188	-216.120	-173.609	63.288
700	25.774	28.856	16.210	9.418	-215.586	-166.529	50.586
800	26.776	32.483	17.618	13.418	-215.041	-159.576	43.594
900	29.564	35.877	19.986	14.302	-214.300	-152.684	37.077
1000	31.298	39.089	21.737	17.352	-213.435	-145.863	31.683

BERYLLIUM DIHYDROXIDE, BETA (β -Be(OH)₂) (CRYSTAL)

OFW = 43.02694

ΔHf° = Unknown

ΔHf°_{298.15} = -216.50 ± 0.5 kcal/mol

S°_{298.15} = [11.0 ± 2] gibbs/mol

Td = [417] °K

Heat of Formation.

The heat of formation is based on ΔHf°_{298.15} = -79.89 ± 0.5 kcal/mol for the reaction Be(c) + 2H₂O(l) = Be(OH)₂(β ,c) + H₂(g). The heat of this reaction is obtained by combination of the calorimetric heats of solution measured by Bear and Turnbull for pure beryllium metal and β -Be(OH)₂ in aqueous HF. Third law analyses of two studies of the decomposition pressure of water vapor over the β -phase are in good agreement with the selected heat of formation, as summarized below. Fricke and Severin observed a decomposition temperature of 105°C at a pressure of 100 mm, while Baur and Lecocq found 223°C for equilibrium with saturated water vapor at 24.2 atm. We have reduced the latter data to a standard state value of ΔG°_{496.15} = -3028 cal/mol for the decomposition reaction given below.

Source	Method	Reaction	T, °K	ΔH° _{298.15} kcal/mol	ΔHf° _{298.15} kcal/mol
1 Bear & Turnbull	Calorimetric	Be(c) + 2H ₂ O(l) → Be(OH) ₂ (β ,c) + H ₂ (g)	294	-79.89	-216.59 ± 0.5
2 Fricke & Severin	Kp	Be(OH) ₂ (β ,c) → BeO(c) + H ₂ O(g)	378	15.68	-216.58
3 Baur & Lecocq	Kp	"	496	15.44	-216.34

Sources.

1. I. J. Bear and A. G. Turnbull, J. Phys. Chem. **69**, 2828-33 (1965).
2. R. Fricke and H. Severin, Z. Anorg. Allgem. Chem. **205**, 287 (1932).
3. A. Baur and A. Lecocq, Comm. Energie At. (France), Rappt. CEA-R2611, 17 pp. (1964).

Heat Capacity and Entropy.

The heat capacity is estimated from that for Mg(OH)₂ by subtracting the values for MgO and adding those for BeO.

The entropy is estimated by extrapolation to beryllium of the differences in S°₂₉₈ between the chlorides and hydroxides of magnesium and calcium. Entropies of Mg(OH)₂, MgCl₂ and BeCl₂ are taken from the JANAF tables, while those of Ca(OH)₂ and CaCl₂ are taken to be 13.9 ± 0.1 and 25.0 ± 1.0 eu, respectively. [Recent low temperature data for SrCl₂ and BaCl₂ suggest that the CaCl₂ extrapolation should be S°₅₀ = 2.4 ± 1.0 eu rather than the original value of S°₅₀ = 4.59 eu used by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. **65**, 782 (1943)]. Confirmation of the adopted entropy is obtained from the good agreement between the calorimetric heat of formation and the third law values derived from the equilibrium data.

Decomposition Data.

Td is calculated as the temperature at which ΔGf° equals zero for Be(OH)₂(β ,c) = BeO(c) + H₂O(g).

Beryllium Dihydroxide (Be(OH)₂)

GFW = 43.02694

(Ideal Gas)

Beryllium Dihydroxide (Be(OH)₂)

(Ideal Gas)

BeH₂O₂

OPW = 43.02694

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	ΔG _f ^c	Log K _p
0	0.000	INFINITE					INFINITE
100	8.576	47.684	69.507	2.989	-154.422	-154.422	153.576
200	11.072	54.378	60.388	2.882	-155.478	-155.478	165.727
298	13.359	59.238	59.238	1.802	-155.935	-155.935	169.562
300	13.398	59.320		1.825	-156.408	-156.408	168.855
400	15.284	63.444	59.787	1.463	-156.814	-156.814	160.335
500	16.751	67.019	60.684	3.068	-157.143	-157.143	151.181
600	17.899	70.178	62.175	4.802	-157.426	-157.426	142.002
700	18.695	72.516	63.673	6.563	-157.596	-157.596	132.728
800	19.405	74.256	64.873	8.363	-157.696	-157.696	123.374
900	20.212	75.925	66.194	10.557	-157.745	-157.745	113.951
1000	20.852	80.091	67.417	12.614	-157.873	-157.873	104.444
1100	21.360	82.103	68.716	14.725	-158.101	-158.101	95.603
1200	21.797	83.782	70.102	16.985	-158.413	-158.413	87.274
1300	22.197	85.252	71.592	19.402	-158.813	-158.813	79.461
1400	22.542	87.400	73.170	21.322	-159.332	-159.332	72.122
1500	22.846	89.966	73.238	23.592	-159.659	-159.659	65.123
1600	23.114	90.449	74.268	25.890	-161.555	-161.555	58.755
1700	23.351	91.198	75.291	30.559	-161.632	-161.632	52.580
1800	23.571	91.958	76.291	33.559	-161.670	-161.670	46.661
1900	23.748	94.477	77.168	32.925	-161.710	-161.710	40.984
2000	23.914	95.700	78.046	35.308	-161.753	-161.753	35.543
2100	24.063	96.870	78.914	37.707	-161.753	-161.753	30.327
2200	24.194	97.971	79.764	40.133	-161.753	-161.753	25.327
2300	24.314	99.071	80.573	42.546	-161.753	-161.753	20.543
2400	24.422	100.108	81.353	44.983	-161.914	-161.914	16.061
2500	24.519	101.107	82.135	47.430	-161.984	-161.984	11.863
2600	24.606	102.070	82.883	49.866	-162.058	-162.058	7.877
2700	24.758	103.000	83.621	52.321	-162.108	-162.108	4.121
2800	24.858	103.900	84.359	54.804	-162.158	-162.158	0.681
2900	24.884	104.770	85.010	57.302	-162.108	-162.108	0.570
3000	24.884	105.612	85.683	59.788	-162.108	-162.108	0.494
3100	24.939	106.429	86.339	62.279	-162.108	-162.108	0.437
3200	25.036	107.221	87.004	64.777	-162.108	-162.108	0.383
3300	25.056	107.981	87.684	67.277	-162.108	-162.108	0.333
3400	25.079	108.739	88.215	69.781	-162.108	-162.108	0.283
3500	25.119	109.467	88.812	72.293	-162.108	-162.108	0.233
3600	25.155	110.175	89.396	74.806	-162.108	-162.108	0.183
3700	25.211	110.867	90.552	77.324	-162.108	-162.108	0.133
3800	25.231	111.537	91.297	79.844	-162.108	-162.108	0.083
3900	25.250	112.192	91.073	82.368	-162.108	-162.108	0.033
4000	25.277	112.832	91.609	84.894	-162.108	-162.108	0.000
4100	25.303	113.457	92.134	87.423	-162.108	-162.108	0.443
4200	25.328	114.063	92.648	89.952	-162.108	-162.108	0.883
4300	25.359	114.653	93.154	92.484	-162.108	-162.108	1.323
4400	25.370	115.246	93.649	95.024	-162.108	-162.108	1.763
4500	25.369	115.816	94.136	97.562	-162.108	-162.108	2.203
4600	25.407	116.374	94.613	100.102	-162.108	-162.108	2.643
4700	25.441	116.925	95.087	102.630	-162.108	-162.108	3.083
4800	25.471	117.466	95.562	105.157	-162.108	-162.108	3.523
4900	25.486	117.981	95.995	107.739	-162.108	-162.108	3.963
5000	25.471	118.486	96.440	110.273	-162.108	-162.108	4.403
5100	25.484	119.000	96.877	112.826	-162.108	-162.108	4.843
5200	25.484	119.511	97.301	115.389	-162.108	-162.108	5.283
5300	25.509	119.981	97.721	117.925	-162.108	-162.108	5.723
5400	25.521	120.488	98.137	120.477	-162.108	-162.108	6.163
5500	25.532	120.926	98.557	123.029	-162.108	-162.108	6.603
5600	25.542	121.386	98.961	125.583	-162.108	-162.108	7.043
5700	25.561	121.823	99.350	128.137	-162.108	-162.108	7.483
5800	25.570	122.293	99.720	130.690	-162.108	-162.108	7.923
5900	25.570	122.720	100.055	133.243	-162.108	-162.108	8.363
6000	25.579	123.150	100.515	135.806	-162.108	-162.108	8.803

Dec. 31, 1960; Sept. 30, 1965; Dec. 31, 1966; Mar. 31, 1967

Point Group [C₂]
S°_{298.15} = [59.2] gibbs/mol
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W ₂ , cm ⁻¹	W ₂ , cm ⁻¹	W ₂ , cm ⁻¹
[3200] (1)	[649] (1)	[1200] (1)
[1000] (1)	[750] (1)	[1800] (1)
[360] (1)	[360] (1)	[3300] (1)

Bond Distances: Be-O = [1.35] Å
O-H = [0.97] Å
Bond Angles: Be-O-H = [100°]
O-B-O = [180°]

σ = 2

Angle between Be-O-H planes = [95°]

Product of the Moments of Inertia: I_AI_BI_C = [32.26] x 10⁻¹¹⁷ g³cm⁶

Heat of Formation

The equilibrium reaction (A) BeO(c) + H₂O(g) → Be(OH)₂(g) has been studied by several investigators; all of them inferred that Be(OH)₂(g) was the major product, but there has been no direct proof of this. D. P. Hildenbrand, L. P. Theard and P. Ju, *Aeronautics*, 3rd Quarterly Technical Report No. U-2331, Contract AF 04(611)-8523, 31 July 1965, have examined the BeO-H₂O system at 2300°C mass-spectroscopically and report only BeO and Be(OH)₂. They report a maximum value of the equilibrium constant for reaction (B) BeO(g) + H₂O(g) → Be(OH)₂(g) of 3.5 x 10⁵ atm⁻¹ at 2327°K; this yields ΔH°_{298.15} (Be(OH)₂,g) ≥ -157.7 ± 10 kcal/mol using JANAF functions.

L. I. Grossweiner and R. L. Seifert, *J. Am. Chem. Soc.* 74, 2701 (1952); W. A. Young, *J. Phys. Chem.* 64, 1003 (1960); and W. I. Stuart and G. H. Price, *J. Nucl. Mater.* 14, 417 (1964), have all studied reaction (A) under similar conditions. Each of these investigators varied and H₂O(g) flow rate without detectable change of K_p values. However, Grossweiner and Seifert used a considerably larger flow rate than the other investigators, and the reaction that they studied may not have been quite at equilibrium. The residence times in all cases were quite comparable. A second and third law analysis of the above data are shown below.

J. Blauer, M. A. Greenbaum and M. Farber, *J. Phys. Chem.* 70, 973 (1966), have also studied reaction (A) using the molecular flow effusion technique. They obtained a large variation of K_p with surface area, although the sample area and size were comparable to that in the earlier investigations. They operated at 300p pressure, which is at the upper limits of the molecular flow regime. Also encountered was an unexpected variation of the blank experiments with sample size. All the samples investigated were relatively coarse with surface areas <60 cm²/g; it seems likely that surface area effects would have been found in the three earlier investigations with up to threefold variation in sample weights. We conclude that the variation observed by Blauer et al. is not wholly caused by sample size. A second and third law analysis of the data are shown below.

O.R.B. Elliott, UCRL 1831 (1952), has also investigated reaction (A), but details of the sample are not available and the results show considerable scatter.

A. Baur and A. Lecoq, *Comm. Energie At. (France)*, Rappt. CEA-R2611, Direction des Matériaux et Combustibles Nucleaires, Nov. 1964, cite the results of Morize, Roudier and Besson, *DM/946*, in equation form.

Reference	No. of Points	Range K	ΔH° ₂₉₈ Kcal/mole	ΔH° _{298.15} Kcal/mole	drift eu
Stuart	15	1338-1653	40.6 ± 0.9	44.53	2.6 ± 0.6
Young	7	1576-1839	43.9 ± 1.5	44.51	0.25 ± 0.9
Grossweiner	24	1472-1873	43.7 ± 1.1	45.22	0.7 ± 0.7
Blauer	11	1673	39.6 ± 4.4	44.62	-155.7
Elliott	6	1567-1808	50.8	47.0	-156.5
Morize	Equation	?	50.8	40.6	-182.7

*calculated using the 3rd law ΔH°₂₉₈

ΔH°₂₉₈(Be(OH)₂,g) = -156.4 ± 5 kcal/mol is adopted, with a large uncertainty to cover errors due to the functions as well as the experimental uncertainty.

Heat Capacity and Entropy

The structure is that assumed by R. L. Altman, *J. Chem. Eng. Data* 8, 534 (1963). One vibrational frequency was reported by M. Farber, M. A. Greenbaum, M. A. Frisch et al., *Rocket Power, Inc., Final Report AFRL-TR-66-220*, Contract AF 04(611)-10929, September 1966. The remaining frequencies were estimated and adjusted to give reasonable agreement between the second and third law heats of reaction. The three principal moments of inertia are I_A = 2.865 x 10⁻⁴⁰, I_B = 10.60 x 10⁻³⁹, and I_C = 10.62 x 10⁻³⁹ g cm².

BeH₂O₂

Ground State Configuration $2\sum^+$
 $\Delta H_f^0 = [56.70] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = [24.6 \pm 5.0] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = [24.7 \pm 5.0] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{E_1 \text{ cm.}^{-1}}{E_2} \quad [2]$$

$$\omega_e = [657] \text{ cm.}^{-1} \quad \omega_e x_e = [3.90] \text{ cm.}^{-1}$$

$$B_e = [0.41894] \text{ cm.}^{-1} \quad \alpha_e = [0.00248] \text{ cm.}^{-1}$$

$$r_e = [2.19] \text{ \AA}$$

Heat of Formation.

The dissociation energy was estimated from the experimental energies for BeF(g), BeCl(g), and the gaseous lithium halides. The resulting value, 79.1 kcal. mole⁻¹, was combined with JANAF heats of formation for Be(g) and I(g) in arriving at ΔH_f^0 238.15.

Heat Capacity and Entropy.

The vibrational frequency was estimated from those of BeF(g), BeCl(g), and the gaseous lithium halides. The ground term was assumed to be similar to that of BeCl(g) and BeF(g), tabulated by G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., New York, 1950. A correlation of the interatomic distances for the alkali halides, BeF(g), and BeCl(g) was employed in deriving r_e .

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(H ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	2.157	24.588	24.588	24.588	INFINITE	INFINITE
100	6.972	48.738	63.156	1.462	24.908	20.777	-45.405	-
200	7.363	53.662	57.409	-	24.894	16.533	-18.175	-
298	7.886	56.703	56.703	0.000	24.700	12.612	-9.244	-
300	7.895	56.732	56.704	0.015	24.696	12.537	-9.133	-
400	8.297	59.077	57.188	0.21	23.881	8.594	-3.405	-
500	8.484	60.946	57.623	1.661	17.052	5.640	-2.465	-
600	8.630	62.506	58.410	2.218	16.918	3.370	-1.227	-
700	8.729	63.853	59.008	3.366	16.764	1.123	-0.351	-
800	8.793	64.957	59.467	5.042	16.595	-0.801	3.900	-
900	8.833	65.856	60.000	6.033	16.404	-3.400	8.401	-
1000	8.855	66.690	60.627	6.333	16.205	-5.479	1.197	-
1100	8.868	67.489	61.545	6.924	15.978	-7.836	-	1.517
1200	8.876	68.257	62.102	7.818	15.720	-1.760	-	2.182
1300	8.880	68.997	62.495	9.015	15.445	-11.979	-	2.339
1400	8.882	69.701	62.834	10.515	15.160	-18.051	-	2.461
1500	8.883	70.374	63.123	11.418	14.875	-18.021	-	2.555
1600	8.884	71.026	63.368	12.524	14.590	-20.777	-	2.639
1700	8.885	71.659	63.574	13.833	14.305	-23.539	-	2.708
1800	8.886	72.274	63.750	15.337	14.020	-26.351	-	2.770
1900	8.887	72.873	63.897	16.945	13.735	-29.204	-	2.825
2000	8.888	73.457	64.018	18.669	13.450	-32.197	-	2.875
2100	8.889	74.026	64.115	20.517	13.165	-35.329	-	2.919
2200	8.890	74.581	64.188	22.499	12.880	-38.591	-	2.958
2300	8.891	75.123	64.238	24.627	12.595	-42.084	-	2.992
2400	8.892	75.653	64.268	26.901	12.310	-45.808	-	3.022
2500	8.893	76.173	64.280	29.321	12.025	-49.761	-	3.050
2600	8.894	76.683	64.283	31.887	11.740	-53.944	-	3.076
2700	8.895	77.184	64.277	34.599	11.455	-58.357	-	3.100
2800	8.896	77.677	64.262	37.457	11.170	-63.000	-	3.122
2900	8.897	78.163	64.238	40.461	10.885	-67.873	-	3.142
3000	8.898	78.642	64.205	43.611	10.600	-73.084	-	3.160
3100	8.899	79.114	64.163	46.904	10.315	-78.633	-	3.177
3200	8.900	79.579	64.112	50.341	10.030	-84.530	-	3.192
3300	8.901	80.038	64.052	53.924	9.745	-90.773	-	3.206
3400	8.902	80.491	63.984	57.653	9.460	-97.361	-	3.219
3500	8.903	80.938	63.908	61.529	9.175	-104.294	-	3.231
3600	8.904	81.380	63.824	65.553	8.890	-111.571	-	3.242
3700	8.905	81.817	63.731	69.724	8.605	-119.192	-	3.253
3800	8.906	82.250	63.629	74.041	8.320	-127.057	-	3.263
3900	8.907	82.679	63.519	78.514	8.035	-135.266	-	3.273
4000	8.908	83.104	63.402	83.143	7.750	-143.819	-	3.282
4100	8.909	83.525	63.279	87.927	7.465	-152.726	-	3.291
4200	8.910	83.942	63.151	92.866	7.180	-161.987	-	3.300
4300	8.911	84.356	63.018	97.959	6.895	-171.602	-	3.309
4400	8.912	84.767	62.880	103.206	6.610	-181.571	-	3.317
4500	8.913	85.174	62.737	108.606	6.325	-191.894	-	3.325
4600	8.914	85.578	62.590	114.159	6.040	-202.571	-	3.333
4700	8.915	85.979	62.438	119.864	5.755	-213.602	-	3.341
4800	8.916	86.377	62.281	125.719	5.470	-224.987	-	3.349
4900	8.917	86.772	62.119	131.724	5.185	-236.726	-	3.356
5000	8.918	87.164	61.952	137.878	4.900	-248.819	-	3.363
5100	8.919	87.553	61.780	144.181	4.615	-261.266	-	3.370
5200	8.920	87.939	61.603	150.632	4.330	-274.071	-	3.377
5300	8.921	88.322	61.421	157.234	4.045	-287.234	-	3.384
5400	8.922	88.702	61.235	163.986	3.760	-300.755	-	3.391
5500	8.923	89.079	61.045	170.888	3.475	-314.634	-	3.398
5600	8.924	89.453	60.850	177.939	3.190	-328.871	-	3.405
5700	8.925	89.824	60.651	185.139	2.905	-343.466	-	3.412
5800	8.926	90.192	60.447	192.487	2.620	-358.419	-	3.419
5900	8.927	90.557	60.238	199.983	2.335	-373.730	-	3.426
6000	8.928	90.919	60.024	207.626	2.050	-389.399	-	3.433
6100	8.929	91.279	59.806	215.414	1.765	-405.426	-	3.440
6200	8.930	91.636	59.583	223.346	1.480	-421.811	-	3.447
6300	8.931	91.991	59.356	231.421	1.195	-438.554	-	3.454
6400	8.932	92.344	59.124	239.638	0.910	-455.655	-	3.461
6500	8.933	92.695	58.888	247.996	0.625	-473.114	-	3.468
6600	8.934	93.044	58.648	256.494	0.340	-490.931	-	3.475
6700	8.935	93.391	58.403	265.131	0.055	-509.106	-	3.482
6800	8.936	93.736	58.154	273.906	-0.230	-527.639	-	3.489
6900	8.937	94.079	57.900	282.819	-0.545	-546.530	-	3.496
7000	8.938	94.420	57.642	291.869	-0.860	-565.779	-	3.503
7100	8.939	94.759	57.380	301.056	-1.175	-585.386	-	3.510
7200	8.940	95.096	57.113	310.379	-1.490	-605.351	-	3.517
7300	8.941	95.431	56.842	319.837	-1.805	-625.674	-	3.524
7400	8.942	95.764	56.567	329.429	-2.120	-646.355	-	3.531
7500	8.943	96.095	56.288	339.154	-2.435	-667.394	-	3.538
7600	8.944	96.424	56.005	349.011	-2.750	-688.691	-	3.545
7700	8.945	96.751	55.718	358.999	-3.065	-710.246	-	3.552
7800	8.946	97.076	55.427	369.117	-3.380	-732.059	-	3.559
7900	8.947	97.399	55.132	379.364	-3.695	-754.130	-	3.566
8000	8.948	97.720	54.834	389.739	-4.010	-776.459	-	3.573
8100	8.949	98.039	54.531	400.241	-4.325	-799.046	-	3.580
8200	8.950	98.356	54.224	410.869	-4.640	-821.891	-	3.587
8300	8.951	98.671	53.913	421.622	-4.955	-844.994	-	3.594
8400	8.952	98.984	53.600	432.499	-5.270	-868.355	-	3.601
8500	8.953	99.295	53.283	443.499	-5.585	-891.974	-	3.608
8600	8.954	99.604	52.962	454.621	-5.900	-915.851	-	3.615
8700	8.955	99.911	52.637	465.864	-6.215	-940.086	-	3.622
8800	8.956	100.216	52.308	477.227	-6.530	-964.589	-	3.629
8900	8.957	100.519	51.975	488.709	-6.845	-989.350	-	3.636
9000	8.958	100.820	51.638	500.309	-7.160	-1014.369	-	3.643
9100	8.959	101.119	51.297	512.026	-7.475	-1039.646	-	3.650
9200	8.960	101.416	50.952	523.859	-7.790	-1065.181	-	3.657
9300	8.961	101.711	50.603	535.807	-8.105	-1090.974	-	3.664
9400	8.962	102.004	50.250	547.869	-8.420	-1116.925	-	3.671
9500	8.963	102.295	49.894	559.944	-8.735	-1143.134	-	3.678
9600	8.964	102.584	49.535	572.131	-9.050	-1169.593	-	3.685
9700	8.965	102.871	49.172	584.429	-9.365	-1196.302	-	3.692
9800	8.966	103.156	48.805	596.837	-9.680	-1223.261	-	3.699
9900	8.967	103.439	48.434	609.354	-9.995	-1250.470	-	3.706
10000	8.968	103.720	48.059	621.979	-10.310	-1277.929	-	3.713

BeI₂

Beryllium Diiodide (BeI₂)
(Crystal) Mol. Wt. = 262.821

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0							
100	17.000	28.800	28.800	0.000	50.600	50.231	36.816
200	17.041	28.905	28.800	0.031	50.600	50.228	36.800
300	18.500	34.039	29.490	1.820	54.422	49.973	27.303
400	19.200	38.247	30.834	3.707	64.562	47.905	20.638
500	19.650	41.790	32.373	5.650	64.058	44.623	16.253
600	20.150	44.757	33.941	7.650	63.243	41.424	12.932
700	20.680	47.517	35.537	9.767	62.481	38.424	9.462
800	20.289	49.899	36.947	11.657	62.539	35.234	6.462
900	20.400	52.042	38.351	13.681	62.050	32.226	4.043
1000	20.484	53.991	39.686	15.736	61.576	29.267	2.815
1100	20.541	55.776	40.952	17.867	61.123	26.350	1.799
1200	20.571	57.421	42.152	19.987	60.688	23.478	0.945
1300	20.574	58.946	43.303	21.901	60.278	20.622	0.219

BERYLLIUM DIIODIDE (BeI₂) (CRYSTAL)

MOL. WT. = 262.821

$\Delta H_f^\circ 0 = \text{Unknown}$
 $\Delta H_f^\circ 298.15 = [-50.6 \pm 8] \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = [5] \text{ kcal. mole}^{-1}$
 $\Delta H_g^\circ 298.15 = 30.3 \pm 2.0 \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = [28.8 \pm 2] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $T_m = 753^\circ \text{K.}$

Heat of Formation.

The heat of formation was estimated from the work of W. Biltz and C. Messermecht, Z. anorg. Chem. 149, 157 (1925) and Biltz, Klatte and Rahlfs, Z. anorg. Chem. 166, 339 (1927) as reported in N.B.S. Circular 500, Washington 1952. They measured the heat of solution of BeI₂ in aq. HCl to an unknown concentration. This value was apparently adjusted and used with Be⁺⁺ and 2I⁻ to obtain ΔH_f° of the crystal. However Be⁺⁺ was estimated by the Bureau and a total uncertainty of 8 kcal. is thought to be realistic.

Heat Capacity and Entropy.

The heat capacity was estimated graphically by comparison with BeCl₂ and BeF₂. The entropy was also estimated by comparing with α-BeCl₂ and BeF₂ and using additive entropy values for the halide ions. K. N. Semenenko and T. N. Naumova, Zhur. Strukt. Khim. 4, 67 (1963) have reported that between 563 and 643°C BeI₂ exists in a β form and above 643°C a β form and an unknown form also exist. No allowance has been made for these modifications in the present table.

Melting Data.

The melting point was reported by O. Rahlfs and W. Fischer, Z. anorg. Chem. 211, 351 (1933). The heat of melting was estimated by comparison with the heats of transition and melting for BeCl₂ and BeF₂.

Sublimation Data.

The heat of sublimation was obtained from a third law analysis of the vapor pressure data of Rahlfs and Fischer, loc. cit. from 578-703°K. This gave ΔH_g° 298 = 30.34 kcal. mole⁻¹ with a drift of 3.2 ± 1.1 cal. mole⁻¹ deg.⁻¹. A second law analysis gave ΔH_g° 298 = 28.1 ± 0.7 kcal. mole⁻¹. No attempt was made to change the functions to eliminate the drift, since a correlation with BeCl₂, BeBr₂ and BeI₂ indicated that the drift was probably due to the data rather than the functions.

BeI₂

T, °K.	C _p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
0					
100					
200					
298	17.000	32.397	32.397	0.000	-48.149
300	17.041	32.502	32.502	0.031	-47.446
400	18.500	37.636	33.087	1.820	-48.153
500	21.000	41.850	34.432	3.704	-48.258
600	27.000	46.772	36.091	6.409	-48.365
700	27.000	50.935	37.921	9.109	-48.450
800	27.000	54.540	39.778	11.809	-48.550
900	27.000	57.720	41.599	14.509	-48.619
1000	27.000	60.585	43.356	17.209	-48.688
1100	27.000	63.138	45.039	19.509	-48.759
1200	27.000	65.487	46.646	22.609	-48.828
1300	27.000	67.649	48.180	25.309	-48.897
1400	27.000	69.649	49.643	28.009	-48.966
1500	27.000	71.512	51.040	30.709	-49.035
1600	27.000	73.255	52.374	33.409	-49.104
1700	27.000	74.892	53.651	36.109	-49.173
1800	27.000	76.435	54.874	38.809	-49.242
1900	27.000	77.895	56.048	41.509	-49.311
2000	27.000	79.280	57.175	44.209	-49.380

BERYLLIUM DIODIDE (BeI₂)

(LIQUID)

MOL. WT. = 262.821

$$\Delta H_f^\circ 298.15 = [-47.45 \pm 3] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = [5] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^\circ = [23] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = [32.4] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_m^\circ = 753^\circ \text{K.}$$

$$T_b^\circ = [755]^\circ \text{K.}$$

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{753}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with the measured value for BeCl₂. A glass transition was assumed at 500°K. below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See BeI₂(c) table for details.

Vaporization Data.

The temperature and heat of vaporization were calculated from the cross over point BeI₂(l) and (g).

Beryllium Diodide (BeI₂)

(Ideal Gas) Mol. Wt. = 262.821

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	0.000	0.000	20.018	20.018	INFINITE
100	11.050	57.007	8.766	2.746	20.018	20.018	20.018	INFINITE
200	12.611	65.254	71.641	1.277	20.010	20.010	20.010	30.945
298	13.364	70.441	70.441	0.000	20.010	20.010	20.010	33.709
300	13.376	70.524	70.524	0.025	20.306	20.306	20.306	23.617
400	14.141	74.441	70.972	1.084	24.553	24.553	24.553	19.814
500	14.166	77.572	71.990	2.781	35.176	35.176	35.176	16.069
600	14.360	80.173	73.143	4.218	35.190	35.190	35.190	14.127
700	14.490	82.397	74.310	5.601	35.216	35.216	35.216	12.295
800	14.579	84.338	75.445	7.115	35.260	35.260	35.260	10.920
900	14.643	86.059	76.530	8.576	35.320	35.320	35.320	9.849
1000	14.690	87.605	77.562	10.043	35.396	35.396	35.396	8.990
1100	14.726	89.007	78.540	11.514	35.498	35.498	35.498	8.286
1200	14.753	90.289	79.466	12.988	35.622	35.622	35.622	7.697
1300	14.771	91.471	80.345	14.464	35.767	35.767	35.767	7.197
1400	14.782	92.566	81.179	15.942	35.937	35.937	35.937	6.767
1500	14.806	93.587	81.973	17.422	36.130	36.130	36.130	6.392
1600	14.818	94.543	82.729	18.904	36.323	36.323	36.323	6.051
1700	14.828	95.442	83.450	20.386	36.528	36.528	36.528	5.737
1800	14.836	96.290	84.140	21.869	36.746	36.746	36.746	5.456
1900	14.843	97.092	84.801	23.353	36.978	36.978	36.978	5.204
2000	14.849	97.854	85.435	24.837	37.226	37.226	37.226	4.977
2100	14.854	98.578	86.044	26.323	37.490	37.490	37.490	4.770
2200	14.858	99.269	86.629	27.808	37.768	37.768	37.768	4.581
2300	14.862	99.930	87.193	29.294	38.060	38.060	38.060	4.408
2400	14.866	100.562	87.737	30.781	38.366	38.366	38.366	4.249
2500	14.869	101.169	88.262	32.267	38.686	38.686	38.686	4.102
2600	14.871	101.753	88.770	33.754	39.020	39.020	39.020	3.966
2700	14.874	102.314	89.261	35.242	39.368	39.368	39.368	3.839
2800	14.876	102.855	89.737	36.730	39.730	39.730	39.730	3.719
2900	14.878	103.377	90.199	38.217	40.107	40.107	40.107	3.604
3000	14.879	103.881	90.646	39.705	40.500	40.500	40.500	3.493
3100	14.881	104.369	91.081	41.193	40.908	40.908	40.908	3.386
3200	14.882	104.842	91.504	42.681	41.332	41.332	41.332	3.283
3300	14.884	105.300	91.915	44.169	41.774	41.774	41.774	3.183
3400	14.885	105.744	92.315	45.657	42.232	42.232	42.232	3.087
3500	14.886	106.175	92.705	47.146	42.706	42.706	42.706	2.995
3600	14.887	106.595	93.085	48.635	43.196	43.196	43.196	2.907
3700	14.888	107.003	93.456	50.123	43.700	43.700	43.700	2.823
3800	14.889	107.400	93.818	51.612	44.218	44.218	44.218	2.743
3900	14.890	107.787	94.171	53.101	44.750	44.750	44.750	2.667
4000	14.890	108.163	94.516	54.590	45.296	45.296	45.296	2.595
4100	14.891	108.531	94.853	56.079	45.856	45.856	45.856	2.527
4200	14.892	108.890	95.183	57.568	46.430	46.430	46.430	2.463
4300	14.892	109.240	95.506	59.058	47.018	47.018	47.018	2.402
4400	14.893	109.583	95.822	60.547	47.620	47.620	47.620	2.344
4500	14.893	109.917	96.132	62.036	48.136	48.136	48.136	2.290
4600	14.894	110.245	96.435	63.526	48.666	48.666	48.666	2.240
4700	14.894	110.565	96.732	65.015	49.210	49.210	49.210	2.193
4800	14.895	110.879	97.024	66.504	49.768	49.768	49.768	2.150
4900	14.895	111.186	97.310	67.994	50.339	50.339	50.339	2.109
5000	14.895	111.487	97.590	69.483	50.924	50.924	50.924	2.071
5100	14.896	111.782	97.865	70.973	51.524	51.524	51.524	2.036
5200	14.896	112.071	98.136	72.463	52.138	52.138	52.138	2.003
5300	14.896	112.355	98.402	73.952	52.766	52.766	52.766	1.972
5400	14.897	112.633	98.662	75.442	53.408	53.408	53.408	1.943
5500	14.897	112.907	98.919	76.931	54.064	54.064	54.064	1.915
5600	14.897	113.175	99.171	78.421	54.734	54.734	54.734	1.889
5700	14.897	113.439	99.419	79.911	55.418	55.418	55.418	1.864
5800	14.898	113.698	99.663	81.401	56.116	56.116	56.116	1.841
5900	14.898	113.952	99.903	82.890	56.828	56.828	56.828	1.819
6000	14.898	114.203	100.139	84.380	57.554	57.554	57.554	1.798

Dec. 31, 1961; June 30, 1965

BeI₂

MOL. WT. = 262.821

(IDEAL GAS)

BERYLLIUM DIODIDE (BeI₂)

Point Group D_{∞h}

S_{298.15}⁰ = [70.44 ± 2] cal. mole⁻¹ deg.⁻¹

Ground State Quantum Weight = 1

ΔH_f⁰ = -20 ± 4 kcal. mole⁻¹

ΔH_f⁰ 298.15 = [-20.3 ± 10] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω₂, cm.⁻¹

[140](1)

[155](2)

[770](1)

σ = 2

Bond Distance: Be-I = 2.12 Å

Bond Angle: I-Be-I = [180°]

Rotational Constant: B₀ = 0.01478 cm.⁻¹

Heat of Formation.

The heat of formation was obtained from that of the crystal plus ΔH₃ 298° see BeI₂ (c) table for details.

Heat Capacity and Entropy.

The linear structure was assumed by analogy with BeCl₂. The bond length was reported by P. A. Akshin, V. P. Spiridonov and O. A. Sobolev, Dokl. Akad. Nauk SSSR, 116, 1134 (1958) from electron diffraction measurements. The vibrational frequencies were estimated by assuming a set of force constants k₁ for the BeF₂, BeCl₂, BeBr₂ and BeI₂ series and also assuming k₁/k₁⁰ = 50 as for BeF₂. The principal moment of inertia is 189.402 x 10⁻⁵⁹ g. cm.²

BeI₂

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.030	INFINITE	101.400	101.400	INFINITE
100	6.958	42.221	56.133	101.741	- 217.311	- 2.173
200	6.958	42.221	56.133	101.741	- 217.311	- 2.173
298	7.192	49.672	64.672	101.981	- 217.311	- 2.173
300	7.197	49.672	64.672	101.981	- 217.311	- 2.173
400	7.514	52.029	50.136	101.981	- 217.311	- 2.173
500	7.620	53.740	50.708	101.981	- 217.311	- 2.173
600	8.069	55.188	51.337	101.981	- 217.311	- 2.173
700	8.264	56.447	51.979	101.981	- 217.311	- 2.173
800	8.414	57.561	52.609	101.981	- 217.311	- 2.173
900	8.531	58.559	53.213	101.981	- 217.311	- 2.173
1000	8.624	59.463	53.796	101.981	- 217.311	- 2.173
1100	8.699	60.289	54.349	100.976	75.368	14.374
1200	8.760	61.048	54.876	100.760	73.050	13.303
1300	8.812	61.752	55.378	100.521	70.750	11.894
1400	8.856	62.406	55.857	100.258	68.469	10.688
1500	8.894	63.019	56.314	99.971	66.208	9.646
1600	8.927	63.594	56.752	99.669	64.046	8.748
1700	8.957	64.136	57.170	99.349	61.999	7.970
1800	8.984	64.649	57.571	99.009	59.965	7.280
1900	9.008	65.135	57.957	98.650	57.944	6.665
2000	9.031	65.598	58.327	98.275	55.935	6.112
2100	9.051	66.039	58.684	97.884	53.938	5.613
2200	9.071	66.460	59.028	97.475	51.952	5.161
2300	9.089	66.864	59.360	97.050	49.979	4.749
2400	9.106	67.251	59.681	96.608	48.017	4.372
2500	9.123	67.623	59.991	96.146	46.062	4.027
2600	9.139	67.981	60.292	95.665	44.122	3.709
2700	9.154	68.326	60.583	95.165	42.190	3.415
2800	9.169	68.650	60.865	94.646	40.275	3.145
2900	9.183	68.962	61.140	94.108	38.375	2.895
3000	9.197	69.263	61.406	93.553	36.487	2.665
3100	9.211	69.555	61.666	92.980	34.613	2.453
3200	9.224	69.838	61.918	92.388	32.754	2.259
3300	9.237	70.112	62.164	91.775	30.913	2.083
3400	9.250	70.448	62.403	91.143	29.083	1.923
3500	9.262	70.716	62.637	90.488	27.263	1.777
3600	9.275	70.977	62.865	89.810	25.453	1.643
3700	9.287	71.231	63.088	89.118	23.653	1.519
3800	9.299	71.470	63.305	88.413	21.863	1.405
3900	9.311	71.721	63.518	87.695	20.083	1.299
4000	9.323	71.957	63.726	86.963	18.323	1.201
4100	9.334	72.187	63.930	86.218	16.583	1.109
4200	9.346	72.412	64.129	85.460	14.853	1.023
4300	9.358	72.632	64.324	84.688	13.133	0.943
4400	9.369	72.847	64.516	83.903	11.423	0.867
4500	9.380	73.056	64.703	83.105	9.733	0.795
4600	9.392	73.264	64.887	82.293	8.063	0.727
4700	9.403	73.466	65.067	81.468	6.413	0.663
4800	9.414	73.665	65.244	80.630	4.783	0.603
4900	9.425	73.859	65.418	79.778	3.173	0.547
5000	9.436	74.049	65.589	78.908	1.583	0.495
5100	9.447	74.236	65.757	78.023	0.013	0.447
5200	9.458	74.420	65.921	77.123	- 1.537	0.403
5300	9.469	74.600	66.084	76.208	- 3.107	0.363
5400	9.480	74.777	66.243	75.278	- 4.697	0.327
5500	9.491	74.951	66.400	74.333	- 6.307	0.295
5600	9.501	75.122	66.554	73.373	- 7.937	0.267
5700	9.512	75.291	66.706	72.400	- 9.587	0.243
5800	9.523	75.456	66.855	71.413	- 11.257	0.223
5900	9.534	75.619	67.000	70.413	- 12.947	0.207
6000	9.545	75.779	67.147	69.400	- 14.657	0.193

Ground State Configuration [³Π]
S_{298.15} = [49.87] cal deg⁻¹ mole⁻¹
ΔH_f⁰ = [101] kcal mole⁻¹
ΔH_f⁰ 298.15 = [102] kcal mole⁻¹

Electronic Levels and Multiplicities

$\frac{\epsilon_i, \text{cm}^{-1}}{0} = \frac{E_i}{(u)}$
ω_e = [1194] cm⁻¹ ω_ex_e = [12.4] cm⁻¹ σ = 1
B_e = [1.885] cm⁻¹ a_e = [0.019] cm⁻¹ r_e = [1.406] Å

Heat of Formation

The heat of formation was estimated by J. S. Gordon, AstroSystems International, Livingston, New Jersey, private communication, April 26, 1963.

Molecular Constants

The molecular constants were taken from J. S. Gordon, loc. cit.

Beryllium Oxide (BeO)

(Crystal) Mol. Wt. = 25.013

BeO

MOL. WT. = 25.013

BERYLLIUM OXIDE (BeO)

(CRYSTAL)

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞.00	INFINITE	-	-142.282	-	INFINITE
100	∞.675	∞.933	-	-142.282	-	307.190
200	3.415	3.856	-	-142.430	-	151.213
298	6.100	3.378	∞.000	-142.913	-136.385	92.775
300	6.144	3.378	∞.111	-143.100	-136.122	99.128
400	8.022	3.644	∞.727	-143.102	-136.079	73.059
500	9.244	7.391	4.204	-143.184	-131.357	57.413
600	10.138	9.163	4.885	-143.130	-128.996	46.984
700	10.778	10.778	6.352	-142.936	-126.912	33.599
800	11.232	12.247	7.716	-142.936	-126.912	23.599
900	11.527	13.588	7.082	-142.821	-121.990	29.622
1000	11.730	14.814	7.019	-142.711	-119.682	26.155
1100	11.900	15.940	8.485	-142.613	-117.384	23.321
1200	12.070	16.983	9.750	-142.534	-115.096	19.964
1300	12.242	17.955	9.791	-142.452	-112.811	17.254
1400	12.418	18.869	10.407	-142.387	-110.534	15.773
1500	12.595	19.732	11.000	-142.332	-108.261	14.466
1600	12.770	20.550	11.571	-145.041	-105.912	13.301
1700	12.940	21.320	12.122	-144.990	-103.471	12.153
1800	13.117	22.074	12.655	-144.950	-101.045	11.023
1900	13.291	22.788	13.170	-144.925	-98.617	10.512
2000	13.465	23.474	13.668	-144.909	-96.204	9.761
2100	13.640	24.136	14.151	-144.890	-93.799	9.080
2200	13.815	24.782	14.617	-144.871	-91.405	8.462
2300	13.988	25.392	15.074	-144.852	-89.023	7.890
2400	14.159	25.932	15.518	-144.833	-86.643	7.368
2500	14.327	26.429	15.950	-144.814	-84.283	6.886
2600	14.491	26.876	16.372	-144.795	-81.930	6.442
2700	14.651	27.266	16.784	-144.776	-79.588	6.034
2800	14.810	27.615	17.186	-144.757	-77.255	5.659
2900	14.968	27.930	17.578	-144.738	-74.933	5.312
3000	15.068	28.239	17.962	-144.719	-72.623	4.985
3100	15.145	28.534	18.337	-144.700	-70.333	4.683
3200	15.215	28.814	18.704	-144.681	-68.063	4.397
3300	15.284	29.086	19.064	-144.662	-65.813	4.133
3400	15.353	29.353	19.414	-144.643	-63.583	3.887
3500	15.437	31.690	19.759	-144.624	-61.373	3.659
3600	15.506	32.126	20.096	-144.605	-59.183	3.447
3700	15.575	32.556	20.427	-144.586	-57.013	3.251
3800	15.641	32.968	20.747	-144.567	-54.863	3.069
3900	15.706	33.375	21.070	-144.548	-52.733	2.902
4000	15.770	33.773	21.383	-144.529	-50.623	2.747

$\Delta H_f^\circ 0 = -142.3 \pm 0.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -143.1 \pm 0.1 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 0.06 \pm 1.0 \text{ kcal. mole}^{-1}$
 $T_m = 2325^\circ\text{K.}$
 $\Delta H_m^\circ = 15.1 \pm 0.4 \text{ kcal. mole}^{-1}$
 $\Delta H_s^\circ 298.15 = 174.1 \pm 3.0 \text{ kcal. mole}^{-1}$

Heat of Formation.

L. A. Cosgrove and P. E. Snyder, *J. Am. Chem. Soc.* 75, 3102 (1953) have reviewed earlier determinations of the heat of formation and have made a very careful oxygen bomb calorimeter determination, their value is adopted here.

Heat Capacity and Entropy.

The high temperature enthalpy of BeO(c) has been reported by A. Magnus and H. Danz, *Ann. Physik.* [4] 81, 407 (1926) up to 1172°K. E. N. Rodigina and K. Z. Gornel'skii, *Zhur. Fiz. Khim.* 35, 1829 (1961) up to 1128°K. V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Ponomarev, *Doklady. Akad. Nauk. S.S.S.R.* 131, 586 (1960) up to 2840°K. B. E. Walker, C. T. Ewing, and R. R. Miller, private communication, U. S. Naval Research Laboratory 18th April 1963 up to 1100°K. A. C. Victor and T. B. Douglas, *J. Res. Natl. Bureau Standards* 67A, 325 (1963) up to 1173°K. A high temperature phase transition has been reported by S. B. Austerman, *Bull. Am. Physical Soc.* 117 (1), 28 (1962) and has been confirmed using high temperature X-rays by T. W. Baker and P. J. Baldock, *Nature* 193, 1172 (1962). K. K. Kelley, *J. Am. Chem. Soc.* 61, 1217 (1939) has reported the low temperature heat capacities from 55.5 to 292.4°K. The heat capacity was assumed to follow the T^3 law below 55.5°K. and this gave $S_{55.5} = 0.045 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The high temperature enthalpy data was smoothed using both 18 and 27 point groupings and was assumed to be discontinuous at 2325°K. The heat capacity obtained from the smoothed enthalpy was itself smoothed graphically so as to fit with the low temperature heat capacity. The data of Kandyba, et al., show no effect of the transition at 2325° and a value of $0.06 \text{ kcal. mole}^{-1}$ was adopted simply to provide a somewhat improved fit of the data above 2700°K. The data above 2700°K. were not included because of apparent premelting effects and the heat capacity curve from 2700 to 2820°K. is extrapolated.

Transition Data.

See heat capacity and entropy.

Melting Data.

Obtained from the enthalpy measurements of Kandyba, et al., loc. cit.

Heat of Sublimation.

The gas above BeO(c) is complex and the value given is for the reaction $\text{BeO(c)} \rightarrow \text{BeO(g)}$ and simply read from the respective tables.

$$\Delta H_f^{298.15} = 8.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = -129.562 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 15.1 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$T_m = 2820^\circ\text{K.}$$

$$T_b = [4060]^\circ\text{K.}$$

Heat of Formation.

The heat of formation was obtained from that of the crystal by adding ΔH_m^0 and the difference between H_{298}^0 for crystal and liquid.

Heat Capacity and Entropy.

The enthalpy of three points in the liquid phase was determined by V. V. Kandyba, P. B. Kantor, R. M. Krasovitskaya and E. N. Pomichev, Dokl. Akad. Nauk. S.S.S.R. 131, 566 (1960). These values were used to obtain a heat capacity for the liquid which was assumed constant. At 1900°K. a glass transition was assumed below which the heat capacity was that of the solid. The entropy at 298°K. was obtained in a manner analogous to the heat of formation.

Melting Data.

See the table for BeO(c).

Vaporization Data.

The vapor composition over BeO(c) at say 2300°K. is composed of Be(g), O(g), BeO(g), (BeO)₂(g), (BeO)₃(g), (BeO)₄(g), (BeO)₅(g), Be₂O(g) and other species and thus a boiling point becomes almost meaningless and the value given here is the point at which the total pressure reaches 1 atm.

Beryllium Oxide (BeO)

(Ideal Gas) Mol. Wt. = 25.013

BeO

BERYLLIUM OXIDE (BeO)

(IDEAL GAS)

MOL. WT. = 25.013

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
0	∞	INFINITE	-2.076	30.429	30.429	INFINITE
100	6.957	36.593	5.418	30.756	28.886	-63.128
200	6.965	44.416	4.849	30.974	26.912	-29.412
298	7.046	47.208	4.687	31.000	26.910	-18.259
300	7.049	47.252	4.709	31.000	24.872	-18.119
400	7.254	48.306	4.787	30.919	22.840	-12.678
500	7.510	50.952	4.821	30.788	20.835	-9.106
600	7.757	52.343	4.828	30.632	18.858	-6.959
700	7.969	53.255	4.817	30.478	16.859	-5.459
800	8.145	54.031	4.804	30.320	14.986	-4.094
900	8.287	54.599	4.784	30.168	13.088	-3.178
1000	8.402	54.978	4.758	29.849	11.213	-2.451
1100	8.497	55.284	4.725	29.460	9.361	-1.860
1200	8.575	55.523	4.687	29.011	7.535	-1.362
1300	8.640	55.715	4.645	28.511	5.735	-0.923
1400	8.695	55.875	4.599	28.070	3.959	-0.615
1500	8.741	56.009	4.542	27.646	2.217	-0.317
1600	8.782	56.125	4.477	27.235	0.515	-0.070
1700	8.818	56.223	4.405	26.832	-1.158	0.172
1800	8.848	56.303	4.328	26.432	-2.807	0.412
1900	8.876	56.364	4.246	26.032	-4.407	0.668
2000	8.901	56.408	4.159	25.629	-5.957	0.909
2100	8.924	56.433	4.067	25.224	-7.460	1.126
2200	8.944	56.449	3.971	24.824	-8.924	1.302
2300	8.963	56.457	3.868	24.428	-10.358	1.446
2400	8.981	56.459	3.759	24.036	-11.766	1.566
2500	8.997	56.456	3.646	23.648	-13.146	1.666
2600	9.013	56.449	3.529	23.264	-14.500	1.746
2700	9.027	56.439	3.408	22.884	-15.832	1.802
2800	9.041	56.425	3.283	22.508	-17.146	1.846
2900	9.054	56.408	3.153	22.128	-18.442	1.877
3000	9.066	56.388	3.018	21.744	-19.722	1.893
3100	9.078	56.364	2.878	21.356	-20.986	1.898
3200	9.089	56.337	2.733	20.964	-22.236	1.893
3300	9.101	56.308	2.583	20.568	-23.472	1.878
3400	9.111	56.278	2.428	20.168	-24.696	1.859
3500	9.122	56.244	2.268	19.764	-25.908	1.836
3600	9.132	56.207	2.103	19.356	-27.108	1.809
3700	9.141	56.168	1.933	18.944	-28.296	1.778
3800	9.151	56.126	1.758	18.528	-29.472	1.742
3900	9.161	56.083	1.578	18.108	-30.636	1.699
4000	9.170	56.039	1.393	17.684	-31.788	1.650
4100	9.179	56.002	1.203	17.256	-32.928	1.596
4200	9.188	55.963	1.008	16.824	-34.056	1.538
4300	9.197	55.923	0.808	16.388	-35.172	1.476
4400	9.205	55.884	0.604	15.948	-36.276	1.410
4500	9.214	55.848	0.396	15.504	-37.368	1.340
4600	9.222	55.811	0.183	15.056	-38.448	1.266
4700	9.231	55.772	0.000	14.604	-39.516	1.188
4800	9.239	55.733	-0.183	14.148	-40.572	1.106
4900	9.247	55.694	-0.364	13.688	-41.616	1.020
5000	9.255	55.655	-0.541	13.224	-42.648	0.930
5100	9.263	55.616	-0.714	12.756	-43.668	0.836
5200	9.271	55.577	-0.884	12.284	-44.676	0.738
5300	9.279	55.538	-1.050	11.808	-45.672	0.636
5400	9.287	55.500	-1.212	11.328	-46.656	0.530
5500	9.295	55.461	-1.371	10.844	-47.628	0.420
5600	9.302	55.422	-1.526	10.356	-48.588	0.306
5700	9.309	55.383	-1.678	9.864	-49.536	0.188
5800	9.318	55.344	-1.826	9.368	-50.472	0.066
5900	9.325	55.305	-1.971	8.868	-51.396	-0.060
6000	9.333	55.266	-2.112	8.364	-52.308	-0.182

Ground State Configuration $1s^2 + s^2$
 $S^2_{298.15} = 47.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_f 0 = 30 \pm 3 \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = 31 \pm 3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ , cm. ⁻¹	g_i
0	1

 $\Delta J_e = 1487.323 \text{ cm.}^{-1}$
 $\Delta J_e = 11.8297 \text{ cm.}^{-1}$
 $\sigma = 1$
 $B_e = 1.6510 \text{ cm.}^{-1}$
 $\alpha_e = 0.0180 \text{ cm.}^{-1}$
 $r_e = 1.3308 \text{ \AA}$

Heat of Formation.

W. A. Chupke, J. Berkowitz, and C. P. Gleason, J. Chem. Phys. 30, 827 (1959) obtained a value of 106 ± 3 kcal. mole⁻¹ for D_0 from the reactions $\text{BeO(g)} \rightarrow \text{Be(g)} + \text{O(g)}$ and $\text{BeO(g)} + \text{O(g)} \rightarrow \text{Be(g)} + \text{O}_2(\text{g})$. The reactions were followed mass spectrometrically at low electron energies in order to eliminate fragmentation of higher polymers. A Lagerqvist, Arkiv. Fysik 1, 473 (1954) had previously reported a value for $D_0 = 110 \pm 10$ kcal. mole⁻¹ based on the dissociation limit of the lowest 1π state which was assumed to dissociate to $\text{Be}(\bar{^1s})$ and $\text{O}(\bar{^1D})$. The $\Delta H^{\circ}_f 298 \text{ BeO(g)} = 31 \pm 3 \text{ kcal. mole}^{-1}$ from $D_0 = 106 \pm 3 \text{ kcal. mole}^{-1}$ was adopted.

Heat Capacity and Entropy.

The spectroscopic constants are from G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York 1950. The ground state configuration has been confirmed by B. A. Thrush, Proc. Chem. Soc. (London), 339 (1960) using absorption spectroscopy.

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-3.102	-284.431	-284.431	INFINITE
100	7.008	4.453	32.600	-2.815	-285.706	-277.563	606.612
200	14.502	11.683	20.326	-1.728	-286.542	-269.021	294.021
298	20.482	18.635	18.635	0.000	-287.000	-260.380	190.864
300	20.581	18.762	18.636	+0.038	-287.005	-260.215	189.566
400	24.828	25.103	19.409	2.322	-287.681	-251.236	137.269
500	27.810	31.180	21.258	4.961	-287.946	-242.088	105.817
600	30.310	36.470	23.360	7.866	-287.950	-232.912	84.898
700	32.500	41.020	25.064	11.067	-287.950	-223.736	70.724
800	34.500	44.863	26.563	14.567	-287.950	-214.560	58.978
900	36.330	48.000	27.863	18.267	-287.950	-205.384	49.877
1000	41.690	54.352	32.332	22.220	-287.958	-195.035	42.625
1100	43.759	58.627	34.539	26.497	-286.465	-184.816	36.710
1200	45.552	62.163	36.493	30.926	-284.971	-174.704	31.704
1300	47.196	65.019	38.239	35.526	-283.137	-164.794	27.704
1400	48.698	67.479	40.012	40.190	-281.384	-154.989	24.195
1500	47.480	72.479	42.935	44.915	-289.609	-145.310	21.172
1600	47.802	75.954	44.904	49.680	-280.485	-135.668	18.531
1700	47.500	78.608	46.974	54.496	-281.384	-126.026	16.149
1800	47.000	81.000	48.674	59.269	-286.828	-116.530	14.149
1900	46.000	84.196	50.475	64.069	-284.971	-107.118	12.321
2000	48.000	86.658	52.424	68.869	-283.130	-97.808	10.688
2100	48.000	89.000	54.920	73.669	-281.385	-88.586	9.219
2200	48.000	91.331	57.424	78.469	-279.499	-79.451	7.893
2300	48.000	93.367	57.163	83.269	-277.707	-70.399	6.689

Sept. 30, 1966

BeO₄S

Heat of Formation.

Bear et al. measured the heats of solution of Be(c) and BeSO₄(α) in concentrated HF and the heat of reaction of H₂SO₄ (aq) with BeSO₄ (aq HF). Combination of these yields reaction (a) below. Taylor et al. measured heats of solution of Be(c) and BeSO₄(α) in H₂SO₄ (aq) which yields reaction (b). Marchal measured the total vapor pressure of BeSO₄(c) in the temperature range 863-1103°K. Partial pressures of SO₃(g) were calculated from Marchal's data using JANAP values for the SO₃ - SO₂ equilibrium. Third law analysis of these data yields ΔH° for reaction (c) as given below. This was converted to ΔH° for α-BeSO₄ using JANAP heats of transition.

Author	Method	Reaction	T°K	ΔH° kcal/mol	ΔH° _{298.15} kcal/mol
1. Bear (1966)	Calorimetric	(a) Be(c) + H ₂ SO ₄ (109 H ₂ O) = H ₂ (g) + α-BeSO ₄	294	-74.47	-286.85 ± 0.5
2. Taylor (1966)	Calorimetric	(b) Be(c) + H ₂ SO ₄ (47.849 H ₂ O) = H ₂ (g) + α-BeSO ₄	298	-76.38	-287.55 ± 0.13
3. Marchal (1925)	Kp (973-1083°K)	(c) BeSO ₄ (γ) = BeO(c) + SO ₃ (g)	298	+43.92	-286.55 ± 0.5

References: 1. I. J. Bear and A. O. Turnbull, J. Phys. Chem. **70**, 711-17 (1966).

2. A. R. Taylor, Jr., B. E. Letson and D. F. Smith, U. S. Bureau of Mines, Report No. 6724, 1966.

3. G. Marchal, J. Chim. Phys. **22**, 502 (1925).

The adopted ΔH°_{298.15} = -287.0 ± 0.8 is an average value of reactions (a) and (b). This value is for relatively finely divided crystals of BeSO₄ as was indicated by Bear et al.

Heat Capacity and Entropy.

Low temperature heat capacities (12-301°K) and high temperature enthalpies (366-864°K) were measured by A. R. Taylor, Jr., T. E. Gardner and D. F. Smith, U. S. Bureau of Mines, Report No. 6240, 1963. These data were joined smoothly at 298°K and extrapolated graphically above 864°K. The entropy was obtained from the heat capacities using S°_{12.56} = 0.034 eu.

Transition Data.

I. I. Bosik, A. V. Novoselova and Yu. P. Simanov, Russ. J. Inorg. Chem. **8**, 1295 (1961), observed two endothermic effects at 863-865°K and 908-913°K on the heating and cooling curves of BeSO₄(c); thus we have adopted T₁(α→β) = 863°K and T₂(β→γ) = 908°K. ΔH°(α→β) = 0.266 kcal/mol was obtained from the single enthalpy point at 863.9°K observed by Taylor, Gardner and Smith. ΔH°(β→γ) = 4.673 kcal/mol was chosen in order to give good agreement with the equilibrium data of Marchal, loc. cit.



Beryllium Sulfate, Beta (β -BeSO₄)

(Crystal) GFW = 105.0738

OPW = 105.0738

(CRYSTAL)

BERYLLIUM SULFATE, BETA (β -BeSO₄)

$\Delta H_f^\circ = \text{Unknown}$
 $\Delta H_{298.15}^\circ = [-286.734] \text{ kcal/mol}$
 $\Delta H_1^\circ = [0.266] \text{ kcal/mol}$
 $\Delta H_2^\circ = [4.673] \text{ kcal/mol}$

$S_{298.15}^\circ = [18.943] \text{ gibbs/mol}$
 $T_1 = 863^\circ\text{K}$
 $T_2 = 908^\circ\text{K}$

Heat of Formation.

The heat of formation was calculated from that of the alpha phase by adding ΔH_1° , since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy.

The heat capacity was assumed to be the same as that of alpha phase. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

See alpha phase.

T, °K	C _p ^o	S ^o - (C ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	20.482	18.943	-0.00	-286.734	-260.206	190.736
300	20.581	18.943	+0.38	-286.739	-260.041	189.440
400	24.828	25.611	2.322	-287.415	-251.093	137.191
500	27.810	31.487	4.961	-287.680	-241.976	105.767
600	30.310	36.778	7.866	-287.684	-232.831	84.808
700	32.980	41.668	11.059	-287.469	-223.680	68.592
800	35.800	46.235	14.467	-287.027	-215.670	58.973
900	38.730	50.620	18.193	-286.984	-208.409	49.880
1000	41.690	54.859	22.220	-287.692	-195.076	42.634
1100	43.759	58.935	26.497	-286.200	-184.869	36.734
1200	45.258	62.478	30.901	-284.526	-174.898	31.458
1300	46.258	65.478	35.526	-282.671	-164.928	26.727
1400	46.984	68.027	40.190	-281.118	-155.154	22.421
1500	47.480	70.186	44.915	-280.343	-145.505	18.542
1600	47.892	72.042	49.680	-280.319	-135.895	15.052
1700	48.192	73.612	54.484	-280.269	-126.325	11.937
1800	48.400	74.908	59.269	-280.192	-116.817	9.163
1900	48.500	76.004	64.069	-280.095	-107.437	6.758
2000	48.600	76.966	68.869	-280.000	-98.158	4.676
2100	48.600	77.808	73.669	-280.000	-88.967	2.950
2200	48.600	78.540	78.469	-280.000	-79.860	1.633
2300	48.600	79.174	83.269	-277.441	-70.839	0.671



T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
100							
200							
298	20.482	24.088	24.088	.000	- 282.061	- 257.067	186.435
300	20.581	24.215	24.088	2.038	- 282.066	- 256.912	187.160
400	24.828	30.456	24.951	2.622	- 282.072	- 256.762	188.452
500	27.810	36.632	26.711	4.961	- 282.097	- 256.875	190.649
600	30.310	41.923	28.812	7.866	- 283.011	- 231.245	84.231
700	32.980	46.793	31.037	11.029	- 282.776	- 222.608	68.501
800	35.490	51.380	33.296	15.157	- 282.534	- 215.327	46.871
900	37.840	55.741	35.584	19.157	- 282.287	- 208.071	25.231
1000	41.490	60.004	37.785	22.220	- 283.019	- 195.548	42.737
1100	43.759	64.080	39.991	26.497	- 281.527	- 185.875	36.930
1200	45.222	67.953	42.162	30.950	- 289.903	- 176.340	32.116
1300	46.588	71.576	44.286	35.488	- 286.198	- 167.884	28.006
1400	47.894	75.071	46.368	40.160	- 286.198	- 157.884	24.006
1500	47.480	78.331	48.398	44.915	- 284.670	- 148.569	21.644
1600	47.802	81.407	50.356	49.680	- 285.646	- 139.454	18.048
1700	47.970	84.310	52.269	54.470	- 283.762	- 130.372	16.761
1800	48.000	87.069	54.128	59.269	- 284.589	- 121.345	15.471
1900	48.000	89.629	55.928	64.069	- 280.032	- 112.539	14.185
2000	48.000	92.111	57.676	68.869	- 278.191	- 103.775	11.340
2100							
2200	48.000	94.453	59.372	73.669	- 276.366	- 95.088	9.897
2300	48.000	96.685	61.018	78.469	- 274.560	- 86.506	8.594
2400	48.000	98.819	62.615	83.269	- 272.768	- 77.999	7.412

ΔH°_{298} = Unknown

$\Delta H^\circ_{298.15} = [292.06] \text{ kcal/mol}$

$\Delta H^\circ_{f1} = [0.286] \text{ kcal/mol}$

$\Delta H^\circ_{f2} = [4.673] \text{ kcal/mol}$

$S^\circ_{298.15} = [24.088] \text{ gibbs/mol}$

$T^\circ_{f1} = 863^\circ\text{K}$

$T^\circ_{f2} = 908^\circ\text{K}$

Heat of Formation.

The heat of formation was calculated from that of the beta phase by adding ΔH°_{f2} , since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy.

The heat capacity was assumed to be the same as that of alpha phase. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

See alpha phase.

Beryllium Tungstate (BeWO₄)
(Crystal) GFW = 256.8598

T, °K	C _p	gibbs/mol S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0							
100	20	21.120	21.120	.000	-361.700	-335.769	246.125
200	23.250	21.120	21.120	.000	-361.701	-335.768	246.490
300	23.350	21.244	21.120	.083	-361.424	-324.816	178.619
400	23.450	21.368	21.083	.2570	-361.424	-318.266	139.114
500	23.520	21.416	21.013	.5401	-361.360	-318.266	112.801
600	31.390	40.370	26.286	8.451	-360.973	-309.662	94.029
700	32.820	45.318	26.658	11.662	-360.511	-301.169	79.051
800	34.150	49.788	31.928	15.081	-359.995	-282.155	60.331
900	35.300	53.674	35.586	18.619	-359.395	-276.050	53.210
1000	36.370	57.074	38.586	22.088	-358.744	-267.816	47.286
1100	37.700	61.213	37.756	25.802	-358.036	-259.046	42.613
1200	38.760	64.539	37.651	29.626	-357.272	-251.508	38.317
1300	39.830	67.685	41.672	33.527	-356.478	-235.534	34.081
1400	40.890	70.607	45.710	37.501	-355.646	-227.566	31.081
1500	41.930	73.533	49.735	41.735	-354.812	-219.326	28.222
1600	43.000	76.273	47.535	45.981	-353.981	-210.703	25.431
1700	44.050	78.911	49.303	50.334	-353.154	-203.703	23.431
1800	45.110	81.629	51.049	54.687	-352.297	-195.497	21.407
1900	46.170	84.319	52.771	59.154	-351.424	-187.286	19.357
2000	47.200	86.980	54.479	64.021	-350.546	-179.071	17.286

BERYLLIUM TUNGSTATE (BeWO₄) (CRYSTAL)

QPW = 256.8598

ΔH° = Unknown

ΔH°_{298.15} = [-361.7 ± 15] kcal/mol

ΔH° = Unknown

S°_{298.15} = [21.12 ± 2] gibbs/molT_m = Unknown

Heat of Formation.

The heat of formation, ΔH°₂₉₈(BeWO₄, c) = -361.7 kcal/mol, is calculated from ΔH°₂₉₈ = -17.1 kcal/mol for BeO(c) + WO₃(c) → BeWO₄(c). The value of ΔH°₂₉₈ is assumed to be the same as that for MgO(c) + WO₃(c) → MgWO₄(c), using -143.7, -143.1, -201.5 and -362.3 kcal/mol for the heats of formation of MgO(c), BeO(c), WO₃(c) and MgWO₄(c), respectively.

Heat Capacity and Entropy.

Heat capacities are estimated by comparison with those of CaWO₄(c)¹, BeO(c)², and CaO(c)³.

The entropy, S°₂₉₈ = 21.12 eu, is calculated from ΔS°₂₉₈ = -0.4 eu for BeO(c) + WO₃(c) → BeWO₄(c). The value of ΔS°₂₉₈ is assumed to be the same as that for MgO(c) + WO₃(c) → MgWO₄(c), using 6.44, 3.38, 18.14 and 24.18 eu for MgO(c), BeO(c), WO₃(c) and MgWO₄(c), respectively.

References.

1. R. A. Yakovleva and T. N. Renukhina, Russ. J. Phys. Chem. (English Transl.) **34**, 390 (1960).
2. JANAF BeO table (Sept. 30, 1965).
3. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	∞.000	∞.000	-176.724	-176.724	INFINITE
100	16.636	65.446	4.819	-176.724	-177.398	367.084
200	24.953	90.850	2.500	-176.724	-177.297	381.287
298	27.974	91.150	∞.000	-176.724	-177.297	126.836
300	27.610	91.321	∞.051	-176.993	-173.003	126.027
400	29.054	99.481	2.891	-178.691	-171.055	93.456
500	29.890	106.062	5.842	-178.454	-169.173	73.942
600	30.406	111.561	8.850	-178.250	-167.336	60.040
700	30.793	116.275	11.917	-178.101	-165.529	51.670
800	30.973	120.396	15.004	-178.076	-163.744	44.731
900	31.136	124.034	18.110	-177.884	-161.969	39.329
1000	31.256	127.342	21.250	-177.832	-160.206	35.011
1100	31.346	130.326	24.460	-177.824	-158.443	31.478
1200	31.416	133.036	27.798	-177.864	-156.681	28.534
1300	31.471	135.572	31.261	-177.947	-154.911	26.042
1400	31.514	137.968	34.762	-178.078	-153.136	23.904
1500	31.550	140.262	38.345	-178.257	-151.350	22.051
1600	31.579	142.419	41.902	-183.094	-149.591	20.405
1700	31.604	144.434	45.461	-184.039	-147.824	18.926
1800	31.624	146.341	49.022	-184.096	-146.059	17.612
1900	31.642	148.152	52.586	-184.162	-144.287	16.435
2000	31.656	149.875	56.151	-184.243	-142.516	15.376
2100	31.669	151.520	59.717	-184.333	-140.743	14.417
2200	31.680	153.093	63.282	-184.438	-138.966	13.545
2300	31.690	154.602	66.842	-184.553	-137.186	12.748
2400	31.699	156.051	70.397	-184.682	-135.406	12.017
2500	31.706	157.450	73.945	-184.827	-133.622	11.344
2600	31.713	158.808	77.487	-184.982	-131.833	10.722
2700	31.719	159.889	81.024	-185.151	-130.044	10.146
2800	31.724	160.839	84.553	-185.335	-128.255	9.617
2900	31.729	161.652	88.077	-185.534	-126.466	9.126
3000	31.734	162.438	91.591	-185.751	-124.677	8.675
3100	31.738	163.069	95.097	-186.000	-122.888	8.266
3200	31.741	163.576	98.597	-186.271	-121.099	7.899
3300	31.744	164.053	102.091	-186.564	-119.310	7.574
3400	31.746	164.501	105.579	-186.878	-117.521	7.289
3500	31.750	164.921	109.061	-187.213	-115.732	7.044
3600	31.753	165.316	112.538	-187.568	-113.943	6.839
3700	31.755	165.686	116.010	-187.943	-112.154	6.666
3800	31.757	166.033	119.477	-188.338	-110.365	6.522
3900	31.759	166.358	122.939	-188.753	-108.576	6.404
4000	31.761	166.661	126.397	-189.188	-106.787	6.311
4100	31.763	166.946	129.851	-189.643	-104.998	6.244
4200	31.764	167.211	133.299	-190.118	-103.209	6.199
4300	31.766	167.459	136.743	-190.613	-101.420	6.174
4400	31.767	167.691	140.183	-191.128	-99.631	6.160
4500	31.768	167.905	143.618	-191.663	-97.842	6.156
4600	31.769	168.099	147.049	-192.218	-96.053	6.161
4700	31.771	168.275	150.475	-192.793	-94.264	6.174
4800	31.772	168.433	153.897	-193.388	-92.475	6.196
4900	31.773	168.575	157.315	-193.993	-90.686	6.229
5000	31.774	168.701	160.729	-194.608	-88.897	6.274
5100	31.774	168.800	164.148	-195.233	-87.108	6.329
5200	31.775	168.889	167.563	-195.868	-85.319	6.394
5300	31.776	168.961	170.974	-196.513	-83.530	6.469
5400	31.776	169.018	174.380	-197.168	-81.741	6.554
5500	31.777	169.061	177.781	-197.833	-79.952	6.649
5600	31.778	169.090	181.177	-198.508	-78.163	6.754
5700	31.779	169.106	184.569	-199.193	-76.374	6.869
5800	31.779	169.111	187.957	-199.888	-74.585	6.994
5900	31.780	169.115	191.341	-200.593	-72.796	7.129
6000	31.780	169.118	194.721	-201.308	-71.007	7.274

Dec. 31, 1960; June 30, 1965

Point Group [D_{2h}]
S_{298.15} = [91.15] cal. mole⁻¹ deg.⁻¹
Ground State Quantum Weight = 1

ΔH_f^o = [-180] kcal. mole⁻¹

ΔH_f^o 298.15 = [-179] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies		
ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
[220](1)	[185](1)	[250](1)
[110](1)	[100](1)	[400](1)
[380](1)	[80](1)	[600](1)
[105](1)	[300](1)	[640](1)

Bond Distance: Be-Cl = [1.71] Å
Bond Angle: Cl'-Be-Cl' (in ring) = [88°]
Product of the Moments of Inertia: I_AI_BI_C = 2.62616 x 10⁻¹¹² g.³ cm.⁶

Be-Cl' (in ring) = [1.81] Å

Cl'-Be-Cl = [136°]

σ = 4

Heat of Formation

The heat of formation was estimated by assuming that the concentration of dimer in equilibrium with the monomer was ~5% at 500°K. as reported by D. L. Hildenbrand, L. P. Theard, E. Murel and F. J. Aeronutronic Div. of Philco Corp., Report U-3068, April 1965 under contract AF 04(611)-8523, giving an effective K_p = 5.5 x 10⁻⁴ for 2BeCl₂(g) → Be₂Cl₄ at 500°K.

Heat Capacity and Entropy

The structure was assumed planar with a D_{2h} symmetry, the bond lengths were estimated from the values for BeCl₂ (g), a lengthening being assumed in the ring. The frequencies were estimated using K₂Cl₂ as a basis for the ring vibrations. Two polymeric frequencies had been observed by A. Snelson, IIT Research Institute, Report No. IITRI-C6013-4, May 1964, under Contract No. DA-31-124-ARO(D)-111. These were observed in matrix isolated BeCl₂ gas and were ascribed to polymeric species on account of their warm up behavior. They are here assigned to the B_{2u} asymmetric stretching mode and the B_{1u} symmetric out of plane wag of the non ring chlorines. The order of the frequencies listed above is arbitrary and not related to their specie types. The individual moments of inertia are: I_A = 18.386 x 10⁻³⁹ g.² cm.², I_B = 110.638 x 10⁻³⁹ g.² cm.² and I_C = 129.034 g.² cm.²

Point Group [D_{∞h}]
 $\Delta H_f^\circ = -15.4 \pm 10 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [52.7] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -15 \pm 10 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [3]

Vibrotional Frequencies and Degeneracies

ω , cm. ⁻¹	g_i
[1100] (1)	
[500] (2)	
[1600] (1)	

Bond distance: Be-O = [1.4] Å

Bond Angle: Be-O-Be = [180°]

Moment of Inertia: $I_A = 5.8656 \times 10^{-39} \text{ g. cm.}^2$ $\sigma = 2$

Heat of Formation.

D. L. Hildenbrand, L. P. Theard, and P. Ju, Ford Motor Co., Aeronutronic Division, Third Quarterly Technical Report U-2231, April-June 1963, have reported the heat of formation. Equilibrium constants were determined in a mass spectrometer for the reactions $2\text{BeO}(c) \rightarrow \text{Be}_2\text{O}(g) + \text{O}(g) - (2)$ and $\text{Be}_2\text{O}_2(g) \rightarrow \text{Be}_2\text{O}(g) + \text{O}(g) - (3)$. Using our own free energy functions we obtain $\Delta H_f^\circ 298 \text{ Be}_2\text{O}(g) = -13.1$, -14.5 , and $-16.7 \text{ kcal. mole}^{-1}$, all ± 10 ; the 2nd law treatment of reaction 1 gives $-16.3 \pm 10 \text{ kcal. mole}^{-1}$. We adopt a median value $-15 \pm 10 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

A. Buchler, J. L. Stauffer, W. Klemperer and C. Wharton, A. D. Little, Inc., Interim Technical Report No. 5, 1963, have shown Li_2O to be linear. Also A. D. Walsh, J. Chem. Soc. London 2269 (1953) predicted that AP_2 molecules with less than 16 bonding electrons would be linear and symmetrical. Thus Be_2O was taken to be linear and symmetrical, with a Be-O bond length of 1.4 Å, which is a little longer than in $\text{BeO}(g)$. The vibrational frequencies were estimated by taking ω_3 to be larger than the stretch in $\text{BeO}(g)$ and then calculating ω_1 from the valence force field assumption. The bending force constant was estimated as $1/20$ th of the stretching force constant. The two outermost electrons were considered unpaired and so gave a $3 \sum$ ground state.

Sept. 30, 1963.

Be₂O

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.000	4.000	2.372	15.399	15.399	15.399	INFINITE
200	7.433	5.054	1.600	10.355	10.355	10.355	27.928
300	7.788	5.911	1.000	6.498	6.498	6.498	16.172
400	8.069	6.527	0.618	4.254	4.254	4.254	16.104
500	8.285	6.953	0.408	3.152	3.152	3.152	15.883
600	8.456	7.254	0.285	2.219	2.219	2.219	15.683
700	8.593	7.454	0.207	1.548	1.548	1.548	15.493
800	8.704	7.579	0.156	1.098	1.098	1.098	15.325
900	8.793	7.630	0.119	0.780	0.780	0.780	15.172
1000	8.865	7.693	0.093	0.554	0.554	0.554	15.030
1100	8.921	7.754	0.074	0.384	0.384	0.384	14.898
1200	8.963	7.811	0.061	0.261	0.261	0.261	14.774
1300	8.993	7.863	0.052	0.174	0.174	0.174	14.658
1400	9.014	7.911	0.045	0.119	0.119	0.119	14.548
1500	9.028	7.954	0.040	0.084	0.084	0.084	14.443
1600	9.036	7.993	0.036	0.061	0.061	0.061	14.343
1700	9.040	8.028	0.033	0.045	0.045	0.045	14.248
1800	9.043	8.059	0.031	0.033	0.033	0.033	14.158
1900	9.045	8.084	0.029	0.024	0.024	0.024	14.073
2000	9.046	8.104	0.028	0.017	0.017	0.017	13.993
2100	9.047	8.120	0.027	0.012	0.012	0.012	13.918
2200	9.048	8.133	0.026	0.008	0.008	0.008	13.848
2300	9.049	8.144	0.025	0.006	0.006	0.006	13.783
2400	9.050	8.153	0.024	0.004	0.004	0.004	13.723
2500	9.051	8.161	0.023	0.003	0.003	0.003	13.668
2600	9.052	8.168	0.022	0.002	0.002	0.002	13.618
2700	9.053	8.174	0.021	0.001	0.001	0.001	13.573
2800	9.054	8.179	0.020	0.001	0.001	0.001	13.533
2900	9.055	8.183	0.020	0.000	0.000	0.000	13.498
3000	9.056	8.186	0.019	0.000	0.000	0.000	13.468
3100	9.057	8.188	0.019	0.000	0.000	0.000	13.443
3200	9.058	8.189	0.018	0.000	0.000	0.000	13.423
3300	9.059	8.190	0.018	0.000	0.000	0.000	13.408
3400	9.060	8.191	0.017	0.000	0.000	0.000	13.398
3500	9.061	8.192	0.017	0.000	0.000	0.000	13.393
3600	9.062	8.193	0.016	0.000	0.000	0.000	13.393
3700	9.063	8.194	0.016	0.000	0.000	0.000	13.398
3800	9.064	8.195	0.015	0.000	0.000	0.000	13.408
3900	9.065	8.196	0.015	0.000	0.000	0.000	13.423
4000	9.066	8.197	0.015	0.000	0.000	0.000	13.443
4100	9.067	8.198	0.014	0.000	0.000	0.000	13.468
4200	9.068	8.199	0.014	0.000	0.000	0.000	13.498
4300	9.069	8.200	0.014	0.000	0.000	0.000	13.533
4400	9.070	8.201	0.013	0.000	0.000	0.000	13.573
4500	9.071	8.202	0.013	0.000	0.000	0.000	13.618
4600	9.072	8.203	0.013	0.000	0.000	0.000	13.668
4700	9.073	8.204	0.012	0.000	0.000	0.000	13.723
4800	9.074	8.205	0.012	0.000	0.000	0.000	13.783
4900	9.075	8.206	0.012	0.000	0.000	0.000	13.848
5000	9.076	8.207	0.011	0.000	0.000	0.000	13.918
5100	9.077	8.208	0.011	0.000	0.000	0.000	13.993
5200	9.078	8.209	0.011	0.000	0.000	0.000	14.073
5300	9.079	8.210	0.010	0.000	0.000	0.000	14.158
5400	9.080	8.211	0.010	0.000	0.000	0.000	14.248
5500	9.081	8.212	0.010	0.000	0.000	0.000	14.343
5600	9.082	8.213	0.009	0.000	0.000	0.000	14.443
5700	9.083	8.214	0.009	0.000	0.000	0.000	14.548
5800	9.084	8.215	0.009	0.000	0.000	0.000	14.658
5900	9.085	8.216	0.008	0.000	0.000	0.000	14.774
6000	9.086	8.217	0.008	0.000	0.000	0.000	14.898

Beryllium Oxide, Dimeric (Be_2O_2)
(Ideal Gas) Mol. Wt. = 50.026

T, °K.	C_p	$S^\circ - (F^\circ - H_{300}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
0	8.000	INFINITE	- 2.726	- 97.716	INFINITE
100	8.089	48.186	- 1.930	- 97.562	214.961
200	8.176	54.897	- 1.054	- 97.732	198.263
298	8.262	59.156	- 0.000	- 98.000	173.034
300	11.831	59.229	59.156	- 98.005	72.611
400	13.689	62.897	59.663	- 98.314	54.738
500	15.105	66.112	60.622	- 98.610	43.979
600	16.146	68.563	61.779	- 98.884	36.787
700	16.911	71.512	62.901	- 99.151	31.635
800	17.477	73.809	64.202	- 99.418	27.761
900	17.904	75.893	65.187	- 99.696	24.739
1000	18.231	77.797	66.454	- 99.966	22.314
1100	18.486	79.267	67.439	- 100.327	20.325
1200	18.687	81.165	68.609	- 100.694	18.661
1300	18.849	82.667	69.717	- 101.097	17.247
1400	18.980	84.069	70.692	- 101.542	16.031
1500	19.088	85.382	71.628	- 102.029	14.972
1600	19.178	86.617	72.557	- 102.571	14.039
1700	19.254	87.782	73.490	- 103.117	13.169
1800	19.318	88.885	74.421	- 103.673	12.374
1900	19.372	89.930	75.350	- 104.240	11.678
2000	19.419	90.925	75.791	- 104.816	11.069
2100	19.460	91.874	76.434	- 105.400	10.478
2200	19.496	92.780	77.252	- 106.000	9.957
2300	19.527	93.647	78.167	- 106.613	9.480
2400	19.555	94.479	78.618	- 107.244	9.041
2500	19.579	95.278	79.269	- 107.897	8.636
2600	19.601	96.046	80.000	- 108.571	8.259
2700	19.620	96.786	80.811	- 109.264	7.910
2800	19.637	97.500	81.615	- 109.981	7.611
2900	19.653	98.189	82.400	- 110.724	7.341
3000	19.667	98.856	83.166	- 111.494	7.104
3100	19.680	99.501	83.922	- 112.296	6.894
3200	19.692	100.126	84.666	- 113.130	6.704
3300	19.702	100.732	85.400	- 113.994	6.535
3400	19.712	101.320	86.125	- 114.887	6.385
3500	19.721	101.892	86.843	- 115.809	6.254
3600	19.729	102.448	87.551	- 116.760	6.139
3700	19.737	102.988	88.250	- 117.740	6.038
3800	19.744	103.515	88.943	- 118.750	5.949
3900	19.750	104.028	89.630	- 119.791	5.870
4000	19.756	104.528	90.312	- 120.862	5.799
4100	19.762	105.016	90.990	- 121.964	5.736
4200	19.767	105.492	91.663	- 123.097	5.680
4300	19.772	105.957	92.332	- 124.261	5.631
4400	19.776	106.412	92.997	- 125.455	5.587
4500	19.781	106.856	93.658	- 126.688	5.548
4600	19.784	107.291	94.315	- 127.960	5.513
4700	19.788	107.717	94.968	- 129.271	5.483
4800	19.792	108.133	95.617	- 130.621	5.456
4900	19.795	108.541	96.262	- 132.010	5.432
5000	19.798	108.941	96.903	- 133.438	5.409
5100	19.801	109.333	97.540	- 134.905	5.388
5200	19.804	109.718	98.173	- 136.410	5.368
5300	19.806	110.095	98.802	- 137.954	5.349
5400	19.809	110.465	99.427	- 139.537	5.331
5500	19.811	110.829	100.048	- 141.159	5.314
5600	19.813	111.186	100.665	- 142.820	5.298
5700	19.815	111.537	101.278	- 144.520	5.283
5800	19.817	111.881	101.885	- 146.259	5.268
5900	19.819	112.220	102.488	- 148.037	5.254
6000	19.821	112.553	103.087	- 149.854	5.240

Dec. 31, 1960; Sept. 30, 1963

Be_2O_2

MOL. WT. = 50.028

(IDEAL GAS)

BERYLLIUM OXIDE DIMERIC (Be_2O_2)

Point Group [V_h]
 $\Delta H_f^\circ = -97.7 \pm 12$ kcal. mole⁻¹
 $\Delta F_f^\circ = -98.15 \pm 12$ kcal. mole⁻¹
 $S^\circ_{298.15} = [59.156]$ cal. deg.⁻¹ mole⁻¹
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[1120] (1)	[460] (1)
[630] (1)	[920] (1)
[760] (1)	[1480] (1)

$\sigma = 4$

Bond Distance: Be-O = [1.63] Å

Bond Angle: Be-O-Be = [90°] O-Be-O = [90°]

Product of the Moments of Inertia: $I_A I_B I_C = [3.0957] \times 10^{-115}$ g.³ cm.⁶

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. P. Glease, J. Chem. Phys. 30, 827 (1959) studied the temperature dependence of the $(\text{BeO})_2^+$ ion in a mass spectrometer and obtained a second law heat of vaporization of 172 ± 8 kcal. mole⁻¹ at 2150°K. No correction was made for fragmentation of higher polymers and this is reflected in the uncertainty. We adopted a heat of sublimation of 176 kcal. mole⁻¹ in order to match more closely the equilibrium constant found by Chupka, et al. However, it was not possible to alter either the heat or entropy sufficiently to obtain exact agreement, the predicted pressure being too high by a factor of 20.

Heat Capacity and Entropy.

A planar ring configuration was assumed which has six vibrational frequencies of the type $2A_g, B_{1g}, B_{2g}, B_{2u}, B_{2u}$, and B_{2u} . These were estimated by comparison with $(\text{H}_2\text{O})_2$ for which values have been calculated by D. White, K. Seshadri, D. P. Dever, D. E. Mann, and M. J. Linevsky, prepublication communication, July, 1963. It seems unlikely that any other structure than that of a ring is possible, as, in order to approach the observed equilibrium constant an even lower entropy is needed. A non-linear chain would have a higher entropy due to the change in symmetry number and the two odd electrons. A linear chain would have approximately the same entropy due to cancellation of opposite effects. The vibrational frequencies were also made as high as possible by normalizing them using B_{2u} equal to the BeO stretch in BeO(g) . The bond length was taken as the sum of the covalent radii of O and Be, which is in general agreement with other polymeric structures which generally increase in bond length by 10-20% in going from monomer to polymer. The bond angle was chosen arbitrarily, however, changes in the angle would change the entropy less than 1 eu.

The individual moments of inertia were $I_A = 7.057$, $I_B = 3.978$, and $I_C = 11.033 \times 10^{-39}$ g. cm.²

Be_2O_2

T, °K.	C_p	S°	$-(H^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	0.000	0.000	INFINITE	-2.972	-503.096	-503.096	INFINITE
100	4.492	1.798	2.76	-2.76	-503.096	-503.096	1.798
200	14.444	7.046	17.172	-1.845	-503.445	-498.581	532.776
298	22.840	15.342	15.342	0.000	-506.029	-478.682	350.866
300	22.968	15.483	15.342	0.042	-506.036	-478.512	348.579
400	26.860	22.946	16.320	2.451	-506.735	-469.299	256.401
500	31.730	29.618	16.795	3.756	-506.168	-460.066	201.095
600	35.604	36.094	20.784	9.162	-505.911	-450.868	164.221
700	37.970	41.732	23.377	12.848	-505.515	-441.725	137.906
800	39.680	46.920	26.000	16.735	-505.016	-432.647	116.188
900	40.810	51.652	28.592	20.763	-504.464	-423.631	102.867
1000	41.600	56.095	31.119	24.885	-503.961	-414.678	90.624
1100	42.150	59.996	33.566	29.074	-503.350	-405.784	80.618
1200	42.590	63.683	35.924	33.312	-502.624	-396.938	72.269
1300	42.934	67.106	38.192	37.598	-502.328	-388.133	65.248
1400	43.200	70.315	40.375	41.837	-501.965	-379.269	59.210
1500	43.472	73.291	42.469	46.023	-501.440	-370.350	53.694
1600	43.702	76.104	44.484	50.592	-500.864	-361.769	49.413
1700	43.930	78.760	46.423	54.973	-500.228	-352.628	45.331
1800	44.156	81.277	48.290	59.376	-500.512	-342.912	41.623
1900	44.378	83.661	50.000	63.784	-500.724	-332.624	38.259
2000	44.600	85.953	51.626	68.253	-500.864	-321.688	35.258
2100	44.812	88.134	53.504	72.724	-500.968	-310.068	32.673
2200	45.024	90.224	55.125	77.216	-501.048	-297.824	30.296
2300	45.236	92.240	56.592	81.729	-501.104	-285.012	28.017
2400	45.448	94.190	58.000	86.269	-501.132	-271.784	25.840
2500	45.660	96.019	59.692	90.818	-501.132	-258.132	23.764
2600	45.872	97.814	61.123	95.395	-501.108	-244.048	21.788
2700	46.084	99.549	62.515	99.993	-501.064	-229.584	20.000
2800	46.296	101.240	63.860	104.616	-501.000	-214.736	18.380
2900	46.508	102.857	65.184	109.242	-500.916	-200.496	17.340
3000	46.720	104.437	66.466	113.913	-500.816	-186.864	16.743

$\Delta H^\circ_f 0 = -503.1 \pm 7 \text{ kcal. mole}^{-1}$
 $\Delta H^\circ_f 298.15 = [-506.0 \pm 7] \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = 15.342 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1853^\circ\text{K.}$

Heat of Formation.

The $\Delta H^\circ_f 298.15$ was estimated from the $\Delta H^\circ_f 298.15$ of Me_2O , Ca and Ba oxides with SiO_2 given by K. K. Kelley in the report of investigations 5801, U. S. Department of the Interior, Bureau of Mines 1962, and from the $\Delta H^\circ_f 298.15$ of $\text{BaO}(c)$ (Sept. 30, 1963) and $\text{SiO}_2(c)$ (Dec. 31, 1962) in JANAF tables. The $\Delta H^\circ_f 298.15 = 0 \pm 7 \text{ kcal. mole}^{-1}$ was estimated for the reaction $2\text{BeO}(c) + \text{SiO}_2(c) \rightarrow \text{Be}_2\text{SiO}_4(c)$.

Heat Capacity and Entropy.

At low temperatures C_p was used from K. K. Kelley, J. Am. Chem. Soc., 81, 1217 (1959). Above 298.15°K. C_p values were estimated by summation of the component oxides using JANAF tables, BaO (Sept. 30, 1963) and SiO_2 (Dec. 31, 1962). The entropy was calculated at 54.7°K. using the Debye and Planck-Einstein functions $D(\frac{422}{T}) + 2E(\frac{257}{T})$ given by K. K. Kelley, J. Am. Chem. Soc., 81, 1217 (1959). The value of $S^\circ_{54.7} = 13.59 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The incongruent melting point was taken from Kubaschewski and Evans, "Metallurgical Thermochemistry" 3rd edition, Pergamon Press., New York 1958.



Beryllium Nitride, Alpha (α -Be₃N₂)
(Crystal) GFW = 55.050

BERYLLIUM NITRIDE, ALPHA (α -Be₃N₂) (CRYSTAL) GFW = 55.050

T, K	Cp°	S°	-(G°-H°)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-1.691	-138.615	-138.615	INFINITE
100	1.460	4.41	17.011	-1.657	-139.504	-296.555	
200	8.482	3.421	9.351	-1.186	-140.143	-131.623	143.831
298	15.382	8.137	0.000	-1.000	-140.600	-127.346	93.387
300	15.484	8.252	8.137	-1.029	-140.605	-127.264	92.711
400	23.166	18.254	10.232	-1.027	-140.821	-125.778	67.083
500	25.458	22.704	11.946	-1.055	-140.746	-113.749	41.433
600	26.989	26.750	13.776	-1.082	-140.563	-109.269	34.118
700	28.150	30.751	15.692	-1.109	-140.390	-105.140	28.572
800	29.073	34.704	17.618	-1.136	-140.226	-101.372	24.076
1000	30.843	49.171	27.300	-1.258	-139.404	-78.208	10.611
1100	30.000	39.710	20.986	-1.059	-139.661	-91.404	18.200
1200	30.335	42.336	22.658	-1.051	-139.511	-87.244	15.669
1300	30.740	44.074	24.266	-1.040	-139.372	-83.582	13.242
1400	30.843	45.074	25.820	-1.027	-139.246	-80.306	10.957
1500	30.843	45.074	27.300	-1.013	-139.130	-77.426	8.714
1600	30.896	51.163	30.730	-0.993	-147.770	-69.516	9.509
1700	30.908	53.037	30.105	-0.983	-147.602	-64.739	8.323
1800	30.910	54.695	32.703	-0.965	-147.423	-59.006	7.157
1900	30.910	56.042	33.932	-0.946	-147.242	-53.269	6.057
2000	30.940	58.062	35.117	-0.925	-147.058	-47.530	5.000
2100	30.949	59.572	36.262	-0.904	-146.873	-41.788	4.019
2200	30.957	61.012	37.368	-0.883	-146.688	-36.046	3.103
2300	30.962	62.386	38.434	-0.862	-146.503	-30.304	2.259
2400	30.966	63.711	39.474	-0.841	-146.318	-24.562	1.474
2500	30.969	64.986	40.479	-0.820	-146.133	-18.820	0.734
2600	30.984	66.186	41.452	-0.800	-145.948	-13.078	0.000
2700	30.989	67.355	42.396	-0.780	-145.763	-7.336	0.000
2800	30.994	68.500	43.316	-0.760	-145.578	-1.594	0.000
2900	30.997	69.621	44.209	-0.740	-145.393	4.148	0.000
3000	31.000	70.621	45.073	-0.720	-145.208	9.890	0.000

$\Delta H^\circ_0 = -138.6 \pm 0.3 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = -140.6 \pm 0.3 \text{ kcal/mol}$
 $\Delta H^\circ = [30.9] \text{ kcal/mol}$

$S^\circ_{298.15} = 8.157 \text{ gibbs/mol}$

$T_m = 2475^\circ \text{K}$

Heat of Formation.

P. Gross, C. Hayman, P. D. Greene and J. N. Bingham, Trans. Faraday Soc. 62, 2719 (1966), have measured the heat of chlorination of α -Be₃N₂ to α -BeCl₂, and the heat of reaction of Be with ammonia. The chlorination reaction (A) of α -Be₃N₂(c) + 3Cl₂(g) \rightarrow 3 α -BeCl₂(c) + $\frac{3}{2}$ N₂(g) had a $\Delta H^\circ_{298} = -210.3 \pm 1.1 \text{ kcal/mol}$, which, combined with the value of α -Be₃N₂(c) + 3H₂(g) \rightarrow 3 α -BeH₂(c) + $\frac{3}{2}$ N₂(g) reported in the same paper, yields $\Delta H^\circ_{298}(\alpha\text{-Be}_3\text{N}_2\text{c}) = -141.0 \pm 1.6 \text{ kcal/mol}$. Reaction (B) 3 Be(c) + 2 NH₃(g) \rightarrow α -Be₃N₂(c) + 3 H₂(g) had a $\Delta H^\circ_{298} = -214.6 \pm 0.3 \text{ kcal/mol}$, which, combined with the JANAP value for NH₃(g), yields $\Delta H^\circ_{298}(\alpha\text{-Be}_3\text{N}_2\text{c}) = -140.3 \pm 0.3 \text{ kcal/mol}$. A weighted mean value of the above two determinations is adopted.

The decomposition Be₃N₂(c) \rightarrow 3 Be(g) + $\frac{1}{2}$ N₂(g) has been studied by R. E. Yates, M. A. Greenbaum and M. Barber, J. Phys. Chem. 69, 2682 (1964), using the torsion effusion technique. The same decomposition has also been investigated by C. L. Hoenig, UCRL-7521, April 1964, using the Knudsen technique. An analysis of these data sets by 2nd and 3rd law methods is given below.

Reference	Range	Points	$\Delta H^\circ_{298} \text{ kcal/mol}$			Drift eu	$\Delta H^\circ_{298.15} \text{ Be}_3\text{N}_2 \text{ kcal/mol}$
			2nd law	3rd law	3rd law		
Yates - 1	1478-1592	9*	364.555.9	374.00	6.045.8	-139.23	
Yates - 2	1541-1652	15*	369.648.3	376.51	4.045.3	-141.74	
Yates - 3	1438-1661	14	347.743.7	374.54	16.942.4	-139.77	
Yates - 4	1450-1646	17*	366.748.9	375.28	4.845.7	-140.51	
Yates	1473-1661	52*	358.945.1	375.41	10.343.3	-140.64	
Hoenig - 1	1767-1946	14	355.043.3	377.77	11.941.8	-143.00	
Hoenig - 2	1660-1891	10	395.045.6	378.69	-9.143.1	-143.92	
Hoenig - 3	1648-1893	10	416.948.4	383.15	-19.544.6	-148.38	

*Points rejected due to failure of statistical test.

**Calculated from 3rd law ΔH°_{298} .

The data of Yates et al. are seen to be in good agreement with the adopted ΔH°_{298} .

Heat Capacity and Entropy.

The low temperature heat capacity of α -Be₃N₂ has been measured, from 25° - 310°K, by B. H. Justice, The Dow Chemical Co., 1st Quarterly Report under Contract AF04611-67-C-0009, April 1967. These measurements are joined smoothly with the high temperature enthalpies reported by T. B. Douglas and W. H. Payne, Natl. Bur. Std. Report 7587, July 1962. Above 1200°K the values were smoothly extrapolated to a limiting value of 6.2 gibbs/g-atom. The entropy at 298° was calculated by integration of the low temperature data based on $S^\circ_{25} = 0.002 \text{ eu}$.

Melting Data.

See Be₃N₂(1) for details.



Beryllium Nitride (Be₃N₂)

(Liquid) GFW = 55.050

BERYLLIUM NITRIDE (Be₃N₂)

(LIQUID)

OPW = 55.050

$$\Delta H_f^{298.15} = [-116.4] \text{ kcal/mol}$$

$$\Delta H_m^\circ = [30.9] \text{ kcal/mol}$$

$$S_{298.15}^\circ = [9.425] \text{ gibbs/mol}$$

$$T_m = 2473^\circ \text{K}$$

Heat of Formation.

The heat of formation of Be₃N₂(l) is calculated from $\Delta H_f^{298} \text{ Be}_2\text{N}_2(c)$ and the difference between $H_{2473} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity is estimated to be constant and slightly greater than the maximum for Be₃N₂(c). The entropy at 298°K is estimated in a manner analogous to that of the heat of formation.

Melting Data.

The melting point was reported by P. Fichter and E. Brunner, Z. Anorg. Allgem. Chem. 93, 84 (1915). The heat of melting was calculated on the assumption that each g-atom contributed 2.5 gibbs to ΔS_m° .

T, °K	C _p °	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log K _p
100	32.000	9.425	9.425	.000	= 116.400	= 103.324	75.885
150	32.000	9.623	9.426	.059	= 116.375	= 103.444	75.359
200	32.000	16.859	10.681	3.259	= 115.180	= 99.320	54.266
250	32.000	25.969	13.051	6.459	= 114.204	= 95.469	41.730
300	32.000	31.804	15.705	9.659	= 113.342	= 91.805	33.440
350	32.000	36.736	18.366	12.859	= 112.586	= 88.278	27.561
400	32.000	41.009	20.935	16.059	= 111.914	= 84.852	23.151
450	32.000	44.779	23.379	19.259	= 111.324	= 81.505	19.762
500	32.000	48.150	25.691	22.459	= 110.818	= 78.220	17.095
550	32.000	51.200	27.873	25.659	= 110.398	= 74.980	14.897
600	32.000	53.984	29.935	28.859	= 110.066	= 71.776	13.072
650	32.000	56.517	31.885	32.059	= 109.813	= 68.596	11.532
700	32.000	58.917	33.732	35.259	= 109.642	= 65.434	10.235
750	32.000	61.125	35.485	38.459	= 109.551	= 62.281	9.074
800	32.000	63.190	37.153	41.659	= 117.804	= 58.993	8.044
850	32.000	65.130	38.742	44.859	= 117.526	= 55.221	7.099
900	32.000	66.959	40.260	48.059	= 117.269	= 51.563	6.261
950	32.000	68.689	41.711	51.259	= 117.031	= 47.918	5.512
1000	32.000	70.331	43.101	54.459	= 116.813	= 44.289	4.860
1100	32.000	71.892	44.435	57.659	= 116.614	= 40.667	4.232
1200	32.000	73.381	45.717	60.859	= 116.434	= 37.056	3.681
1300	32.000	74.803	46.951	64.059	= 116.272	= 33.447	3.178
1400	32.000	76.167	48.140	67.259	= 116.127	= 29.847	2.709
1500	32.000	77.471	49.288	70.459	= 116.004	= 26.259	2.278
1600	32.000	78.726	50.386	73.659	= 115.895	= 22.667	1.905
1700	32.000	79.934	51.448	76.859	= 115.800	= 19.083	1.545
1800	32.000	81.098	52.505	80.059	= 124.812	= 15.482	.951
1900	32.000	82.221	53.511	83.259	= 127.984	= 11.883	.067
2000	32.000	83.306	54.466	86.459	= 127.105	= 10.381	.756
2100	32.000	84.355	55.433	89.659	= 126.180	= 21.611	= 1.524
2200	32.000	85.371	56.392	92.859	= 125.260	= 32.433	= 2.242
2300	32.000	86.356	57.287	96.059	= 124.791	= 48.020	= 2.915
2400	32.000	87.311	58.117	99.259	= 124.411	= 63.516	= 3.516
2500	32.000	88.238	58.904	102.459	= 124.236	= 78.932	= 4.141
2600	32.000	89.140	59.760	105.659	= 122.481	= 77.447	= 4.702
2700	32.000	90.017	60.595	108.859	= 121.735	= 88.540	= 5.230
2800	32.000	90.870	61.381	112.059	= 121.006	= 99.620	= 5.729
2900	32.000	91.711	62.117	115.259	= 120.298	= 110.628	= 6.201
3000	32.000	92.511	62.897	118.459	= 120.592	= 121.728	= 6.651

Dec. 31, 1960; Mar. 31, 1963; Sept. 30, 1964; Mar. 31, 1967

Beryllium Oxide, Trimeric (Be_3O_3)
(Ideal Gas) Mol. Wt. = 75.039

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	8.460	52.000	INFINITE	-	3.1874	-250.668	-250.668	INFINITE
100	8.465	52.000	76.193	-	2.3174	-250.668	-250.668	16.318
200	11.980	59.926	66.588	-	1.3333	-251.350	-248.859	271.927
298	15.167	65.304	65.304	0.000	-	-252.000	-247.515	181.425
300	15.226	65.398	65.405	0.028	-	-252.012	-247.487	180.286
400	18.400	72.577	67.238	3.675	-	-253.337	-244.084	106.684
500	20.861	74.588	67.238	3.675	-	-253.337	-244.084	106.684
600	23.091	76.606	68.602	5.882	-	-253.909	-242.176	88.208
700	24.745	78.295	70.470	8.277	-	-254.397	-240.182	74.985
800	26.018	80.066	72.163	10.818	-	-254.838	-238.123	65.049
900	27.011	81.811	73.684	13.491	-	-255.237	-236.026	57.137
1000	27.770	83.596	75.084	16.212	-	-255.677	-233.844	51.104
1100	28.376	85.372	77.081	19.020	-	-256.119	-231.639	46.020
1200	28.861	87.148	78.627	21.883	-	-256.595	-229.394	41.776
1300	29.253	88.926	80.120	24.789	-	-257.110	-227.106	38.178
1400	29.563	90.704	81.561	27.731	-	-257.673	-224.779	35.088
1500	29.808	92.482	82.951	30.702	-	-258.268	-222.409	32.403
1600	30.060	94.260	84.291	33.697	-	-267.225	-219.759	30.016
1700	30.246	96.038	85.584	36.713	-	-267.612	-216.780	27.868
1800	30.405	97.816	86.832	39.745	-	-268.007	-213.779	25.955
1900	30.538	99.594	88.031	42.796	-	-268.411	-210.751	24.241
2000	30.658	101.372	89.190	45.853	-	-268.825	-207.713	22.697
2100	30.759	103.150	90.331	48.924	-	-269.250	-204.645	21.297
2200	30.848	104.928	91.453	52.004	-	-269.692	-201.559	20.022
2300	30.926	106.706	92.565	55.093	-	-270.146	-198.448	18.856
2400	31.003	108.484	93.667	58.182	-	-270.613	-195.317	17.785
2500	31.078	110.262	94.760	61.292	-	-271.106	-192.178	16.793
2600	31.151	112.040	95.853	64.400	-	-271.612	-189.044	15.886
2700	31.223	113.818	96.946	67.514	-	-272.131	-185.817	15.040
2800	31.295	115.596	98.039	70.632	-	-272.662	-182.589	14.253
2900	31.367	117.374	99.132	73.754	-	-273.206	-179.358	13.520
3000	31.438	119.152	100.225	76.880	-	-273.762	-176.127	12.841
3100	31.509	120.930	101.318	80.010	-	-274.329	-172.896	12.212
3200	31.579	122.708	102.411	83.142	-	-274.906	-169.665	11.631
3300	31.649	124.486	103.504	86.278	-	-275.493	-166.434	11.096
3400	31.719	126.264	104.597	89.415	-	-276.090	-163.203	10.606
3500	31.789	128.042	105.690	92.556	-	-276.697	-160.000	10.156
3600	31.859	129.820	106.783	95.698	-	-277.314	-156.807	9.744
3700	31.929	131.598	107.876	98.842	-	-277.941	-153.634	9.368
3800	31.999	133.376	108.969	101.989	-	-278.578	-150.481	9.032
3900	32.069	135.154	110.062	105.136	-	-279.225	-147.348	8.732
4000	32.139	136.932	111.155	108.284	-	-279.882	-144.225	8.468
4100	32.209	138.710	112.248	111.437	-	-280.549	-141.122	8.238
4200	32.279	140.488	113.341	114.589	-	-281.226	-138.049	8.038
4300	32.349	142.266	114.434	117.743	-	-281.913	-135.006	7.864
4400	32.419	144.044	115.527	120.897	-	-282.610	-132.000	7.712
4500	32.489	145.822	116.620	124.053	-	-283.317	-129.022	7.578
4600	32.559	147.600	117.713	127.210	-	-284.034	-126.084	7.460
4700	32.629	149.378	118.806	130.368	-	-284.761	-123.187	7.356
4800	32.699	151.156	119.899	133.527	-	-285.498	-120.330	7.266
4900	32.769	152.934	121.000	136.686	-	-286.245	-117.512	7.188
5000	32.839	154.712	122.101	139.846	-	-286.992	-114.734	7.120
5100	32.909	156.490	123.202	143.006	-	-287.749	-112.000	7.062
5200	32.979	158.268	124.303	146.169	-	-288.516	-109.312	7.014
5300	33.049	160.046	125.404	149.332	-	-289.293	-106.669	6.974
5400	33.119	161.824	126.505	152.497	-	-290.080	-104.072	6.942
5500	33.189	163.602	127.606	155.662	-	-290.877	-101.525	6.916
5600	33.259	165.380	128.707	158.827	-	-291.684	-99.028	6.894
5700	33.329	167.158	129.808	161.992	-	-292.491	-96.581	6.876
5800	33.399	168.936	130.909	165.157	-	-293.308	-94.184	6.862
5900	33.469	170.714	132.010	168.322	-	-294.135	-91.837	6.850
6000	33.539	172.492	133.111	171.487	-	-294.972	-89.540	6.840
6100	33.609	174.270	134.212	174.652	-	-295.819	-87.293	6.832
6200	33.679	176.048	135.313	177.817	-	-296.676	-85.096	6.826
6300	33.749	177.826	136.414	180.982	-	-297.543	-82.949	6.822
6400	33.819	179.604	137.515	184.147	-	-298.410	-80.852	6.818
6500	33.889	181.382	138.616	187.312	-	-299.287	-78.805	6.814
6600	33.959	183.160	139.717	190.477	-	-300.174	-76.808	6.810
6700	34.029	184.938	140.818	193.642	-	-301.071	-74.861	6.806
6800	34.099	186.716	141.919	196.807	-	-301.978	-72.964	6.802
6900	34.169	188.494	143.020	200.000	-	-302.895	-71.117	6.800
7000	34.239	190.272	144.121	203.193	-	-303.822	-69.320	6.798
7100	34.309	192.050	145.222	206.386	-	-304.759	-67.573	6.796
7200	34.379	193.828	146.323	209.579	-	-305.706	-65.876	6.794
7300	34.449	195.606	147.424	212.772	-	-306.663	-64.229	6.792
7400	34.519	197.384	148.525	215.965	-	-307.630	-62.632	6.790
7500	34.589	199.162	149.626	219.158	-	-308.607	-61.085	6.788
7600	34.659	200.940	150.727	222.351	-	-309.594	-59.588	6.786
7700	34.729	202.718	151.828	225.544	-	-310.591	-58.141	6.784
7800	34.799	204.496	152.929	228.737	-	-311.598	-56.744	6.782
7900	34.869	206.274	154.030	231.930	-	-312.615	-55.397	6.780
8000	34.939	208.052	155.131	235.123	-	-313.642	-54.100	6.778
8100	35.009	209.830	156.232	238.316	-	-314.679	-52.853	6.776
8200	35.079	211.608	157.333	241.509	-	-315.726	-51.656	6.774
8300	35.149	213.386	158.434	244.702	-	-316.783	-50.509	6.772
8400	35.219	215.164	159.535	247.895	-	-317.840	-49.412	6.770
8500	35.289	216.942	160.636	251.088	-	-318.907	-48.365	6.768
8600	35.359	218.720	161.737	254.281	-	-319.984	-47.368	6.766
8700	35.429	220.498	162.838	257.474	-	-321.071	-46.421	6.764
8800	35.499	222.276	163.939	260.667	-	-322.168	-45.524	6.762
8900	35.569	224.054	165.040	263.860	-	-323.275	-44.677	6.760
9000	35.639	225.832	166.141	267.053	-	-324.392	-43.880	6.758
9100	35.709	227.610	167.242	270.246	-	-325.519	-43.133	6.756
9200	35.779	229.388	168.343	273.439	-	-326.656	-42.436	6.754
9300	35.849	231.166	169.444	276.632	-	-327.803	-41.789	6.752
9400	35.919	232.944	170.545	279.825	-	-328.960	-41.192	6.750
9500	35.989	234.722	171.646	283.018	-	-330.127	-40.645	6.748
9600	36.059	236.500	172.747	286.211	-	-331.304	-40.148	6.746
9700	36.129	238.278	173.848	289.404	-	-332.491	-39.701	6.744
9800	36.199	240.056	174.949	292.597	-	-333.688	-39.304	6.742
9900	36.269	241.834	176.050	295.790	-	-334.895	-38.957	6.740
10000	36.339	243.612	177.151	298.983	-	-336.112	-38.660	6.738

Dec. 31, 1960; Sept. 30, 1963

Be_3O_3

MOL. WT. = 75.039

BERYLLIUM OXIDE TRIMERIC (Be_3O_3) (IDEAL GAS)

Point Group [D_{3h}]
 $\Delta H_f^o = -250.7 \pm 9 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = -252 \pm 9 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = [65.3] \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$(\omega_e) \text{ cm}^{-1}$	$(\omega_e) \text{ cm}^{-1}$
[730] (1)	[1380] (2)
[990] (1)	[1450] (2)
[1480] (1)	[610] (2)
[1100] (1)	[320] (2)

$\sigma = [6]$

Bond Distances: Be-O = [1.63] Å

Bond Angle: Be-O-Be = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [9.0658] \times 10^{-114} \text{ g}^3 \text{ cm}^6$

Heat of Formation

W. A. Chupka, J. Berkowitz, and C. P. Olase, J. Chem. Phys. **30**, 827 (1959) measured the change in the intensity of the $(\text{BeO})^+$ ion with temperature and obtained a second law heat of vaporization of $161 \pm 6 \text{ kcal. mole}^{-1}$ at 2150°K. The uncertainty is large because of an approximate correction of 8 kcal. mole⁻¹ and the neglect of fragmentation effects. We adopted a heat of sublimation at 2150°K. of $163 \text{ kcal. mole}^{-1}$ in order to bring the equilibrium vapor pressure into agreement with that measured by Chupka, et al.

Heat Capacity and Entropy

The assumed D_{3h} symmetry implies eight vibrational frequencies of the types $2A_1$, A_2 , $3E'$, and E_2' . The frequencies were estimated by comparison with the values for the $\text{B}_2\text{O}_3(\text{O}^-)$ skeleton as given by J. L. Parsons, J. Chem. Phys. **33**, 1860 (1960) and the partial assignment of Boronine by S. K. Gupta and R. P. Porter, J. Phys. Chem. **67**, 1286 (1963). The bond length was taken as that in $\text{Be}_2\text{O}_2(\text{g})$, while the bond angle was arbitrarily taken as 120°. The individual moments of inertia were $I_A = I_B = 16.550$, $I_C = 33.010 \times 10^{-59} \text{ g}^2 \text{ cm}^2$.

Be_3O_3

(Ideal Gas) Mol. Wt. = 100.052

BERYLLIUM OXIDE TETRAMERIC (Be₄O₄) (IDEAL GAS)

MOL. WT. = 100.052

T, °K. C_p cal. mole⁻¹ deg.⁻¹ S° (F°-H₂₉₈)/T H°-H₂₉₈ ΔH_f° kcal. mole⁻¹ ΔF_f° Log K_p

Point Group [D_{4h}]
 $\Delta H_f^\circ = -378 \pm 12 \text{ kcal. mole}^{-1}$
 $S_{298}^\circ = [72.3] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = -380 \pm 12 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 288.15$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e , cm. ⁻¹	ω_e , cm. ⁻¹
[700] (1)	[200] (2)
[850] (1)	[900] (1)
[1400] (1)	[400] (1)
[1000] (1)	[500] (1)
[800] (1)	[1150] (2)
[1000] (1)	[1200] (2)
[800] (1)	[800] (2)

Bond Distance: Be-O = [1.63] Å $\sigma = [8]$

Bond Angle: Be-O-Be = [115°] O-Be-O = [135°]

Product of the Moments of Inertia: $I_A I_B I_C = [1.11656] \times 10^{-112} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation

W. A. Chupka, J. Berkowitz, and C. P. Giese, J. Chem. Phys. 30, 827 (1959) measured the variation of intensity of the (BeO)₄⁺ ion with temperature in a mass spectrometer. They reported a second law heat of vaporization of $177 \pm 8 \text{ kcal. mole}^{-1}$ at 2150°K., which included an approximate correction of 9 kcal. mole⁻¹, and this value was adopted here.

Heat Capacity and Entropy

The assumed D_{4h} structure has 14 vibrational frequencies of the type 2A_{1g}, A_{2g}, 2B_{1g}, 2B_{2g}, E_g, A_{2u}, B_{2u}, B_{1u}, and 3E_u. The frequencies were estimated by comparison with (BeO)₃ and cyclobutane from G. W. Nathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, J. Am. Chem. Soc. 75, 5634 (1953). The estimated structure and frequencies gave an entropy which was in excellent agreement with the experimental heat and equilibrium constant determined by Chupka, et al.

The bond lengths were taken equal to those in Be₂O₂(g) and the angles were chosen so that O-Be-O was almost linear. The individual moments of inertia were calculated to be $I_A = I_B = 38.219$, $I_C = 76.438 \times 10^{-39} \text{ g. cm.}^2$

Dec. 31, 1960; Sept. 30, 1963

(Ideal Gas) Mol. Wt. = 150.078

(IDEAL GAS)

BERYLLIUM OXIDE HEXAMERIC (Be₆O₆)

MOL. WT. = 150.078

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	12.043	INF. INITE.	5.133	-	-	-632.101	-632.101	INF. INITE.
100	20.631	60.456	4.223	-	-	-626.917	-626.917	1370.000
200	21.158	84.556	2.585	-	-	-634.619	-634.619	677.463
298	31.459	82.000	0.000	-	-	-636.000	-636.000	448.991
300	31.664	82.195	0.058	-	-	-636.023	-636.023	446.105
400	40.551	92.573	3.687	-	-	-637.161	-637.161	330.177
500	47.149	102.371	8.610	-	-	-637.974	-637.974	260.510
600	51.851	111.408	13.054	-	-	-638.528	-638.528	214.016
700	55.682	120.214	17.076	-	-	-639.242	-639.242	170.682
800	57.682	127.214	20.076	-	-	-639.742	-639.742	155.852
900	59.499	134.117	22.933	-	-	-639.823	-639.823	136.434
1000	60.874	140.461	25.955	-	-	-639.822	-639.822	120.901
1100	61.935	146.315	29.098	-	-	-640.180	-640.180	108.186
1200	62.769	151.721	32.366	-	-	-640.539	-640.539	98.581
1300	63.434	156.732	35.746	-	-	-641.153	-641.153	90.606
1400	63.972	161.513	39.117	-	-	-641.790	-641.790	84.905
1500	64.413	165.943	42.486	-	-	-642.543	-642.543	79.222
1600	64.778	170.112	45.857	-	-	-643.408	-643.408	73.587
1700	65.085	174.026	49.227	-	-	-644.383	-644.383	68.003
1800	65.344	177.776	52.598	-	-	-645.468	-645.468	62.468
1900	65.565	181.315	56.069	-	-	-646.663	-646.663	57.083
2000	65.754	184.684	59.540	-	-	-647.968	-647.968	51.848
2100	65.919	187.895	63.011	-	-	-649.383	-649.383	46.763
2200	66.062	190.965	66.482	-	-	-650.908	-650.908	41.818
2300	66.187	193.904	69.953	-	-	-652.543	-652.543	37.023
2400	66.297	196.724	73.424	-	-	-654.288	-654.288	32.378
2500	66.395	199.432	76.895	-	-	-656.143	-656.143	27.883
2600	66.482	202.038	80.366	-	-	-658.108	-658.108	23.538
2700	66.550	204.548	83.837	-	-	-660.183	-660.183	19.343
2800	66.609	206.970	87.308	-	-	-662.368	-662.368	15.298
2900	66.662	209.310	90.779	-	-	-664.663	-664.663	11.403
3000	66.710	211.572	94.250	-	-	-667.068	-667.068	7.658
3100	66.800	213.761	97.721	-	-	-669.583	-669.583	4.063
3200	66.887	215.884	101.192	-	-	-672.208	-672.208	0.618
3300	66.969	217.940	104.663	-	-	-674.943	-674.943	-2.827
3400	67.046	219.938	108.134	-	-	-677.788	-677.788	-6.182
3500	67.118	221.878	111.605	-	-	-680.743	-680.743	-13.537
3600	67.186	223.765	115.076	-	-	-683.808	-683.808	-20.892
3700	67.250	225.601	118.547	-	-	-686.983	-686.983	-28.247
3800	67.309	227.389	122.018	-	-	-690.268	-690.268	-35.602
3900	67.363	229.131	125.489	-	-	-693.663	-693.663	-42.957
4000	67.414	230.830	128.960	-	-	-697.168	-697.168	-50.312
4100	67.461	232.487	132.431	-	-	-700.783	-700.783	-57.667
4200	67.505	234.105	135.902	-	-	-704.508	-704.508	-65.022
4300	67.546	235.684	139.373	-	-	-708.343	-708.343	-72.377
4400	67.584	237.229	142.844	-	-	-712.288	-712.288	-79.732
4500	67.621	238.739	146.315	-	-	-716.343	-716.343	-87.087
4600	67.655	240.217	149.786	-	-	-720.508	-720.508	-94.442
4700	67.686	241.662	153.257	-	-	-724.783	-724.783	-101.797
4800	67.715	243.078	156.728	-	-	-729.168	-729.168	-109.152
4900	67.742	244.465	160.199	-	-	-733.663	-733.663	-116.507
5000	67.767	245.824	163.670	-	-	-738.268	-738.268	-123.862
5100	67.791	247.156	167.141	-	-	-742.983	-742.983	-131.217
5200	67.812	248.462	170.612	-	-	-747.808	-747.808	-138.572
5300	67.831	249.744	174.083	-	-	-752.743	-752.743	-145.927
5400	67.848	251.002	177.554	-	-	-757.788	-757.788	-153.282
5500	67.863	252.238	181.025	-	-	-762.943	-762.943	-160.637
5600	67.876	253.451	184.496	-	-	-768.208	-768.208	-167.992
5700	67.888	254.642	187.967	-	-	-773.583	-773.583	-175.347
5800	67.899	255.814	191.438	-	-	-779.068	-779.068	-182.702
5900	67.909	256.965	194.909	-	-	-784.663	-784.663	-190.057
6000	67.918	258.097	198.380	-	-	-790.368	-790.368	-197.412

Dec. 31, 1960/ Sept. 30, 1963

ΔH_f^o 0 = -632 ± 22 kcal. mole⁻¹ΔH_f^o 298.15 = -636 ± 22 kcal. mole⁻¹Point Group [D_{6h}]S_{298.15} = [82] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω _v , cm ⁻¹	ω _v , cm ⁻¹	ω _v , cm ⁻¹	ω _v , cm ⁻¹
[700] (1)	[600] (2)	[900] (1)	[1100] (2)
[850] (1)	[750] (2)	[1100] (1)	[1200] (2)
[1400] (1)	[850] (2)	[1000] (1)	[1500] (2)
[500] (1)	[850] (2)	[900] (1)	[200] (2)
[400] (1)	[950] (2)	[1400] (1)	[250] (2)

Bond Distance: Be-O = [1.63] Å

Bond Angle: Be-O-Be = [110°] O-Be-O = [190°]

Product of the Moments of Inertia: I_AI_BI_C = [3.1266] X 10⁻¹¹¹ g.³ cm.⁶

Heat of Formation.

W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. **30**, 827 (1959) measured the temperature dependence of the (BeO)₆⁺ ion in a mass spectrometer. They calculated a second law heat of vaporization of 203 ± 15 kcal. mole⁻¹ which was adopted here. The uncertainty reflects in part an approximate correction of 10 kcal. mole⁻¹ and the small observed intensities.

Heat Capacity and Entropy.

The assumed symmetry D_{6h} has 20 vibrational frequencies of the type 2A_{1g}, A_{2g}, E_{1g}, E_{2g}, 4E_{2g}, A_{2u}, 2E_{1u}, 2E_{2u}, 3E_{1u}, and 2E_{2u}. The frequencies were estimated by comparison with similar motions in other ring molecules including benzene, (BeO)₃ and (BeO)₄. The assumed structure and vibrational frequencies gave an entropy in good agreement with the heat and equilibrium constant determined by Chupka, et al. The bond length was taken equal to that in BeO₂(s) the angles were chosen so that the O-Be-O angle was almost linear but with the Be-O-Be angle less than 120°. The individual moments of inertia were calculated to be I_A = I_B = 116.089, I_C = 232.118 X 10⁻³⁹ g.² cm.²

Bromine, Monatomic (Br)
(Ideal Gas) Mol. Wt. = 79.916

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔF° ₂₉₈	Log K _p
0	4.000	0.000	INFINITE	1.461	28.188	INFINITE
100	4.968	36.378	46.222	1.944	28.357	55.415
200	4.968	41.805	41.805	1.000	28.188	14.440
298	4.968	41.805	41.805	1.000	28.188	14.440
300	4.968	41.805	41.805	1.000	28.188	14.440
400	4.968	43.265	42.000	1.506	23.110	16.044
500	4.971	44.374	42.368	1.003	23.185	16.771
600	4.979	45.261	42.780	1.500	23.216	15.481
700	4.987	46.050	43.194	1.999	23.271	14.194
800	5.026	46.719	43.593	2.500	23.324	12.894
900	5.063	47.313	43.974	3.005	23.379	11.587
1000	5.107	47.848	44.335	3.513	23.438	10.274
1100	5.153	48.337	44.677	4.026	23.500	8.954
1200	5.199	48.788	45.001	4.544	23.566	7.639
1300	5.243	49.206	45.309	5.066	23.635	6.322
1400	5.284	49.596	45.601	5.592	23.709	5.009
1500	5.320	49.961	45.880	6.122	23.785	3.692
1600	5.351	50.306	46.146	6.656	23.864	2.374
1700	5.377	50.631	46.400	7.192	23.945	1.059
1800	5.398	50.939	46.644	7.731	24.029	-0.253
1900	5.415	51.231	46.878	8.272	24.113	-1.566
2000	5.428	51.509	47.102	8.814	24.199	-2.879
2100	5.437	51.775	47.319	9.357	24.285	-4.192
2200	5.443	52.028	47.527	9.901	24.371	-5.507
2300	5.446	52.270	47.728	10.446	24.457	-6.822
2400	5.447	52.501	47.922	10.991	24.543	-8.136
2500	5.445	52.724	48.110	11.535	24.628	-9.450
2600	5.442	52.937	48.291	12.080	24.712	-10.764
2700	5.438	53.143	48.467	12.624	24.796	-12.078
2800	5.432	53.340	48.638	13.167	24.878	-13.392
2900	5.425	53.531	48.803	13.710	24.959	-14.706
3000	5.418	53.715	48.964	14.252	25.039	-16.020
3100	5.410	53.892	49.120	14.794	25.116	-17.334
3200	5.402	54.064	49.272	15.334	25.195	-18.648
3300	5.393	54.230	49.420	15.874	25.271	-19.962
3400	5.384	54.391	49.563	16.413	25.346	-21.276
3500	5.375	54.547	49.704	16.951	25.419	-22.590
3600	5.366	54.698	49.840	17.488	25.490	-23.904
3700	5.357	54.845	49.973	18.024	25.561	-25.218
3800	5.348	54.988	50.104	18.559	25.630	-26.532
3900	5.339	55.126	50.231	19.093	25.697	-27.846
4000	5.330	55.261	50.355	19.627	25.763	-29.160
4100	5.321	55.393	50.478	20.159	25.827	-30.474
4200	5.312	55.521	50.595	20.691	25.890	-31.788
4300	5.304	55.646	50.711	21.222	25.952	-33.102
4400	5.295	55.769	50.824	21.752	26.013	-34.416
4500	5.287	55.887	50.935	22.281	26.072	-35.730
4600	5.279	56.003	51.044	22.809	26.130	-37.044
4700	5.271	56.116	51.151	23.337	26.184	-38.358
4800	5.264	56.227	51.256	23.863	26.241	-39.672
4900	5.256	56.336	51.359	24.389	26.295	-40.986
5000	5.249	56.442	51.459	24.915	26.348	-42.300
5100	5.242	56.546	51.557	25.439	26.399	-43.614
5200	5.236	56.647	51.654	25.963	26.449	-44.928
5300	5.229	56.747	51.749	26.486	26.499	-46.242
5400	5.223	56.845	51.843	27.009	26.546	-47.556
5500	5.217	56.940	51.935	27.531	26.593	-48.870
5600	5.211	57.034	52.025	28.052	26.638	-50.184
5700	5.205	57.126	52.114	28.573	26.683	-51.498
5800	5.199	57.217	52.203	29.093	26.728	-52.812
5900	5.194	57.306	52.287	29.613	26.769	-54.126
6000	5.189	57.393	52.371	30.132	26.810	-55.440

September 30, 1961

Bromine, Monatomic (Br)
(Ideal Gas)
MOL. WT. = 79.916

ΔH°₁₀ = 28.188 ± 0.070 kcal. mole⁻¹
Ground State = ²S_{1/2}
ΔH°₂₉₈ = 28.740 kcal. mole⁻¹
S°₂₉₈ = 41.805 cal. mole⁻¹ deg.⁻¹

Electronic Levels and Multiplicities

ω, cm. ⁻¹	g ₁	ω, cm. ⁻¹	g ₁	ω, cm. ⁻¹	g ₁
0.00	4	74666	6	86430	2
3685.00	2	75531	22	87500	10
83429.82	6	76736	4	88561	38
64900.50	4	77317	10	89700	56
66877.16	2	78540	14	90371	44
67176.87	4	79517	10	91737	70
68963.52	2	85724	30	92735	12

Thermodynamic Functions.

Thermodynamic functions were calculated using electronic levels and multiplicities listed by C. E. Moore [Nat. Bur. Standards Circ. 467 (1949)]. Higher levels were averaged. The results are in good agreement with W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 147 (1955)], who used essentially the same data.

Heat of Formation.

The heat of formation is calculated from the dissociation energy of bromine selected by Evans, Munson, and Wagman (loc. cit.) and the heat of sublimation derived for diatomic bromine. Evans, Munson, and Wagman list experimental vapor density measurements from the literature which agree with the spectroscopic value within their estimated uncertainty.

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0	∞.000	∞.000	∞.000	∞.000	5.279	5.279	∞.000
100	7.101	48.926	2.247	1.550	5.282	3.303	7.218
200	8.484	54.059	1.800	1.512	5.287	1.512	1.512
300	8.369	57.337	1.515	1.486	5.290	0.257	0.180
400	8.611	59.833	1.302	1.466	5.291	0.000	0.000
500	8.744	61.771	1.134	1.450	5.292	0.193	0.384
600	8.826	63.373	0.991	1.438	5.293	0.193	0.370
700	8.881	64.738	0.879	1.430	5.294	0.193	0.352
800	8.921	65.926	0.790	1.424	5.295	0.193	0.347
900	8.952	66.979	0.721	1.419	5.296	0.194	0.342
1000	8.977	67.923	0.661	1.415	5.297	0.194	0.338
1100	8.998	68.780	0.608	1.412	5.298	0.195	0.334
1200	9.016	69.563	0.561	1.409	5.299	0.196	0.330
1300	9.033	70.286	0.518	1.406	5.300	0.197	0.326
1400	9.048	70.956	0.477	1.403	5.301	0.198	0.322
1500	9.063	71.581	0.438	1.400	5.302	0.199	0.318
1600	9.076	72.166	0.401	1.397	5.303	0.201	0.314
1700	9.089	72.717	0.366	1.394	5.304	0.202	0.310
1800	9.102	73.236	0.333	1.391	5.305	0.203	0.306
1900	9.114	73.729	0.301	1.388	5.306	0.204	0.302
2000	9.126	74.197	0.270	1.385	5.307	0.207	0.298
2100	9.137	74.642	0.241	1.382	5.308	0.208	0.294
2200	9.148	75.068	0.213	1.379	5.309	0.211	0.290
2300	9.160	75.474	0.187	1.376	5.310	0.214	0.286
2400	9.171	75.865	0.163	1.373	5.311	0.217	0.282
2500	9.182	76.239	0.140	1.370	5.312	0.221	0.278
2600	9.192	76.599	0.118	1.367	5.313	0.224	0.274
2700	9.203	76.947	0.097	1.364	5.314	0.229	0.270
2800	9.214	77.281	0.077	1.361	5.315	0.235	0.266
2900	9.224	77.605	0.058	1.358	5.316	0.241	0.262
3000	9.235	77.918	0.040	1.355	5.317	0.248	0.258
3100	9.245	78.221	0.023	1.352	5.318	0.257	0.254
3200	9.256	78.514	0.007	1.349	5.319	0.266	0.250
3300	9.266	78.799	0.000	1.346	5.320	0.276	0.246
3400	9.276	79.076	0.000	1.343	5.321	0.287	0.242
3500	9.287	79.345	0.000	1.340	5.322	0.299	0.238
3600	9.297	79.607	0.000	1.337	5.323	0.312	0.234
3700	9.307	79.862	0.000	1.334	5.324	0.325	0.230
3800	9.317	80.110	0.000	1.331	5.325	0.339	0.226
3900	9.328	80.352	0.000	1.328	5.326	0.352	0.222
4000	9.338	80.589	0.000	1.325	5.327	0.367	0.218
4100	9.348	80.819	0.000	1.322	5.328	0.382	0.214
4200	9.358	81.045	0.000	1.319	5.329	0.397	0.210
4300	9.368	81.265	0.000	1.316	5.330	0.412	0.206
4400	9.378	81.481	0.000	1.313	5.331	0.427	0.202
4500	9.389	81.691	0.000	1.310	5.332	0.442	0.200
4600	9.399	81.898	0.000	1.307	5.333	0.457	0.196
4700	9.409	82.100	0.000	1.304	5.334	0.472	0.192
4800	9.419	82.298	0.000	1.301	5.335	0.487	0.188
4900	9.429	82.492	0.000	1.298	5.336	0.502	0.184
5000	9.439	82.683	0.000	1.295	5.337	0.517	0.180
5100	9.449	82.870	0.000	1.292	5.338	0.532	0.176
5200	9.459	83.054	0.000	1.289	5.339	0.547	0.172
5300	9.469	83.234	0.000	1.286	5.340	0.562	0.168
5400	9.479	83.410	0.000	1.283	5.341	0.577	0.164
5500	9.490	83.585	0.000	1.280	5.342	0.592	0.160
5600	9.500	83.756	0.000	1.277	5.343	0.607	0.156
5700	9.510	83.925	0.000	1.274	5.344	0.622	0.152
5800	9.520	84.090	0.000	1.271	5.345	0.637	0.148
5900	9.530	84.252	0.000	1.268	5.346	0.652	0.144
6000	9.540	84.413	0.000	1.265	5.347	0.667	0.140

Sept. 30, 1982; Sept. 30, 1985

Ground State Configuration 1Σ⁺
S_{298.15} = 57.337 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = 5.28 ± 0.30 kcal. mole⁻¹
ΔH°_f 298.15 = 3.50 ± 0.3 kcal. mole⁻¹

Electronic Levels and Quantum Weight

Electronic Levels and Quantum Weight
E, cm.⁻¹ g.
0 1
Δx_e = 1.8 cm.⁻¹
Δx_e = 0.000757 cm.⁻¹
E₀ = 2.136 Å

Heat of Formation.

The average ΔH°_f 298.15 = -0.406 kcal. mole⁻¹ for the reaction Br₂(g) + Cl₂(g) = 2BrCl(g) and the ΔH°_f 298.15 = 3.694 kcal. mole⁻¹ for 1/2 Br₂(g) from JANAP tables were used to calculate the ΔH°_f 298.15 = 3.5 ± 0.3 kcal. mole⁻¹. Other equilibrium measurements not included below have been summarized by Beeson and Yost, loc. cit.

Third Law ΔH°_f 298.15

Source	T°K	Method	kcal. mole ⁻¹
1	301	Light absorption	-0.51
2	298	Light absorption	-0.34
3	372-492	Total pressure Run III	-0.39
3	372-492	Total pressure Run II	-0.47
4	313-5	Mass spectrometric	-0.32
Average			-0.406

Source

- 1 H. G. Veesper and G. K. Rollefson, J. Am. Chem. Soc. 56, 620 (1934).
- 2 G. Braune and E. Victor, Z Elektrochem. 41, 508 (1935).
- 3 C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. 61, 1432 (1939).
- 4 H. C. Matraw, C. P. Pachucki and N. J. Hawkins, General Electric Co., Report No. KAPL-1016 (1953) Knolls Atomic Power Laboratory, Schenectady, New York.

Heat Capacity and Entropy.

All spectroscopic and molecular constants were obtained from W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. of Standards, 55, 147 (1955) except ν_e which was calculated from B_e. The value of ν_e was reported to be 2.13 Å and 2.11 Å by C. M. Beeson and D. M. Yost, J. Am. Chem. Soc. 61, 1432 (1939) and L. O. Cole and G. W. Elverum Jr., J. Chem. Phys., 20, 1543 (1952), respectively. Ground state configuration was taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

Bromine Monofluoride (BrF)

(Ideal Gas) Mol. Wt. = 98.9074

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(H ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	Log K _p
0	-0.000	INFINITE	-	2.156	-12.144	-	INFINITE
100	6.970	46.743	14.366	1.460	-12.130	-10.872	30.872
200	7.352	51.653	15.404	.748	-12.354	-16.402	17.529
298	7.877	54.700	16.700	.000	-13.073	-17.636	12.927
300	7.885	54.749	16.700	.015	-13.082	-17.658	12.863
400	8.225	55.014	17.422	.523	-13.679	-18.535	9.903
500	8.498	56.041	18.019	1.061	-14.686	-19.557	7.971
600	8.640	60.503	18.306	2.518	-17.689	-18.347	6.682
700	8.744	61.843	18.387	3.387	-17.691	-18.456	5.762
800	8.810	63.015	18.456	4.566	-17.694	-18.565	5.071
900	8.850	64.086	18.516	5.955	-17.698	-18.674	4.554
1000	8.892	64.995	18.568	7.542	-17.701	-18.782	4.195
1100	8.960	65.848	18.612	9.355	-17.703	-18.891	3.753
1200	9.019	66.659	18.652	11.371	-17.705	-18.999	3.460
1300	9.067	67.434	18.686	13.584	-17.707	-19.105	3.212
1400	9.106	68.176	18.714	15.989	-17.710	-19.211	2.999
1500	9.137	68.884	18.738	18.584	-17.714	-19.321	2.815
1600	9.161	69.559	18.758	21.369	-17.718	-19.427	2.654
1700	9.179	70.201	18.773	24.344	-17.723	-19.534	2.511
1800	9.193	70.812	18.784	27.509	-17.728	-19.642	2.385
1900	9.204	71.394	18.792	30.866	-17.733	-19.750	2.274
2000	9.216	71.948	18.798	34.415	-17.738	-19.858	2.169
2100	9.216	72.473	18.798	38.156	-17.743	-19.966	2.077
2200	9.216	72.969	18.798	42.089	-17.749	-20.065	1.993
2300	9.216	73.439	18.798	46.214	-17.755	-20.170	1.916
2400	9.216	73.884	18.798	50.531	-17.761	-20.274	1.844
2500	9.216	74.304	18.798	55.140	-17.768	-20.380	1.782
2600	9.216	74.680	18.798	59.941	-17.776	-20.482	1.722
2700	9.216	75.010	18.798	64.934	-17.783	-20.588	1.666
2800	9.216	75.296	18.798	70.119	-17.790	-20.691	1.613
2900	9.216	75.539	18.798	75.496	-17.796	-20.791	1.562
3000	9.216	75.740	18.798	81.066	-17.800	-20.898	1.512
3100	9.216	75.900	18.798	86.829	-17.805	-21.002	1.461
3200	9.216	76.020	18.798	92.784	-17.810	-21.103	1.411
3300	9.216	76.100	18.798	98.931	-17.813	-21.205	1.361
3400	9.216	76.140	18.798	105.270	-17.815	-21.307	1.311
3500	9.216	76.148	18.798	111.800	-17.815	-21.407	1.261
3600	9.216	76.113	18.798	118.521	-17.815	-21.505	1.211
3700	9.216	76.040	18.798	125.434	-17.815	-21.601	1.161
3800	9.216	75.929	18.798	132.539	-17.815	-21.694	1.111
3900	9.216	75.784	18.798	139.846	-17.815	-21.784	1.061
4000	9.216	75.606	18.798	147.354	-17.815	-21.871	1.011
4100	9.216	75.394	18.798	155.064	-17.815	-21.956	0.961
4200	9.216	75.148	18.798	162.976	-17.815	-22.038	0.911
4300	9.216	74.869	18.798	171.091	-17.815	-22.117	0.861
4400	9.216	74.559	18.798	179.409	-17.815	-22.192	0.811
4500	9.216	74.219	18.798	187.931	-17.815	-22.264	0.761
4600	9.216	73.849	18.798	196.658	-17.815	-22.332	0.711
4700	9.216	73.449	18.798	205.591	-17.815	-22.397	0.661
4800	9.216	73.019	18.798	214.730	-17.815	-22.459	0.611
4900	9.216	72.559	18.798	224.074	-17.815	-22.518	0.561
5000	9.216	72.069	18.798	233.624	-17.815	-22.574	0.511
5100	9.216	71.549	18.798	243.379	-17.815	-22.627	0.461
5200	9.216	70.989	18.798	253.339	-17.815	-22.677	0.411
5300	9.216	70.399	18.798	263.504	-17.815	-22.724	0.361
5400	9.216	69.779	18.798	273.874	-17.815	-22.768	0.311
5500	9.216	69.129	18.798	284.449	-17.815	-22.809	0.261
5600	9.216	68.449	18.798	295.229	-17.815	-22.847	0.211
5700	9.216	67.739	18.798	306.214	-17.815	-22.882	0.161
5800	9.216	67.009	18.798	317.404	-17.815	-22.914	0.111
5900	9.216	66.259	18.798	328.799	-17.815	-22.943	0.061
6000	9.216	65.489	18.798	340.399	-17.815	-22.969	0.011

June 30, 1962; Sept. 30, 1965

BROMINE MONOFLUORIDE (BrF)

(IDEAL GAS)

MOL. WT. = 98.9074

Ground State Configuration $1\Sigma^+$ $\Delta H_f^o = -12.1 \pm 0.4$ kcal. mole⁻¹

$S_{298.15}^o = 54.700$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^o 298.15 = -14.0 \pm 0.4$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

ϵ , cm.⁻¹ g_i

$\omega_e x_e = 4$ cm.⁻¹ $\sigma = 1$

$\omega_e = 0.356319$ cm.⁻¹ $r_e = 1.7555$ Å

Heat of Formation.

The equilibrium constant for the reaction $Br_2(g) + BrF_3(g) = 3BrF(g)$ has been measured over the temperature range 328-380°K. by R. K. Steunenberg, R. C. Vogel and J. Fischer, J. Am. Chem. Soc. **79**, 1320 (1957). Third law analysis of the data yields $\Delta H_f^o 298 = 11.785 \pm 0.2$ kcal. mole⁻¹, with a drift of -0.6 ± 1.2 cal. mole⁻¹ deg.⁻¹. Second law analysis yields $\Delta H_f^o 298 = 11.98 \pm 0.45$ kcal. mole⁻¹, thus it is obvious that the data is thermodynamically self consistent. There is uncertainty in the entropy of $BrF_3(g)$ of ± 1 cal. mole⁻¹ deg.⁻¹ but this corresponds only to ± 0.35 kcal. mole⁻¹ in $\Delta H_f^o 298$, thus a best value of $\Delta H_f^o 298 = 11.78 \pm 0.5$ kcal. mole⁻¹ is adopted. This yields $\Delta H_f^o 298 BrF = -13.973 \pm 0.4$ kcal. mole⁻¹, the uncertainty in the heat of formation being a maximum value comprising the sum of the uncertainties in Br_2 , BrF_3 and ΔH_f^o .

Attempts have been made to analyze the spectra of BrF to obtain a D^o value. P. H. Brodersen and J. E. Sicre, Z. Physik **141**, 515 (1955) obtained two dissociation limits for BrF of 68.52 kcal. mole⁻¹ and 54.98 kcal. mole⁻¹. The difference corresponds to the $Br(F_{1/2}) - Br(F_{3/2})$ excitation energy, indicating that the upper state goes to $F(F_{3/2})$ and $Br(F_{1/2})$. This yields a heat of formation of BrF of -10.23 kcal. mole⁻¹. Since this value is well outside the possible uncertainty limits of the equilibrium data we must conclude that the extrapolation is in error. W. H. Evans, T. R. Munson and D. D. Wagman, J. Res. Natl. Bur. Std. **55**, 147 (1955) have also analyzed the spectra and conclude that a heat of formation of -14.4 kcal. mole⁻¹ is possible. However M. H. Evans, private communication Nov. 1965, now believes that the dissociating state was too strongly perturbed for meaningful extrapolation.

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards **55**, 147 (1955) except r_e and ground state configuration which were taken from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

BROMINE TRIFLUORIDE (BrF₃) (IDEAL GAS)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	$\int_0^T (C_p - H_{298}^0)/T$	$H - H_{298}^0$ kcal. mole ⁻¹	ΔH_f°	ΔF_f°	Log K _f
0	0.000	INFINITE	-	-58.404	-	INFINITE
100	5.271	2.587	-58.404	-57.835	-126.395	126.395
200	13.436	6.4017	-59.451	-56.501	-61.730	61.730
298	15.893	69.867	-60.867	-54.687	-	-
300	15.929	69.966	-60.868	-54.789	-39.912	39.912
400	18.145	78.127	-64.573	-48.755	-23.314	23.314
500	18.478	82.081	-64.573	-45.616	-16.615	16.615
600	18.936	84.978	-64.573	-42.494	-13.267	13.267
800	19.415	91.823	-64.573	-39.396	-10.762	10.762
1000	19.908	98.748	-64.573	-36.306	-8.267	8.267
1100	19.478	93.676	-64.573	-33.253	-5.767	5.767
1200	19.960	99.373	-64.573	-30.207	-3.267	3.267
1300	19.957	99.392	-64.573	-27.173	-0.767	0.767
1400	19.957	99.392	-64.573	-24.142	-0.267	0.267
1500	19.658	98.748	-64.573	-21.114	-0.267	0.267
1600	19.684	101.017	-64.573	-18.087	-0.267	0.267
1700	19.705	102.211	-64.573	-15.060	-0.267	0.267
1800	19.728	103.405	-64.573	-12.033	-0.267	0.267
1900	19.748	104.599	-64.573	-9.006	-0.267	0.267
2000	19.751	105.417	-64.573	-6.980	-0.267	0.267
2100	19.762	106.381	-64.573	-4.954	-0.267	0.267
2200	19.772	107.301	-64.573	-2.928	-0.267	0.267
2300	19.780	108.177	-64.573	-0.902	-0.267	0.267
2400	19.788	109.022	-64.573	1.124	-0.267	0.267
2500	19.795	109.830	-64.573	3.149	-0.267	0.267
2600	19.800	110.606	-64.573	5.174	-0.267	0.267
2700	19.806	111.354	-64.573	7.199	-0.267	0.267
2800	19.811	112.076	-64.573	9.224	-0.267	0.267
2900	19.815	112.769	-64.573	11.249	-0.267	0.267
3000	19.818	113.441	-64.573	13.274	-0.267	0.267
3100	19.822	114.091	-64.573	15.299	-0.267	0.267
3200	19.826	114.719	-64.573	17.324	-0.267	0.267
3300	19.828	115.331	-64.573	19.349	-0.267	0.267
3400	19.830	115.923	-64.573	21.374	-0.267	0.267
3500	19.833	116.497	-64.573	23.399	-0.267	0.267
3600	19.835	117.056	-64.573	25.424	-0.267	0.267
3700	19.839	117.599	-64.573	27.449	-0.267	0.267
3800	19.843	118.129	-64.573	29.474	-0.267	0.267
3900	19.846	118.644	-64.573	31.499	-0.267	0.267
4000	19.842	119.146	-64.573	33.524	-0.267	0.267
4100	19.845	119.636	-64.573	35.549	-0.267	0.267
4200	19.848	120.116	-64.573	37.574	-0.267	0.267
4300	19.846	120.581	-64.573	39.599	-0.267	0.267
4400	19.847	121.038	-64.573	41.624	-0.267	0.267
4500	19.848	121.484	-64.573	43.649	-0.267	0.267
4600	19.850	121.920	-64.573	45.674	-0.267	0.267
4700	19.851	122.347	-64.573	47.699	-0.267	0.267
4800	19.851	122.765	-64.573	49.724	-0.267	0.267
4900	19.852	123.174	-64.573	51.749	-0.267	0.267
5000	19.853	123.575	-64.573	53.774	-0.267	0.267
5100	19.854	123.968	-64.573	55.799	-0.267	0.267
5200	19.854	124.354	-64.573	57.824	-0.267	0.267
5300	19.855	124.732	-64.573	59.849	-0.267	0.267
5400	19.856	125.103	-64.573	61.874	-0.267	0.267
5500	19.856	125.468	-64.573	63.899	-0.267	0.267
5600	19.857	125.825	-64.573	65.924	-0.267	0.267
5700	19.858	126.177	-64.573	67.949	-0.267	0.267
5800	19.858	126.522	-64.573	69.974	-0.267	0.267
5900	19.859	126.862	-64.573	71.999	-0.267	0.267
6000	19.859	127.195	-64.573	74.024	-0.267	0.267

June 30, 1962; Sept. 30, 1965

Point Group C_{2v}
 $\Delta H_f^\circ = -58.4 \pm 0.7$ kcal. mole⁻¹
 $\Delta F_f^\circ = -61.1 \pm 0.7$ kcal. mole⁻¹
 $S_{298.15}^\circ = 69.867$ cal. deg.⁻¹ mole⁻¹

Vibrational Frequencies and Degeneracies

(ν), cm. ⁻¹	(ν), cm. ⁻¹
674 (1)	613 (1)
528 (1)	384 (1)
300 (1)	289 (1)

Bond Distances: Br-F₁ = Br-F₃ = 1.8061 Å Br-F₂ = 1.721 Å
Bond Angle: F₁-Br-F₂ = 86° 12.6' F₂-Br-F₃ = 187° 34.8'
Product of the Moment of Inertia: I_AI_BI_C = 4.51825 X 10⁻¹¹⁴ g.³ cm.⁶

Heat Capacity and Entropy.
The ΔH_f° 298.15 = -61.087 ± 0.7 kcal. mole⁻¹ is from L. Stein, J. Phys. Chem. 66, 288 (1962) and was derived from heats of reaction of F₂ with Br₂ which were measured in an adiabatic calorimeter. Stein's value for the ΔH_f° 298.15 = -64.78 kcal. mole⁻¹ was based upon gaseous Br₂, which has been adjusted to the liquid Br₂ reference state at 298.15°K.

D. W. Magnuson, Report No. K-1179, Carbide and Carbon Chemicals Co., K-25 plant, Oak Ridge, Tennessee (December, 1954) determined the moments of inertia and quadrupole coupling coefficients of both Br⁷⁹F₃ and Br⁸¹F₃ from a number of microwave transitions. From the moment of inertia the bromine trifluoride molecule was found to have a distorted -T- structure with one short, 1.721 Å, and two long, 1.810 Å Br-F bonds. The FBrF angle was found to be 86° 12.6'.

H. H. Claassen, B. Weinstock, and J. G. Malm, J. Chem. Phys. 28, 285 (1958), observed two of the six vibrational levels in the vapor, and calculated the other four levels from a normal coordinate treatment of the molecule. They also obtained a measured entropy of BrF₃(g), from low temperature data combined with vapor pressure data and an approximate correction for dimerization. This value is 71.9 e.u. at 316.27°K. compared with a value of 70.82 e.u. from this table, the difference is probably within the uncertainty of the data. The three principal moments of inertia are: I_A = 7.7514 X 10⁻³⁹, I_B = 2.0579 X 10⁻³⁸ and I_C = 2.83306 X 10⁻³⁸ g. cm.²

BrF₃

Bromine Pentafluoride (BrF₅)
(Ideal Gas) Mol. Wt. = 174.901

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	∞	∞	∞
100	11.313	58.201	95.297	-4.584	-98.846	INFINITE
200	16.311	68.612	79.417	-2.421	-100.043	207.712
298	28.236	77.337	-0.000	-102.466	-98.004	98.004
300	28.236	77.337	-0.000	-102.466	-98.004	98.004
400	27.005	84.888	78.328	-2.624	-102.473	61.000
500	28.424	91.092	80.278	-5.407	-105.614	42.039
600	29.439	96.380	82.532	-8.309	-105.237	30.480
700	30.419	100.966	84.118	-11.284	-102.485	22.700
800	30.697	105.002	85.118	-14.307	-104.425	17.133
900	30.697	108.602	86.308	-17.364	-104.007	13.250
1000	30.699	111.847	87.403	-20.444	-103.590	10.086
1100	31.050	114.709	88.398	-23.525	-103.178	7.566
1200	31.258	117.005	89.101	-26.582	-102.764	5.212
1300	31.331	118.824	89.621	-29.575	-102.344	3.202
1400	31.331	120.224	90.000	-32.504	-101.935	2.370
1500	31.390	121.248	90.261	-35.364	-101.531	1.735
1600	31.439	121.915	90.422	-38.162	-101.131	1.243
1700	31.476	122.225	90.500	-40.900	-100.734	0.864
1800	31.513	122.283	90.557	-43.582	-100.346	0.580
1900	31.542	122.027	90.630	-46.215	-99.959	0.367
2000	31.566	121.546	90.653	-48.800	-99.578	0.217
2100	31.588	120.987	90.623	-51.343	-99.203	0.136
2200	31.606	120.356	90.543	-53.843	-98.833	0.086
2300	31.622	119.662	90.415	-56.300	-98.468	0.053
2400	31.636	118.908	90.243	-58.715	-98.109	0.032
2500	31.649	118.100	90.030	-61.090	-97.757	0.020
2600	31.660	117.251	89.782	-63.425	-97.409	0.014
2700	31.670	116.366	89.500	-65.715	-97.065	0.009
2800	31.678	115.448	89.188	-67.960	-96.727	0.006
2900	31.685	114.500	88.843	-70.160	-96.395	0.004
3000	31.694	113.524	88.468	-72.317	-96.071	0.003
3100	31.700	112.521	88.063	-74.432	-95.749	0.002
3200	31.706	111.490	87.629	-76.506	-95.434	0.001
3300	31.711	110.433	87.167	-78.537	-95.125	0.000
3400	31.716	109.350	86.678	-80.523	-94.820	0.000
3500	31.721	108.242	86.163	-82.465	-94.523	0.000
3600	31.725	107.110	85.623	-84.363	-94.230	0.000
3700	31.729	105.956	85.057	-86.217	-93.942	0.000
3800	31.732	104.779	84.468	-88.027	-93.660	0.000
3900	31.735	103.579	83.845	-89.793	-93.386	0.000
4000	31.738	102.356	83.188	-91.515	-93.115	0.000
4100	31.741	101.110	82.500	-93.193	-92.845	0.000
4200	31.744	99.846	81.782	-94.827	-92.575	0.000
4300	31.746	98.564	81.035	-96.417	-92.306	0.000
4400	31.748	97.268	80.268	-97.962	-92.038	0.000
4500	31.750	95.958	79.482	-99.462	-91.771	0.000
4600	31.752	94.633	78.678	-100.917	-91.505	0.000
4700	31.754	93.294	77.855	-102.327	-91.240	0.000
4800	31.756	91.942	76.999	-103.693	-90.975	0.000
4900	31.758	90.579	76.113	-105.015	-90.710	0.000
5000	31.760	89.206	75.197	-106.293	-90.445	0.000
5100	31.761	87.824	74.251	-107.527	-90.180	0.000
5200	31.762	86.433	73.276	-108.717	-89.915	0.000
5300	31.763	85.035	72.272	-109.862	-89.650	0.000
5400	31.764	83.630	71.239	-110.962	-89.385	0.000
5500	31.766	82.218	70.178	-112.017	-89.120	0.000
5600	31.767	80.794	69.089	-113.027	-88.855	0.000
5700	31.768	79.359	67.972	-113.992	-88.590	0.000
5800	31.769	77.915	66.827	-114.912	-88.325	0.000
5900	31.770	76.462	65.652	-115.787	-88.060	0.000
6000	31.770	75.000	64.457	-116.617	-87.795	0.000

Sept. 30, 1962 Sept. 30, 1965

BrF₅

MOL. WT. = 174.901

(IDEAL GAS)

BROMINE PENTAFLUORIDE (BrF₅)

Point Group C_{4v}
S_{298.15} = 77.34 cal. deg.⁻¹ mole⁻¹
ΔH_f° 0 = -98.8 ± 0.5 kcal. mole⁻¹
ΔH_f° 298.15 = -102.5 ± 0.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

W, cm. ⁻¹	W, cm. ⁻¹	W, cm. ⁻¹
693 (1)	535 (1)	644 (2)
587 (1)	[281](4)	415 (2)
369 (1)	312 (1)	245 (2)

Bond Distance: Br-F_(equatorial) = 1.79 Å Br-F_(axial) = 1.68 Å
Bond Angle: F_(equatorial)-Br-F_(equatorial) = [90°] and F_(axial)-Br-F_(equatorial) = [90°]
Product of the Moment of Inertia: I_AI_BI_C = 3.2035 X 10⁻¹¹³ g.³ cm.⁶

Heat of Formation.
The ΔH_f° 298.15 = -102.466 ± 0.5 kcal. mole⁻¹ is from L. Stein J. Phys. Chem. 66, 288 (1962) and was derived from heats of reaction of F₂ with Br₂ which were measured in an adiabatic calorimeter. Stein's value for the ΔH_f° 298.15 = -106.16 kcal. mole⁻¹ was based upon gaseous Br₂ which has been adjusted to the liquid Br₂ reference state at 298.15°K.

Heat Capacity and Entropy.
O. M. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2235 (1965) report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for the similar molecules BrF₃, IF₅, ClF₃ and XeOF₄. The fundamental frequencies are taken from Begun, et al., except for ν_g which was beyond the range of their infrared measurements. The value ν_g = 245 cm.⁻¹ for the gas has been observed by R. S. McDowell and L. B. Asprey, J. Chem. Phys. 37, 165 (1962) and is confirmed by 237 cm.⁻¹ found in the Raman spectra of the liquid. Raman values from the liquid were used for the infrared inactive fundamentals ν₄ and ν₅. One Raman active frequency, presumably ν₆, is not observed in any of the four molecules. The value ν₅ = 281 cm.⁻¹ was obtained from the normal coordinate calculation. Previous Raman studies were reported by C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 1830 (1952).

A tetragonal pyramidal structure (C_{4v} symmetry) with the above parameters was used by Begun, et al., in the analysis of the spectra. This symmetry is consistent with the NMR spectra of H. S. Outowsky and C. J. Hoffman, J. Chem. Phys. 19, 1259 (1951), with the dipole moment determined by M. T. Rogers, R. D. Pruett, H. B. Thompson and J. L. Speirs, J. Am. Chem. Soc. 78, 44 (1956), and with the X-ray crystal structure obtained by R. D. Burbank and F. N. Benesey, Jr., J. Chem. Phys. 27, 962 (1957). Bond distances were based on those in the crystal and the bond angle was assumed to be 90°, slightly larger than those in the crystal (90.5-96.5°). Begun, et al., indicate that the angle in the gaseous molecule is probably not exactly 90° but that the normal coordinate calculations are not sensitive to this angle. The three principal moments of inertia are: I_A = 2.61497 X 10⁻³⁸, I_B = 2.61497 X 10⁻³⁸ and I_C = 4.04277 X 10⁻³⁸ g.² cm.²

BrF₅

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	INFINITE	-	2.067	6.836	-	INFINITE
100	6.959	39.861	53.655	1.379	6.861	-	19.635
200	6.961	44.685	48.102	-.683	7.052	-	12.072
298	6.965	47.465	47.465	∞.000	7.710	-	9.372
300	6.965	47.508	47.465	-.013	8.720	-	12.810
400	6.984	49.514	47.739	1.710	12.490	-	7.324
500	7.040	51.078	48.256	1.411	12.580	-	5.955
600	7.139	52.369	48.937	2.120	12.665	-	5.036
700	7.272	53.479	49.422	2.840	12.743	-	4.374
800	7.423	54.660	49.992	3.575	12.809	-	3.876
900	7.576	55.943	50.538	4.325	12.864	-	3.486
1000	7.725	55.149	51.060	5.090	12.908	-	3.173
1100	7.863	56.892	51.557	5.869	12.942	-	2.917
1200	7.989	57.582	52.030	6.662	12.968	-	2.702
1300	8.103	58.226	52.482	7.466	12.988	-	2.520
1400	8.205	58.830	52.914	8.282	13.003	-	2.364
1500	8.296	59.399	53.328	9.107	13.014	-	2.229
1600	8.378	59.937	53.724	9.941	13.024	-	2.110
1700	8.451	60.448	54.105	10.782	13.031	-	2.006
1800	8.517	60.933	54.471	11.631	13.037	-	1.913
1900	8.577	61.395	54.823	12.486	13.041	-	1.829
2000	8.630	61.836	55.163	13.346	13.045	-	1.754
2100	8.679	62.258	55.491	14.212	13.048	-	1.686
2200	8.724	62.663	55.808	15.082	13.052	-	1.625
2300	8.765	63.052	56.114	15.956	13.056	-	1.568
2400	8.803	63.426	56.411	16.835	13.060	-	1.517
2500	8.838	63.786	56.699	17.717	13.065	-	1.469
2600	8.870	64.133	56.978	18.602	13.070	-	1.425
2700	8.890	64.468	57.250	19.491	13.075	-	1.384
2800	8.929	64.792	57.513	20.382	13.082	-	1.347
2900	8.955	65.106	57.770	21.276	13.088	-	1.311
3000	8.980	65.410	58.019	22.173	13.095	-	1.278
3100	9.004	65.705	58.262	23.072	13.103	-	1.248
3200	9.027	65.991	58.500	23.974	13.111	-	1.219
3300	9.048	66.269	58.731	24.877	13.121	-	1.192
3400	9.069	66.540	58.957	25.783	13.131	-	1.166
3500	9.088	66.803	59.177	26.691	13.142	-	1.142
3600	9.107	67.059	59.392	27.601	13.155	-	1.119
3700	9.125	67.309	59.603	28.513	13.168	-	1.098
3800	9.143	67.553	59.809	29.426	13.182	-	1.077
3900	9.160	67.790	60.011	30.341	13.198	-	1.058
4000	9.176	68.023	60.208	31.258	13.215	-	1.039
4100	9.192	68.249	60.401	32.176	13.232	-	1.022
4200	9.208	68.471	60.591	33.096	13.251	-	1.005
4300	9.223	68.688	60.777	34.018	13.271	-	.989
4400	9.238	68.900	60.959	34.941	13.292	-	.973
4500	9.252	69.108	61.138	35.866	13.314	-	.959
4600	9.266	69.311	61.313	36.791	13.338	-	.945
4700	9.280	69.511	61.485	37.719	13.362	-	.931
4800	9.294	69.706	61.655	38.647	13.388	-	.918
4900	9.307	69.896	61.821	39.576	13.414	-	.906
5000	9.320	70.086	61.984	40.509	13.442	-	.894
5100	9.333	70.271	62.145	41.442	13.471	-	.882
5200	9.346	70.452	62.303	42.375	13.501	-	.871
5300	9.358	70.629	62.459	43.311	13.532	-	.860
5400	9.370	70.802	62.613	44.248	13.564	-	.849
5500	9.383	70.977	62.762	45.185	13.597	-	.840
5600	9.395	71.147	62.910	46.124	13.632	-	.831
5700	9.407	71.313	63.056	47.064	13.667	-	.821
5800	9.419	71.477	63.200	48.005	13.703	-	.812
5900	9.431	71.637	63.341	48.948	13.741	-	.803
6000	9.442	71.796	63.481	49.891	13.779	-	.795

Sept. 30, 1961; Sept. 30, 1965

Ground State Configuration $1\sum^+$
 $S_{298.15}^0 = 47.465 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = -6.84 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 298.15 = -8.71 \pm 0.10 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{E}{\text{cm.}^{-1}} = \frac{g_1}{0} \frac{1}{1}$$

$\omega_e = 2849.218 \pm 0.016 \text{ cm.}^{-1}$
 $\omega_e x_e = 45.246 \pm 0.008 \text{ cm.}^{-1}$
 $\omega_e = 1.414 \text{ Å}$
 $\alpha_e = 0.23248 \pm 7 \times 10^{-5} \text{ cm.}^{-1}$
 $B_e = 8.46571 \pm 1.8 \times 10^{-4} \text{ cm.}^{-1}$
 $\sigma = 1$

Heat of Formation

The enthalpy change, $\Delta H_f^0 376.2 = -12.47 \pm 0.13 \text{ kcal. mole}^{-1}$, for the reaction $(1) 1/2 \text{ H}_2(\text{g}) + 1/2 \text{ Br}_2(\text{g}) = \text{HBr}(\text{g})$ was reported by J. R. Lacher, L. Cassali, and J. D. Park, J. Phys. Chem. 50, 608 (1956). Using $\Delta H_f^0 298.15$ (Br₂, g) = 7.59 kcal. mole⁻¹, the $\Delta H_f^0 298.15$ (HBr, g) was derived as $-8.71 \pm 0.13 \text{ kcal. mole}^{-1}$.

The heat of oxidation of aqueous sulfur dioxide with gaseous chlorine and liquid bromine were determined by calorimetric methods by W. H. Johnson and J. R. Ambrose, J. Res. Natl. Bur. Std. 67A, 427 (1963) and W. H. Johnson and S. Sunner, Acta Chem. Scand., 17, 1917 (1963), respectively. The results were given as $\Delta H_f^0 298.15 = -77.28 \pm 0.14 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Cl}_2(\text{g})$) and $-55.47 \pm 0.11 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Br}_2(\text{l})$) for the reaction $\text{X}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l}) = \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l}) = \text{H}_2\text{SO}_4 + 2 \text{ H}_2\text{O}(\text{l})$. The enthalpy change for the reaction $\text{Cl}_2(\text{g}) + 2 \text{ (HBr-1250 H}_2\text{O)} = \text{Br}_2(\text{l}) + 2 \text{ (HCl-1250 H}_2\text{O)}$ was calculated to be $-21.82 \pm 0.18 \text{ kcal. mole}^{-1}$. Using $\Delta H_f^0 298.15$ (HCl-1250 H₂O) = $-39.93 \pm 0.05 \text{ kcal. mole}^{-1}$, the heat of formation for HBr-1250 H₂O was derived to be $-28.53 \pm 0.10 \text{ kcal. mole}^{-1}$. Employing ΔH_f^0 (HBr-1250 H₂O) = $-28.53 \pm 0.10 \text{ kcal. mole}^{-1}$, leads to $\Delta H_f^0 298.15$ (HBr-∞H₂O) = $-29.016 \pm 0.10 \text{ kcal. mole}^{-1}$. Based on the value, $\Delta H_f^0 298.15 = -20.350 \pm 0.012 \text{ kcal. mole}^{-1}$ for the reaction $\text{HBr}(\text{g}) = \text{HBr}(\infty \text{ H}_2\text{O})$ reported by C. E. Vandervee and J. D. Nutter, J. Phys. Chem. 67, 2521 (1963), the heat of formation ($\Delta H_f^0 298.15$) for HBr(g) was evaluated as $-8.67 \pm 0.10 \text{ kcal. mole}^{-1}$.

The heats of oxidation of As_2O_3 to As_2O_5 in aqueous solution with $\text{Br}_2(\text{l})$ and $\text{Cl}_2(\text{g})$ were measured by L. Bjellerup, S. Sunner and I. Wedberg, Acta Chem. Scand. 17, 1761 (1963) and S. Thoren, Symposium on Thermodynamics and Thermochemistry, Lund, Sweden, July, 1963. Using the values $\Delta H_f^0 = -56.61 \pm 0.11 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Br}_2(\text{l})$) and $-100.09 \pm 0.08 \text{ kcal. mole}^{-1}$ ($\text{X}_2 = \text{Cl}_2(\text{g})$) for the reaction $\text{As}_2\text{O}_3(\text{aq.}) + 2 \text{ X}_2 + 2 \text{ H}_2\text{O}(\text{eq.}) \rightarrow \text{As}_2\text{O}_5(\text{aq.}) + 4 \text{ HX}(\text{aq.})$ obtained from H. A. Skinner, Pure Appl. Chem. 5, 95 (1964), the enthalpy change for the reaction $2\text{Br}_2(\text{l}) + 4 \text{ HX}(\text{aq.}) = 2\text{Cl}_2(\text{g}) + 4\text{HBr}(\text{aq.})$ was calculated to be $+3.48 \pm 0.14 \text{ kcal. mole}^{-1}$. Based on $\Delta H_f^0 298.15$ (HCl, ∞H₂O) = $-39.95 \pm 0.05 \text{ kcal. mole}^{-1}$, the value of $\Delta H_f^0 298.15$ (HBr, ∞H₂O) was derived to be $-28.06 \pm 0.06 \text{ kcal. mole}^{-1}$, yielding $\Delta H_f^0 298.15$ (HBr, g) = $-8.71 \pm 0.06 \text{ kcal. mole}^{-1}$.

The value of $\Delta H_f^0 298.15$ (HBr, g) adopted is $-8.71 \pm 0.10 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

The values of ω_e , $\omega_e x_e$, B_e and α_e were taken from T. C. James and R. J. Thibault, J. Chem. Phys. 42, 1450 (1965), and corrected to the average isotopic species. Submillimeter-wave spectra of HBr were measured by G. Jones and M. Gordy, Phys. Rev. 135, A 1229 (1964). The molecular constants derived were close to the values adopted. The ground state configuration was obtained from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950, in which molecular constants for HBr(g) were also given. A precise measurement of the infrared fundamental bands of HBr has been made by E. K. Plyler, J. Res. Natl. Bur. Std., 64, 377 (1960). The corresponding rotational and vibrational constants have been calculated from the observed data. The moment of inertia is $3.30514 \times 10^{-40} \text{ g. cm.}^2$.

Ammonium Bromide (NH₄Br)

(Crystal) Mol. Wt. = 97.94758

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	4.052	-60.939	-60.939	INFINITE
100	10.584	43.950	3.542	-62.623	-56.049	122.490
200	18.525	28.875	2.053	-63.277	-49.203	53.764
298	21.194	26.970	0.000	-64.900	-42.085	30.847
300	21.246	27.101	0.039	-64.910	-41.943	30.954
400	22.160	33.381	2.224	-68.581	-33.532	18.320
500	25.840	39.597	4.542	-68.055	-24.908	10.887
600	28.480	43.728	7.213	-67.984	-16.279	5.029
700	27.500	47.531	9.814	-67.597	-7.687	2.009
800	30.300	51.591	12.707	-66.935	-8.827	0.226
900	32.700	55.300	15.859	-66.036	-9.247	2.245
1000	34.900	58.651	19.241	-64.927	-17.554	3.836
1100	36.831	62.279	22.839	-63.634	-25.741	5.114
1200	38.600	65.561	26.602	-62.183	-33.805	6.154
1300	40.183	68.714	30.542	-60.589	-41.739	7.017
1400	41.650	71.746	34.634	-58.868	-49.547	7.734
1500	43.000	74.667	38.868	-57.035	-57.228	8.338

AMMONIUM BROMIDE (NH₄Br)

(CRYSTAL)

MOL. WT. = 97.94758



ΔH_f^o 0 = -60.9 ± 0.3 kcal. mole⁻¹
 ΔH_f^o 298.15 = -64.9 ± 0.3 kcal. mole⁻¹
 ΔH_f^o = 0.77 kcal. mole⁻¹
 ΔH_m^o = Unknown

S_{298.15} = 26.97 cal. deg.⁻¹ mole⁻¹

T_c = 411°K.

T_m = 815.2°K.

T_d = 670°K.

Heat of Formation.

The equilibrium pressures for the reaction NH₄Br(c) → NH₃(g) + HBr(g) have been measured by several investigators. Using the densi-tensimeter, A. Smith and R. Purcell, J. Chem. Soc. 2944 (1928), determined both the equilibrium pressures and vapor densities of the decomposition products, simultaneously, at several temperatures. In order to check the density values obtained, the authors applied the "extrapolation method", from which it was calculated that the corresponding vapor density agreed with complete dissociation. Based on this conclusion, the reported equilibrium pressures were employed to evaluate the enthalpy changes (ΔH_f^o) of the decomposition reaction by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	Equipment Used
Smith and Calvert (1)	576.40-676.02	45.12 ± 0.13	44.93	Isoteniscope
Smith and Purcell (2)	604.95-668.15	45.50 ± 0.17	45.08	Densit-tensimeter
Johnson (3)	573.15-667.76	45.41 ± 0.44	44.85	Spiral Manometer
(1) A. Smith and R. P. Calvert, J. Am. Chem. Soc. 50, 1363 (1928).				
(2) A. Smith and R. Purcell, J. Chem. Soc. 2944 (1928).				
(3) F. W. G. Johnson, Z. physik. Chem. 65, 38 (1909).				

The value of ΔH_f^o 298.15 adopted is 45.2 ± 0.2 kcal. mole⁻¹. Using ΔH_f^o 298.15 = -10.97 and -8.71 kcal. mole⁻¹ for NH₃(g) and HBr(g), respectively, the value of ΔH_f^o 298.15 for NH₄Br(c) is evaluated as -64.9 ± 0.3 kcal. mole⁻¹. The corresponding ΔH_f^o 298.15 value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of the Univalent Electrolytes", NBS-NBS2, National Bureau of Standards, April 1, 1965, is 45.5 ± 0.2 kcal. mole⁻¹.

The vapor densities (573-661°K.) of dissociation products of NH₄Br(c) were also measured by A. Smith and R. H. Lombard, J. Am. Chem. Soc. 51, 38 (1929). Using the equilibrium pressures reported by A. Smith and R. P. Calvert, loc. cit., they derived the corresponding degrees of dissociation of NH₄Br(c) at different temperatures. The calculated results indicated that only 48% of NH₄Br(c) decomposed at 573°K. and as reaction temperatures increased to 661°K. the degree of dissociation decreased to 10%. This conclusion was stated to be erroneous by Smith and Purcell, loc. cit., probably because of incorrect density determinations.

Heat Capacity and Entropy.

The low temperature (13-305°K.) heat capacities and S_{298.15} were obtained from M. Sorai, H. Suga and S. Seki, Bull. Chem. Soc. Japan, 38, 1125 (1965). The C_p values above 305°K. were estimated by comparison with those for NaCl(c), NaBr(c) and NH₄Cl(c). The low temperature heat capacities were also measured by R. Ewald, Ann. Physik, 44, 1213 (1914), 139-301°K., and P. Simon, C. V. Simon and M. Ruhemann, Z. phys. Chem. 129, 339 (1927), 201.2-277.1°K.

Transition Data.

The temperature (T_c) and heat of transition (ΔH_f^o) were given by P. W. Bridgman, Proc. Am. Acad. Arts Sci. 52, 91 (1916-17). T_c = 419.5 ± 0.6°K. was reported by M. M. Markowitz and D. A. Boryte, J. Phys. Chem. 66, 1477 (1962), which was determined by differential thermal analysis. According to Sorai, Suga and Seki, loc. cit., there are 3 solid phase transitions, namely Phase IV (CaCl₂) → Phase III (tetragonal) at 108°K., Phase III (tetragonal) → Phase II (CaCl₂) at 235°K. and Phase II (CaCl₂) → Phase I (NaCl) at 411°K.

Melting Temperature.

The value of T_m was taken from H. Rasow, Z. anorg. Chem. 114, 117 (1920), determined under pressure.

Mar. 31, 1962, Sept. 30, 1965

Temperature of Decomposition.

The temperature of decomposition (T_d) was calculated as the temperature at which the total pressure of the decomposition products for the reaction NH₄Br(c) → NH₃(g) + HBr(g) equals 1 atm. T_d = 674 and 688.4°K. were reported by N. W. Laft. Ind. Chemist, 31, 502 (1955) and M. M. Markowitz and D. A. Boryte, loc. cit., respectively.



Iodine Monobromide (IBr)
(Ideal Gas)

GFW = 206.8134

IODINE MONOBROMIDE (IBr)

(IDEAL GAS)

GFW = 206.8134

Ground State Configuration $1\Sigma^+$ $S_{298.15}^\circ = 61.86 \text{ gibbs/mol}$ $\Delta H_f^\circ = 11.91 \pm 0.02 \text{ kcal/mol}$ $\Delta H_f^\circ = 9.77 \pm 0.02 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	$\epsilon_2, \text{cm}^{-1}$	$\epsilon_3, \text{cm}^{-1}$	$\epsilon_4, \text{cm}^{-1}$	ϵ_5
0	1	16980	1	1
12230	6	[51677]	2	2
[16155]	5	[56349]	2	2

$w_e = 267.38 \text{ cm}^{-1}$
 $B_e = 0.05568 \text{ cm}^{-1}$
 $w_e X_e = 0.774 \text{ cm}^{-1}$
 $\sigma_e = 1$
 $r_e = 2.485 \text{ \AA}$

Heat of Formation

The equilibrium constants for the reaction (A) $I_2(g) + Br_2(g) = 2 IBr(g)$ were determined to be 0.01124 and 0.01303 at 547.7 and 578°K, respectively, by M. Müller, Z. Physik. Chem. 123, 1 (1926), who studied the rate of reaction between $H_2(g)$ and $Br_2(g)$ in the presence of $I_2(g)$. M. Bodenstein and A. Schmidt, Z. Physik. Chem. 123, 26 (1926), derived two values of the equilibrium constants at 1495°K for the same reaction by vapor density studies on the system I_2, I, Br_2, Br and BrI . The equilibrium between $CuBr_2(c), I_2(g), CuBr(c)$ and $IBr(g)$ was investigated by J. Morris and D. M. Yost, J. Am. Chem. Soc. 53, 2625 (1931), and the equilibrium constants at 115.0, 151.2 and 176.0°C for reaction (A) were evaluated. Based on these reported equilibrium constants, the corresponding enthalpy changes for reaction (A) are calculated by both the second and third law methods.

R. M. Bader and D. M. Yost, Phys. Rev. 37, 1548 (1931), observed the infrared bands of IBr and classified them as the $A\Pi_2 = X\Sigma^+$ transition. They have shown that the dissociation products of the upper state are normal atoms. M. O. Brown, Phys. Rev. 42, 355 (1932), assigned a faint set of bands in the red as the $B^1\Pi_g = X^1\Sigma^+$ system. By means of a vibrational analysis he found that the absorption spectrum of IBr is analogous to that of ICl . The heat of dissociation for IBr was evaluated to be $14,660 \pm 5 \text{ cm}^{-1}$ or 1.817 eV . Hence the enthalpy change for the reaction (B) $IBr(g) = I(g) + Br(g)$ is calculated as 41.92 kcal/mol .

The heats of formation for $BrI(g)$ derived from the enthalpy changes for reaction (A) and (B) are presented in the following table. The value of $\Delta H_f^\circ(298.15^\circ K, IBr, g)$ adopted is $9.77 \pm 0.02 \text{ kcal/mol}$.

Investigator	Reaction	Temperature °K	No. of Points	$\Delta H_f^\circ(298.15^\circ K, \text{kcal/mol})$	Second Law Value	Third Law Value	Drift eu	$\Delta H_f^\circ(298.15^\circ K, \text{kcal/mol})$
Müller (1926)	(A)	547.7, 578	2	-3.07	-3.38	-0.55	9.47	9.77
Bodenstein and Schmidt (1926)	"	1495	1	-	-2.92	-	9.70	9.70
McMorris and Yost (1931)	(B)	388.2-449.2	14	-2.46	-2.85	-0.9 \pm 0.4	9.73	9.73
Brown (1932)	"	298	-	-	41.92**	-	9.77**	9.77**

Calculation based on third law $\Delta H_f^\circ(298.15^\circ K)$ value.The value is derived from $D_0^\circ(I-Br)$.

Heat Capacity and Entropy

The ground state configuration, electronic levels, quantum weights, w_e and $w_e X_e$ are obtained from O. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., New York, 1950. The values of B_e, σ_e (corrected to the average isotopic species) and r_e were reported by T. S. Jaseja, J. Mol. Spectry, 5, 445 (1960), who analyzed the microwave spectrum of IBr , corresponding to the transitions $J = 4 \rightarrow 5$ and $J = 5 \rightarrow 6$, for the two isotopic species, $^{127}\text{Br}^{79}\text{I}$ and $^{127}\text{Br}^{81}\text{I}$. The moment of inertia is $5.007 \times 10^{-38} \text{ g cm}^2$.

The infrared absorption spectrum of IBr at 8000 - 6800 \AA , associated with a $^3\Pi_1 \rightarrow ^1\Sigma^+$ transition, was observed by L. E. Selin, Arkiv Fysik 22, 479 (1962). The derived rotational constants are different from those reported by Jaseja, loc. cit.

T, °K	C_p°	$S^\circ - (G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	-0.00	INFINITE	-2.370	11.906	11.906	INFINITE
100	7.425	52.434	69.408	11.921	8.010	17.505
200	8.457	58.428	62.656	11.558	4.232	6.624
298	8.731	61.864	61.864	9.770	0.887	0.650
300	8.734	61.918	61.864	9.758	0.833	0.606
400	8.919	66.432	62.662	1.785	1.382	0.912
500	9.061	68.062	63.597	1.381	2.227	0.811
600	9.193	68.446	64.336	1.379	2.369	0.740
700	9.319	68.649	64.876	1.377	2.511	0.686
800	9.441	68.781	65.252	1.375	2.653	0.641
900	9.559	68.846	65.511	1.373	2.795	0.601
1000	9.668	68.846	65.691	1.372	2.936	0.563
1100	9.768	68.791	65.801	1.370	3.079	0.525
1200	9.859	68.681	65.841	1.368	3.221	0.487
1300	9.941	68.520	65.817	1.365	3.363	0.450
1400	10.015	68.317	65.731	1.362	3.505	0.412
1500	10.081	68.071	65.581	1.359	3.647	0.375
1600	10.139	67.791	65.371	1.356	3.789	0.337
1700	10.189	67.481	65.111	1.352	3.931	0.299
1800	10.231	67.141	64.801	1.348	4.073	0.261
1900	10.265	66.781	64.441	1.344	4.215	0.223
2000	10.291	66.401	64.041	1.339	4.357	0.185
2100	10.309	65.991	63.601	1.334	4.500	0.147
2200	10.319	65.551	63.121	1.328	4.642	0.109
2300	10.321	65.081	62.601	1.321	4.784	0.071
2400	10.315	64.591	62.041	1.313	4.926	0.033
2500	10.301	64.081	61.441	1.304	5.068	0.000
2600	10.279	63.551	60.801	1.294	5.210	-0.038
2700	10.249	62.991	60.121	1.282	5.352	-0.076
2800	10.211	62.401	59.401	1.269	5.494	-0.114
2900	10.165	61.781	58.641	1.254	5.636	-0.152
3000	10.111	61.131	57.841	1.237	5.778	-0.189
3100	10.049	60.451	57.001	1.218	5.920	-0.227
3200	9.979	59.741	56.121	1.197	6.062	-0.265
3300	9.901	59.001	55.201	1.174	6.204	-0.303
3400	9.815	58.231	54.241	1.149	6.346	-0.341
3500	9.721	57.441	53.241	1.121	6.488	-0.379
3600	9.619	56.621	52.201	1.090	6.630	-0.417
3700	9.509	55.781	51.121	1.056	6.772	-0.455
3800	9.391	54.911	50.001	1.019	6.914	-0.493
3900	9.255	54.011	48.841	0.979	7.056	-0.531
4000	9.101	53.081	47.641	0.935	7.200	-0.569
4100	8.929	52.121	46.401	0.887	7.342	-0.607
4200	8.749	51.131	45.121	0.835	7.484	-0.645
4300	8.561	50.111	43.801	0.778	7.626	-0.683
4400	8.365	49.061	42.441	0.716	7.768	-0.721
4500	8.161	47.981	41.041	0.649	7.910	-0.759
4600	7.949	46.871	39.601	0.577	8.052	-0.797
4700	7.729	45.731	38.121	0.500	8.194	-0.835
4800	7.501	44.561	36.601	0.418	8.336	-0.873
4900	7.265	43.371	35.041	0.331	8.478	-0.911
5000	7.021	42.151	33.441	0.239	8.620	-0.949
5100	6.769	40.911	31.801	0.141	8.762	-0.987
5200	6.509	39.641	30.121	0.039	8.904	-1.025
5300	6.241	38.341	28.401	-0.069	9.046	-1.063
5400	5.965	37.011	26.641	-0.171	9.188	-1.101
5500	5.681	35.651	24.841	-0.269	9.330	-1.139
5600	5.389	34.271	23.001	-0.361	9.472	-1.177
5700	5.089	32.871	21.121	-0.449	9.614	-1.215
5800	4.781	31.441	19.201	-0.531	9.756	-1.253
5900	4.465	30.001	17.241	-0.609	9.898	-1.291
6000	4.141	28.541	15.241	-0.681	10.040	-1.329

Potassium Bromide (KBr)

POTASSIUM BROMIDE (KBr)

(CRYSTAL)

OPW = 119.011

GFW = 119.011

(Crystal)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	2.919	- 92.417	- 92.417	INFINITE
100	10.312	10.265	33.595	2.333	- 92.579	- 92.111	201.307
200	11.920	18.047	24.052	1.201	- 92.652	- 91.615	100.112
298	12.500	22.930	22.930	0.000	- 94.120	- 90.924	66.649
300	12.510	23.007	22.930	0.023	- 94.126	- 90.908	66.223
400	12.860	26.655	23.425	1.292	- 94.292	- 88.980	48.616
500	13.205	29.558	24.371	2.593	- 94.175	- 86.566	37.882
600	13.470	31.986	25.444	3.927	- 94.011	- 84.378	30.735
700	13.660	34.091	26.533	5.295	- 93.807	- 82.251	25.639
800	13.800	35.981	27.537	6.708	- 93.553	- 79.997	21.927
900	15.222	37.725	28.626	8.188	- 97.233	- 77.709	18.870
1000	16.255	39.380	29.620	9.760	- 96.833	- 75.561	16.514
1100	17.460	40.987	30.500	11.440	- 115.283	- 74.490	14.890
1200	18.400	42.500	31.280	13.120	- 113.466	- 74.704	10.894
1300	19.030	44.025	32.420	15.113	- 113.466	- 74.704	10.894
1400	19.550	45.474	33.302	17.042	- 112.486	- 61.089	9.536
1500	20.000	46.839	34.159	19.020	- 111.459	- 57.454	8.371

Dec. 31, 1961; Mar. 31, 1967

Heat of Sublimation.

The heats of sublimation to monomer and dimer are calculated as the enthalpy changes for the following two reactions: $\text{KBr}(g) = \text{KBr}(c)$ and $2 \text{KBr}(c) = \text{K}_2\text{Br}_2(g)$.

BrK

Melting Data.

See KBr(1) table for details.

Heat Capacity and Entropy.

The low temperature heat capacities, 2.9 - 272.2°K, were measured by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A 242, 467 (1957), using an adiabatic calorimeter. The high temperature heat capacities, 325.25 - 711.75°K, are taken from A. Mustafa, Ann. Acad. Sci. Penicase, Ser. A I, 98, 7 (1951). These two sets of Cp data are joined smoothly at 298°K. The Cp values at temperatures, 720 - 1007°K, are extrapolated graphically, so that the derived enthalpy change ($H^{\circ}_{1007} - H^{\circ}_{298}$) = 9.9 kcal/mol agrees with that determined by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Dec. 1, 1964. The derived enthalpies at 700, 800 and 900°K are also in good agreement with those measured by S. M. Skuratov and S. A. Lapushkin, J. Gen. Chem. USSR (Eng. Transl.) 21, 2465 (1951). The Cp values above 1007°K are obtained by graphical extrapolation.

The S°_{298} is calculated from the adopted low temperature Cp, based on $S^{\circ}_{2,9} = 0.0015$ eu.

The heat capacities of KBr(c) were also measured by W. Nemat and P. A. Lindemann, Z. Elektrochem. 17, 817 (1911), 78.7 - 89.2°K; F. Korf, Ann. Physik 4, 49 (1911), 137 - 234°K; and K. Clausius, J. Goldmann, and A. Perlick, Z. Naturforsch. 4b, 424 (1949). The enthalpies of KBr(c) were determined by A. Magnus, Phys. Z. 14, 5 (1913), and C. B. Cooper, J. Chem. Phys. 21, 777 (1953). The results are in reasonable agreement with the adopted functions except for those reported by Cooper.

Heat of Formation.

The heat of solution (ΔH_{soln}) of KBr(c) in $\text{H}_2\text{O}(l)$ has been measured by many investigators. The results were reviewed in detail by V. B. Parker, U. S. Natl. Bur. Std. NBS-NSB-2, 1965. Eight pertinent ΔH_{soln}° values are reproduced in the table below. Adopting the best value, $\Delta H_{298}^{\circ} = 4.75 \pm 0.02$ kcal/mol for the reaction $\text{KBr}(c) + \text{K}^+(\infty \text{H}_2\text{O}) + \text{Br}^-(\infty \text{H}_2\text{O})$, we derive $\Delta H_{298}^{\circ} = -94.12$ kcal/mol for KBr(c). The auxiliary values $\Delta H_{298}^{\circ} = -80.32$ and -29.05 kcal/mol for $\text{K}^+(\infty \text{H}_2\text{O})$ and $\text{Br}^-(\infty \text{H}_2\text{O})$, respectively, are obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.

ΔH°	Temperature °C	m*	Investigator
4.727	16.6	0.28	P. T. Walden, Z. Physik. Chem. 58, 479 (1907).
4.777	25	0.37	J. Wüst and E. Lange, Z. Physik. Chem. 116, 161 (1925).
4.753	25	0.09	H. R. Chipman, F. M. G. Johnson, and O. Maass, Proc. Trans. Nova Scotian Inst. Sci. 17, 149 (1929).
4.684	20	0.19	M. M. Popov, A. Bundel, and V. Cholier, Z. Physik. Chem. 147, 302 (1930).
4.989	23.5	0.14	A. S. Fedorov and O. P. Sil'chenko, Ukrain. Khim. Zhur. 12, 53 (1937).
4.783	25	0.13	E. Lange and W. Martin, Z. Physik. Chem. 180, 233 (1937).
4.542	20.5	0.12	M. M. Popov, S. M. Skuratov, and M. M. Strel'tsova, Zhur. Obshchei Khim. 10, 2023 (1940).
4.739	25	0.28	J. Hetala, Ann. Acad. Sci. Fennicae Ser. A VI No. 63, 1 (1960).

*Values are adjusted to 298.15°K and to infinite dilution.

**Lowest experimental molality.

Potassium Bromide (KBr)

(Liquid) GFW = 119.011

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	kcal/mol ΔH°	ΔG°	Log Kp
0					
100					
200					
298	16,700	25,225	0.000	- 89.984	64.119
300					
400	16,700	25,328	0.031	- 89.983	63.712
500	16,700	30,133	1.701	- 85.826	46.893
600	16,700	33,959	3.371	- 83.261	36.674
700	16,700	36,908	5.081	- 82.077	29.497
800	16,700	39,478	6.711	- 80.336	25.082
900	16,700	41,708	8.361	- 78.470	21.492
1000	16,700	43,675	10.051	- 77.065	18.714
1100	16,700	45,435	11.721	- 75.519	16.505
1200	16,700	47,026	13.391	- 72.994	14.503
1300	16,700	48,479	15.061	- 69.740	12.701
1400	16,700	49,816	16.731	- 66.546	11.187
1500	16,700	51,054	18.401	- 63.406	9.898
1600	16,700	52,208	20.071	- 60.318	8.786
1700	16,700	53,284	21.741	- 57.277	7.824
1800	16,700	54,286	23.411	- 54.283	7.076
1900	16,700	55,251	25.081	- 51.330	6.232
2000	16,700	56,154	26.751	- 48.417	5.569
2100	16,700	57,010	28.421	- 45.540	4.976
2200	16,700	57,825	30.091	- 42.700	4.444
2300	16,700	58,602	31.761	- 39.693	3.963
2400	16,700	59,344	33.431	- 37.119	3.527
2500	16,700	60,055	35.101	- 34.375	3.130
2600	16,700	60,737	36.771	- 31.562	2.768

POTASSIUM BROMIDE (KBr)

(LIQUID)

OPW = 119.011

S°_{298.15} = 25.225 gibbs/mol

Tm = 1007°K

Tb = 1671°K

ΔHf°_{298.15} = -89.984 kcal/mol

ΔHm° = 6.1 kcal/mol

ΔHv° = 35.65 kcal/mol

Heat of Formation.

The heat of formation (ΔHf°₂₉₈) for KBr(l) is obtained from ΔHf°₂₉₈(KBr, c) by adding ΔHm° and the difference between H°₁₀₀₇ - H°₂₉₈ for crystal and liquid.

J. Togruri, H. Flood and T. Forland, Acta Chem. Scand. **17**, 1502 (1963), studied the chemical equilibrium for the reaction KBr(l) + HCl(g) = KCl(l) + HBr(g). They obtained ΔH°₁₀₇₃ = 3.50 ± 0.08 and 3.54 kcal/mol from partial pressure data and emf data, respectively. The corresponding value calculated from these tables is 3.78 kcal/mol. Combination of the experimental results with JANAF auxiliary data leads to -89.70 and -89.74 kcal/mol for ΔHf°₂₉₈.

Heat Capacity and Entropy.

The heat capacity of 16.7 gibbs/mol was derived by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, Dec. 1, 1964, from enthalpy data in the range 1010 - 1100°K. This Cp value is adopted here for the temperature range 298 - 2500°K.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The adopted Tm and ΔHm° were determined by J. W. Johnson and M. A. Bredig, J. Phys. Chem. **62**, 604 (1958), and A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960), respectively.

Heats of melting of 6.2 kcal/mol from phase diagram studies and 6.7 kcal/mol from calorimetric measurements were obtained by E. Aukrust, B. Bjorge, H. Flood, and T. Forland, Annals of the New York Academy of Sciences **79**, Art. 11, 830 (1960).

Vaporization Data.

The boiling point, Tb = 1671°K, is calculated as the temperature at which the sum of the partial pressures of KBr(g) and K₂Br₂(g) over KBr(l) equals one atmosphere. The value of ΔHv° is calculated as the heat required to produce one mole of vapor mixture, which contains 19.5% dimer (K₂Br₂) and 80.5% monomer (KBr).

Tb was reported to be 1648 and 1668°K by H. von Wartenberg and P. Albrecht, Z. Elektrochem. **27**, 162 (1921), and O. Ruff and S. Mugdan, Z. Anorg. Chem. **117**, 147 (1921), respectively.

Potassium Bromide (KBr)

POTASSIUM BROMIDE (KBr)

(IDEAL GAS)

OPW = 119.011

(Ideal Gas) GFW = 119.011

Ground State Configuration 1^1S $\Delta H_f^\circ = -40.83 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^\circ = -40.83 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^\circ = -43.04 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^\circ = -43.04 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$w = 218.47 \text{ cm}^{-1}$
 $w_e = 0.7533 \text{ cm}^{-1}$
 $\nu_e = 0.000401 \text{ cm}^{-1}$
 $\nu_e = 2.821 \text{ Å}$

Heat of Formation

The heat of formation is derived from the sublimation and vaporization data analyzed below. Numerous investigators have obtained total pressures by static methods or "apparent" pressures by effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see $K_2\text{Br}_2(\text{g})$ table] which are consistent with the dimer-monomer equilibrium data of Hagemark et al.(6). Second and third law analyses of the monomer pressures show remarkable consistency over temperatures from 637 to 1668 K. The selected value of $\Delta H_f^\circ = -43.0 \pm 0.5 \text{ kcal/mol}$ may be compared with -43.8 kcal/mol derived from $D_0 = 3.95 \text{ eV}$ which is reported by Gaydon(14) based on atomic fluorescence data.

Investigator	Reaction	Temperature, °K	No. of Points	ΔH_f° , kcal/mol	Drift	ΔH_f° , kcal/mol
1. Wartenberg-Albrecht	(A)	1366-15-1654-15	14	48.28±0.31	46.70	-1.140-2
2. Ruff-Mugdan	"	1361-15-1668-15	10	49.06±0.56	47.16	-1.440-4
3. Flock-Rodebush	"	1179-15-1335-75	10	47.80±0.05	46.95	-0.740-1
4. Hintz-Jellinek	"	1523-15	1	-	47.34	-
5. Murgulescu-Marta	"	1373-15-1473-15	5	46.20±1.15	47.69	1-140-8
6. Hagemark et al.	"	1158-95-1416-02	26	47.15±0.49	46.94	-0.240-4
7. Nilsa	(B)	823-15-923-15	6	48.04±0.51	51.67	4-110-6
8. Mayer-Mintner	"	884.90-929.40	6	56.15±3.17	51.49	-5.23-5
9. Zimm-Mayer	"	636.94-900.09	15	50.71±0.21	50.58	-0.140-2

*Based on the third law ΔH_f° value. (A) $KBr(1) = KBr(g)$, (B) $KBr(c) = KBr(g)$.

Heat Capacity and Entropy

Rusk and Gordy(10) have investigated the pure rotational spectra of KBr in the 1.5 to 5.0 mm range of the microwave region by millimeter wave molecular beam spectroscopy. The reported values of w , w_e , ν_e and ν_e are adopted here and corrected to the average isotopic species. The value of a_g is obtained from Fabricand et al.(11). Molecular constants for $KBr(g)$ have also been reported by Herzberg(12) and Rice and Klemperer(13). They are in good agreement with the values adopted. Herzberg(12) also lists an A state at 31770 cm^{-1} based on observed electronic spectra. The moment of inertia is $3.4604 \times 10^{-38} \text{ g cm}^2$.

References

1. H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921).
2. O. Ruff and S. Mugdan, Z. Anorg. Chem. 117, 147 (1921).
3. E. P. Flock and W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).
4. H. Hintz and K. Jellinek, Z. Elektrochem. 42, 187 (1936).
5. I. G. Murgulescu and L. Marta, Rev. Roumaine chim. 11, 457 (1966). The authors adopted total vapor pressures reported by Wartenberg and Albrecht, loc. cit., for the evaluation of the partial pressures of $KBr(g)$ and $K_2Br_2(g)$. We use the KBr partial pressures derived from JANAF table thermodynamic functions for evaluation.
6. K. I. Hagemark, M. Elander and E. B. Luchinsinger, J. Phys. Chem. 70, 276 (1966), and K. I. Hagemark, private communication, 3M Company, St. Paul, Minnesota, Feb. 6, 1967.
7. K. Nilsa, "Vapor Pressures of Alkali-Halides," J. Fac. Sci., Hokkaido Imperial Univ., Ser. III, 2, 201 (1938).
8. J. E. Mayer and I. H. Wintner, J. Chem. Phys. 5, 301 (1938).
9. B. H. Zimm and J. E. Mayer, J. Chem. Phys. 12, 362 (1944).
10. J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).
11. P. B. Fabricand, R. O. Carlson, C. A. Lee, and I. I. Rabi, Phys. Rev. 91, 1403 (1953).
12. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, 1950.
13. S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957).
14. A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

Dec. 31, 1961, Mar. 31, 1967

Lithium Bromide (LiBr)

(Crystal)

GFW = 86.848

T, °K	Cp	gibbs/mol S	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
298	11.692	17.700	17.700	0.000	-83.870	-81.650	59.851
300	11.710	17.772	17.700	0.022	-83.876	-81.636	59.472
400	12.245	21.216	18.166	1.220	-87.419	-80.155	43.795
500	12.770	24.003	19.063	2.470	-88.028	-78.279	34.216
600	13.405	26.385	20.089	3.777	-87.876	-76.342	27.607
700	14.038	28.385	21.149	5.149	-87.443	-74.443	22.643
800	14.605	30.093	22.189	6.643	-87.299	-72.573	19.629
900	15.165	31.565	23.117	8.233	-86.846	-70.759	17.183
1000	15.660	32.827	24.221	9.906	-86.315	-68.998	15.080
1100	17.580	35.778	25.197	11.659	-85.721	-67.295	13.370
1200	18.250	38.280	26.061	13.522	-84.907	-64.055	10.760
1300	18.770	40.139	27.067	15.232	-83.707	-62.516	9.759
1400	19.470	41.418	28.003	17.069	-82.990	-61.028	8.892
1500	19.600	42.022	29.029	20.788	-82.261	-59.587	8.139
1600	19.590	42.820	30.047	24.556	-81.568	-58.179	7.420
1700	19.780	43.829	31.098	28.516	-80.848	-56.848	6.801
1800	19.810	45.845	31.942	26.415	-114.721	-49.942	5.745
1900	18.620	46.810	32.661	28.257	-113.794	-46.558	5.088

BrLi

LITHIUM BROMIDE (LiBr)

(CRYSTAL)

GFW = 86.848

ΔHf° = Unknown

ΔHf°_{298.15} = -83.87 ± 0.1 kcal/mol

ΔHm° = 4.22 kcal/mol

S°_{298.15} = [17.7] gibbs/mol

Tm = 823°K

Heat of Formation.

The heat of formation, ΔHf°₂₉₈ (LiBr, c) = -83.87 kcal/mol, was calculated from the heat of solution of lithium bromide (c) at infinite dilution and the ionic heats of formation of Li⁺(∞H₂O) and Br⁻(∞H₂O).

V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-NS-2, April 1, 1955, reviewed the heat of solution data in the literature and gave the "best" value, ΔHso = -11.670 ± 50 cal/mol for LiBr(c) → LiBr(∞H₂O) at 298.15°K. The ionic heat of formation, ΔHf°₂₉₈ (Li⁺·∞H₂O) = -66.49 kcal/mol, was calculated from ΔHf°₂₉₈ (LiOH·∞H₂O) = -121.46 kcal/mol (see JANAP LIOH(c) table, Mar. 31, 1958) with ΔHf°₂₉₈ (OH⁻·∞H₂O) = -54.97 kcal/mol from NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Oct. 1, 1955. The value ΔHf°₂₉₈ (Br⁻·∞H₂O) = -29.05 kcal/mol was also obtained from NBS Technical Note 270-1. Combination of the ionic heats of formation of Li⁺(∞H₂O) and Br⁻(∞H₂O) gives the heat of formation of LiBr(∞H₂O), ΔHf°₂₉₈ = -85.54 kcal/mol.

Heat Capacity and Entropy.

A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has measured the enthalpy changes by the drop method (723-883°K), yielding H₂₉₈-H₂₉₈ = 7.0 kcal/mol for the crystal at the melting point. Heat capacities derived from his data were Cp 773° = 15.1 and Cp 853° = 15.6 gibbs/mol for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of LiCl(c), NaCl(c) and NaBr(c).

The entropy, S°_{298.15} = 17.7 eu, was estimated by adding the entropy difference between NaBr(c) and NaCl(c) to the entropy of lithium chloride (c) at 298.15°K. Comparisons with other alkali halides give results within ± 0.5 eu of this value. K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) and 592 (1961), has estimated the heat capacities (Cp = 11.50 + 3.02 × 10⁻⁵T gibbs/mol) and the entropy (S°₂₉₈ = 16.0 ± 0.5 eu)

Melting Data.

The selected heat of fusion (ΔHf°₂₉₈ = 4.22 kcal/mol) was obtained from enthalpy measurements in a drop calorimeter by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

K. K. Kelley, U. S. Bur. Mines Bull. 393 (1936), reviewed some phase diagram studies of the lithium bromide system in the literature, and gave the heat of fusion ΔHf°₂₉₈ = 2.30 kcal/mol. M. Blanc, Compt. rend. 246, 570 (1958), reported the heat of fusion ΔHf°₂₉₈ = 3.095 kcal/mol by a cryoscopic method. Both values are too low.

BrLi

T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
100							
200							
298							
300	15.600	20.220	20.220	0.000	- 80.839	- 79.370	98.180
400	15.600	20.316	20.220	0.029	- 80.838	- 79.161	97.614
500	15.600	24.804	20.632	1.389	- 84.019	- 78.190	42.721
600	15.600	26.285	21.086	3.149	- 84.318	- 76.710	33.530
700	15.600	31.230	23.281	4.709	- 83.015	- 75.226	27.401
800	15.600	34.617	24.811	7.679	- 82.082	- 73.811	22.954
900	15.600	37.455	27.023	10.380	- 82.062	- 71.153	19.078
1000	15.600	39.098	28.130	10.949	- 82.242	- 69.896	15.276
1100	15.600	40.585	29.214	12.509	- 81.821	- 68.682	13.646
1200	15.600	41.958	30.269	14.069	- 81.399	- 67.519	12.117
1300	15.600	43.191	31.169	15.629	- 80.979	- 66.365	11.117
1400	15.600	44.347	32.070	17.189	- 80.557	- 65.237	10.187
1500	15.600	45.424	32.924	18.749	- 80.134	- 64.180	9.351
1600	15.600	46.421	33.737	20.309	- 79.710	- 63.100	8.614
1700	15.600	47.376	34.512	21.869	- 79.287	- 62.000	7.970
1800	15.600	48.268	35.252	23.429	- 78.864	- 60.880	7.418
1900	15.600	49.111	35.959	24.989	- 78.441	- 59.743	6.948
2000	15.600	49.912	36.637	26.549	- 78.018	- 58.580	6.552
2100	15.600	50.673	37.288	28.109	- 77.595	- 57.400	6.228
2200	15.600	51.398	37.913	29.669	- 77.172	- 56.210	5.972
2300	15.600	52.092	38.514	31.229	- 76.749	- 55.010	5.782
2400	15.600	52.756	39.094	32.789	- 76.326	- 53.800	5.652
2500	15.600	53.393	39.653	34.349	- 75.903	- 52.590	5.582
2600	15.600	54.004	40.193	35.909	- 75.480	- 51.380	5.570
2700	15.600	54.593	40.716	37.469	- 75.057	- 50.170	5.620
2800	15.600	55.161	41.222	39.029	- 74.634	- 48.960	5.730
2900	15.600	55.708	41.712	40.589	- 74.211	- 47.750	5.890
3000	15.600	56.237	42.187	42.149	- 73.788	- 46.540	6.100

$S_{298.15}^{\circ} = [20.220] \text{ gibbs/mol}$
 $T_m = 823^{\circ}\text{K}$
 $T_b(\text{to equilibrium mixture}) = 1562^{\circ}\text{K}$
 $T_b(\text{to monomer only}) = [1611]^{\circ}\text{K}$

$\Delta H_{298.15}^{\circ} = -80.839 \text{ kcal/mol}$
 $\Delta H_m^{\circ} = -4.22 \text{ kcal/mol}$
 $\Delta H^{\circ}(\text{to equilibrium mixture}) = 25.6 \text{ kcal/mol}$
 $\Delta H^{\circ}(\text{to monomer only}) = [35.2] \text{ kcal/mol}$

Heat of Formation.
 The heat of formation was calculated from that of the crystal by adding the heat of fusion and the difference between H_{823}° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy.
 A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1964, has derived the heat capacity ($C_p = 15.6 \text{ gibbs/mol}$) from enthalpy measurements ($823^{\circ} - 893^{\circ}\text{K}$) by the drop method. The liquid heat capacity was assumed to be a constant, 15.6 gibbs/mol . The entropy ($S_{298}^{\circ} = 20.220 \text{ eu}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.
 See LiBr(c) table for detail.

Vaporization Data.
 $T_b(\text{to monomer only})$ is taken as the temperature at which the calculated Gibbs energy change is zero for $\text{LiBr(l)} \rightarrow \text{LiBr(g)}$, while $\Delta H_v^{\circ}(\text{to monomer only})$ is the corresponding heat of reaction.

$T_b(\text{to equilibrium mixture})$ is taken as the temperature at which the sum of the calculated partial vapor pressures of LiBr(g) and $\text{Li}_2\text{Br}_2(\text{g})$ reaches one atmosphere (trimer and higher polymers have been neglected in calculation). This value (1562°K) is in good agreement with the boiling point of 1583°K obtained from total vapor pressure measurements by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 588 (1921), and also the boiling point of 1558°K by O. Ruff and S. Migdan, Z. anorg. Chem. 117, 147 (1921). $\Delta H_v^{\circ}(\text{to equilibrium mixture})$ at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 29.23 mole percent of dimer. For detailed information see LiBr(g) and $\text{Li}_2\text{Br}_2(\text{g})$ table.

Lithium Bromide (LiBr)

(Ideal Gas)

GFW = 86.848

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	kcal/mol ΔH°	ΔG°	Log Kp
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	7.002	45.454	∞.000	2.193	34.959	34.959	∞.000
200	7.575	50.460	54.319	1.498	34.716	34.716	84.015
298	8.115	53.593	53.593	.772	35.016	42.070	45.972
300	8.122	53.643	53.593	.845	35.016	45.281	33.192
400	8.446	56.028	53.016	.845	36.812	45.334	33.026
500	8.637	57.935	54.515	1.700	40.724	47.385	29.890
600	8.758	59.321	55.238	2.570	42.015	50.381	18.344
700	8.830	60.403	56.249	3.458	42.781	51.732	16.151
800	8.878	61.244	57.000	4.346	43.024	52.137	15.595
900	8.911	61.884	57.503	5.230	43.024	52.517	15.047
1000	8.930	62.359	57.832	6.127	43.024	52.860	14.500
1100	8.938	62.718	58.029	7.028	43.262	53.169	14.000
1200	8.938	62.998	58.131	7.928	43.430	53.430	13.500
1300	8.938	63.200	58.154	8.828	43.530	53.650	13.000
1400	8.938	63.330	58.154	9.728	43.590	53.830	12.500
1500	8.938	63.400	58.154	10.628	43.610	53.970	12.000
1600	8.938	63.420	58.154	11.528	43.610	54.080	11.500
1700	8.938	63.420	58.154	12.428	43.610	54.160	11.000
1800	8.938	63.420	58.154	13.328	43.610	54.220	10.500
1900	8.938	63.420	58.154	14.228	43.610	54.260	10.000
2000	8.938	63.420	58.154	15.128	43.610	54.280	9.500
2100	8.938	63.420	58.154	16.028	43.610	54.280	9.000
2200	8.938	63.420	58.154	16.928	43.610	54.260	8.500
2300	8.938	63.420	58.154	17.828	43.610	54.220	8.000
2400	8.938	63.420	58.154	18.728	43.610	54.160	7.500
2500	8.938	63.420	58.154	19.628	43.610	54.080	7.000
2600	8.938	63.420	58.154	20.528	43.610	54.000	6.500
2700	8.938	63.420	58.154	21.428	43.610	53.900	6.000
2800	8.938	63.420	58.154	22.328	43.610	53.780	5.500
2900	8.938	63.420	58.154	23.228	43.610	53.640	5.000
3000	8.938	63.420	58.154	24.128	43.610	53.480	4.500
3100	8.938	63.420	58.154	25.028	43.610	53.300	4.000
3200	8.938	63.420	58.154	25.928	43.610	53.100	3.500
3300	8.938	63.420	58.154	26.828	43.610	52.880	3.000
3400	8.938	63.420	58.154	27.728	43.610	52.640	2.500
3500	8.938	63.420	58.154	28.628	43.610	52.380	2.000
3600	8.938	63.420	58.154	29.528	43.610	52.100	1.500
3700	8.938	63.420	58.154	30.428	43.610	51.800	1.000
3800	8.938	63.420	58.154	31.328	43.610	51.480	.500
3900	8.938	63.420	58.154	32.228	43.610	51.140	.000
4000	8.938	63.420	58.154	33.128	43.610	50.780	.000
4100	8.938	63.420	58.154	34.028	43.610	50.400	.000
4200	8.938	63.420	58.154	34.928	43.610	50.000	.000
4300	8.938	63.420	58.154	35.828	43.610	49.580	.000
4400	8.938	63.420	58.154	36.728	43.610	49.140	.000
4500	8.938	63.420	58.154	37.628	43.610	48.680	.000
4600	8.938	63.420	58.154	38.528	43.610	48.200	.000
4700	8.938	63.420	58.154	39.428	43.610	47.700	.000
4800	8.938	63.420	58.154	40.328	43.610	47.180	.000
4900	8.938	63.420	58.154	41.228	43.610	46.640	.000
5000	8.938	63.420	58.154	42.128	43.610	46.080	.000
5100	8.938	63.420	58.154	43.028	43.610	45.500	.000
5200	8.938	63.420	58.154	43.928	43.610	44.900	.000
5300	8.938	63.420	58.154	44.828	43.610	44.280	.000
5400	8.938	63.420	58.154	45.728	43.610	43.640	.000
5500	8.938	63.420	58.154	46.628	43.610	42.980	.000
5600	8.938	63.420	58.154	47.528	43.610	42.300	.000
5700	8.938	63.420	58.154	48.428	43.610	41.600	.000
5800	8.938	63.420	58.154	49.328	43.610	40.880	.000
5900	8.938	63.420	58.154	50.228	43.610	40.140	.000
6000	8.938	63.420	58.154	51.128	43.610	39.380	.000

Sept. 30, 1961; June 30, 1966

LITHIUM BROMIDE (LiBr)

(IDEAL GAS)

GFW = 86.848

Ground State Configuration 1Σ

S^{298.15} = 53.593 gibbs/molΔH_f⁰ = -35.0 ± 3 kcal/molΔH_f^{298.15} = -36.8 ± 3 kcal/mol

Electronic Levels and Quantum Weights

ε, cm ⁻¹	g _i
0	1

σ = 1

ω_ex_e = 3.53 cm⁻¹ω_e = 563.16 cm⁻¹B_e = 0.56112 cm⁻¹r_e = 2.1704 Å

Heat of Formation.

The heat of formation (ΔH_f²⁹⁸ (LiBr, g) = -36.8 ± 3 kcal/mol) was calculated from the selected heat of vaporization and the heat of formation for lithium bromide (1). Lithium bromide vaporizes to a mixture of monomeric and dimeric gases. (Higher polymers have been neglected in the calculation.) The heats of vaporization to monomer and to dimer were chosen to satisfy (1) the total vapor pressure data measured by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921), and O. Ruff and S. Mugdan, Z. anorg. Chem. 117, 147 (1921); (2) the partial vapor pressures of monomer and dimer derived from R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956), 28, 881 (1958), in an analysis of the velocity distribution of molecules in alkali halide vapor. The selected heats of vaporization are ΔH_v²⁹⁸ (to monomer) = 44.0 ± 3 kcal/mol and ΔH_v²⁹⁸ (to dimer) = 42.0 ± 5 kcal/mol which combine with the heat of formation of lithium bromide (1) (ΔH_f²⁹⁸ = -80.64 kcal/mol) to give the standard heats of formation of LiBr(g) and Li₂Br₂(g) = -36.8 and -119.7 kcal/mol, respectively. The derived heat of dissociation is ΔH_d²⁹⁸ = 46.0 kcal/mol for Li₂Br₂(g) → 2LiBr(g).

J. Berkowitz, H. A. Tiesman and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962), have measured mass-spectrometrically the heat of dissociation ΔH_d⁸⁵⁰ = 45.9 kcal/mol (ΔH_d²⁹⁸ = 46.9 kcal/mol) for Li₂Br₂(g) → 2LiBr(g) in a double oven apparatus by the second law method. D. L. Hildenbrand, L. P. Theard, W. F. Hall and N. D. Potter, Philco Report U-2289, under Contract N061-0905-C, Sept. 15, 1963, have determined mass-spectrometrically the heats of sublimation of lithium bromide by the second law method as ΔH_s⁰ (to monomer) = 46.9 and ΔH_s⁷⁴⁰ (to dimer) = 45.0 kcal/mol (equivalent to ΔH_v²⁹⁸ (to monomer) = 45.82 kcal/mol and ΔH_v²⁹⁸ (to dimer) = 41.93 kcal/mol). These values are in reasonable agreement with those selected in the tabulation.

Heat Capacity and Entropy.

The bond distance (r_e) was obtained from the microwave studies by A. Honig, M. Mandel, M. L. Stich and C. H. Townes, Phys. Rev. 95, 829 (1954). The vibrational constants (ω_e and ω_ex_e) were determined from the infrared spectrum by W. Klempner, W. G. Norris, A. Blicher, and A. G. Emile, J. Chem. Phys. 33, 1534 (1960). The rotational constants which have been corrected to the average isotopic species were obtained by A. J. Herbert, P. W. Breivogel, Jr., and K. Street, Jr., J. Chem. Phys. 41, 2368 (1964), using microwave spectra. Their data are in good agreement with those reported by Honig et al., loc. cit., and J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by R. L. Wilkins, J. Chem. Eng. Data 5, 337 (1960), who used slightly different molecular constants.

BrLi

T, °K	C _p ^o	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	4.000	INFINITE	INFINITE	2.489	-	-	INFINITE
100	7.224	49.893	65.740	11.589	-	11.104	52.926
200	8.104	55.157	59.269	.418	-	19.163	20.961
298	8.517	58.481	58.481	.000	-	22.682	16.627
300	8.522	58.554	58.481	.016	-	22.762	16.568
400	8.715	61.401	58.481	.079	-	25.403	13.770
500	8.820	62.472	59.460	1.746	-	27.259	11.915
600	8.884	64.506	60.184	2.641	-	29.273	10.663
700	8.922	65.913	60.723	3.422	-	31.475	9.455
800	8.946	67.211	62.425	4.222	-	33.868	8.319
900	8.964	68.415	64.295	5.324	-	35.489	7.269
1000	9.011	69.415	65.495	6.224	-	36.769	6.314
1100	9.031	70.415	67.540	7.126	-	38.359	5.461
1200	9.049	71.415	69.540	8.028	-	40.191	4.711
1300	9.062	72.415	71.540	8.930	-	42.165	4.069
1400	9.071	73.415	73.540	9.832	-	44.284	3.526
1500	9.079	74.415	75.540	10.734	-	46.548	3.084
1600	9.104	75.415	77.540	11.636	-	48.964	2.741
1700	9.127	76.415	79.540	12.538	-	51.532	2.485
1800	9.147	77.415	81.540	13.440	-	54.254	2.298
1900	9.164	78.415	83.540	14.342	-	57.130	2.161
2000	9.180	79.415	85.540	15.244	-	60.162	2.063
2100	9.195	80.415	87.540	16.146	-	63.350	1.994
2200	9.209	81.415	89.540	17.048	-	66.694	1.944
2300	9.222	82.415	91.540	17.950	-	70.194	1.904
2400	9.234	83.415	93.540	18.852	-	73.848	1.874
2500	9.245	84.415	95.540	19.754	-	77.656	1.844
2600	9.256	85.415	97.540	20.656	-	81.618	1.814
2700	9.266	86.415	99.540	21.558	-	85.734	1.784
2800	9.275	87.415	101.540	22.460	-	90.004	1.754
2900	9.284	88.415	103.540	23.362	-	94.428	1.724
3000	9.292	89.415	105.540	24.264	-	99.006	1.694
3100	9.301	90.415	107.540	25.166	-	103.738	1.664
3200	9.314	91.415	109.540	26.068	-	108.624	1.634
3300	9.328	92.415	111.540	26.970	-	113.664	1.604
3400	9.342	93.415	113.540	27.872	-	118.858	1.574
3500	9.356	94.415	115.540	28.774	-	124.206	1.544
3600	9.371	95.415	117.540	29.676	-	129.708	1.514
3700	9.386	96.415	119.540	30.578	-	135.364	1.484
3800	9.402	97.415	121.540	31.480	-	141.174	1.454
3900	9.419	98.415	123.540	32.382	-	147.138	1.424
4000	9.436	99.415	125.540	33.284	-	153.256	1.394
4100	9.454	100.415	127.540	34.186	-	159.528	1.364
4200	9.471	101.415	129.540	35.088	-	165.954	1.334
4300	9.489	102.415	131.540	35.990	-	172.534	1.304
4400	9.514	103.415	133.540	36.892	-	179.268	1.274
4500	9.535	104.415	135.540	37.794	-	186.158	1.244
4600	9.558	105.415	137.540	38.696	-	193.204	1.214
4700	9.581	106.415	139.540	39.598	-	200.406	1.184
4800	9.606	107.415	141.540	40.500	-	207.764	1.154
4900	9.631	108.415	143.540	41.402	-	215.278	1.124
5000	9.658	109.415	145.540	42.304	-	222.948	1.094
5100	9.685	110.415	147.540	43.206	-	230.774	1.064
5200	9.714	111.415	149.540	44.108	-	238.758	1.034
5300	9.743	112.415	151.540	45.010	-	246.898	1.004
5400	9.774	113.415	153.540	45.912	-	255.194	0.974
5500	9.805	114.415	155.540	46.814	-	263.646	0.944
5600	9.838	115.415	157.540	47.716	-	272.254	0.914
5700	9.871	116.415	159.540	48.618	-	281.018	0.884
5800	9.905	117.415	161.540	49.520	-	290.038	0.854
5900	9.941	118.415	163.540	50.422	-	299.314	0.824
6000	9.977	119.415	165.540	51.324	-	308.846	0.794

Ground State Configuration 2Σ
 $S_{298.15}^{\circ} = 58.481 \pm 0.5$ gibbs/mol
 $\Delta H_f^{\circ} = -11$ kcal/mol
 $\Delta H_f^{\circ} = -13 \pm 7$ kcal/mol

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	g_1
0	2
25800	4
39200	4

$\omega_e = 373.8$ cm⁻¹
 $\omega_e x_e = 1.34$ cm⁻¹
 $B_e = [0.165182]$ cm⁻¹
 $\alpha_e = [0.000809]$ cm⁻¹
 $\sigma^{\circ} = 1$
 $r_e = [2.34] \text{ \AA}$

Heat of Formation.

The heat of formation was calculated from that of $MgBr_2(g)$ using the relation $D(MgBr)/\Delta H_{atom}(MgBr_2) = 0.46 \pm 0.04$ which has been shown to apply to several dihalides. This results in $\Delta H_f^{\circ} = -13 \pm 7$ and $D_0 = 74.4 \pm 7$ kcal/mol. The selected value is in good agreement with D_0 of 77 kcal/mol obtained from predissociation by G. Herzberg, "Spectra of Diatomic Molecules," second edition, D. van Nostrand Co., Inc., New York, 1950, and with the linear Birge-Sponner extrapolation of $D_0 = 74$ kcal/mol given by A. G. Gaydon, "Dissociation Energies," second edition, Chapman and Hall Ltd, London, 1953. Gaydon's selected value of $D_0 = 88 \pm 23$ kcal/mol was discounted since it would require the unlikely ratio $D(MgBr)/\Delta H_{atom}(MgBr_2) = 0.28$.

Heat Capacity and Entropy.

The molecular constants ω_e , $\omega_e x_e$ and ground state configuration (2Σ) were taken from G. Herzberg, loc. cit., while α_e was calculated from the above constants. The bond distance was estimated to be the same as in $MgBr_2(g)$.

Nitrogen Monobromide (NBr)

(Ideal Gas) Mol. Wt. = 93.924

BrN

MOL. WT. = 93.924

(IDEAL GAS)

NITROGEN MONOBROMIDE (NBr)

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-	2.148	73.700	73.700	INFINITE
100	6.967	48.233	52.815	1.145	73.111	73.111	-1.753
200	7.310	53.240	56.956	-	73.492	68.232	-3.560
298	7.819	56.256	56.256	+0.00	71.883	67.357	-49.372
300	7.828	56.305	56.256	+0.14	71.874	67.329	-49.047
400	8.433	65.641	56.568	+8.11	68.209	66.563	-36.370
500	8.830	68.627	57.168	1.649	66.248	66.154	-28.914
600	8.981	62.018	57.851	2.500	68.299	65.731	-23.941
700	8.683	63.349	58.544	3.364	68.352	65.298	-20.386
800	8.755	64.514	59.219	4.236	68.404	64.858	-17.718
900	8.789	65.581	60.000	5.119	68.456	64.410	-15.634
1000	8.819	66.478	60.881	5.997	68.500	63.960	-13.978
1100	8.881	67.323	61.065	6.884	68.542	63.504	-12.616
1200	8.967	68.097	61.619	7.773	68.579	63.045	-11.481
1300	8.959	68.811	62.146	8.665	68.613	62.582	-10.521
1400	8.964	69.481	62.646	9.559	68.643	62.117	-9.696
1500	8.964	70.091	63.122	10.454	68.670	61.649	-8.982
1600	8.979	70.670	63.575	11.352	68.695	61.181	-8.357
1700	8.992	71.215	64.009	12.250	68.717	60.711	-7.805
1800	9.004	71.729	64.424	13.150	68.737	60.239	-7.314
1900	9.016	72.216	64.821	14.051	68.755	59.768	-6.875
2000	9.026	72.679	65.203	14.953	68.771	59.293	-6.479
2100	9.036	73.120	65.569	15.856	68.787	58.819	-6.121
2200	9.045	73.540	65.922	16.760	68.800	58.344	-5.786
2300	9.054	73.943	66.262	17.665	68.812	57.868	-5.468
2400	9.062	74.331	66.593	18.571	68.823	57.393	-5.166
2500	9.071	74.698	66.907	19.478	68.833	56.910	-4.875
2600	9.079	75.054	67.214	20.385	68.842	56.439	-4.744
2700	9.087	75.397	67.510	21.293	68.850	55.962	-4.530
2800	9.095	75.728	67.798	22.203	68.857	55.484	-4.331
2900	9.103	76.047	68.077	23.112	68.864	55.007	-4.145
3000	9.110	76.356	68.346	24.023	68.871	54.529	-3.972
3100	9.117	76.654	68.611	24.934	68.876	54.051	-3.810
3200	9.124	76.944	68.867	25.846	68.881	53.572	-3.659
3300	9.132	77.225	69.116	26.759	68.885	53.093	-3.516
3400	9.139	77.497	69.362	27.673	68.889	52.615	-3.382
3500	9.146	77.763	69.595	28.587	68.892	52.136	-3.255
3600	9.152	78.020	69.825	29.502	68.895	51.657	-3.136
3700	9.159	78.271	70.050	30.417	68.898	51.178	-3.023
3800	9.166	78.515	70.270	31.334	68.900	50.700	-2.916
3900	9.173	78.754	70.484	32.251	68.902	50.222	-2.814
4000	9.180	78.986	70.694	33.168	68.903	49.741	-2.718
4100	9.186	79.213	70.899	34.087	68.904	49.262	-2.626
4200	9.193	79.434	71.099	35.006	68.904	48.783	-2.538
4300	9.199	79.651	71.296	35.925	68.905	48.305	-2.455
4400	9.206	79.864	71.490	36.845	68.906	47.826	-2.375
4500	9.213	80.069	71.677	37.766	68.904	47.346	-2.299
4600	9.219	80.272	71.861	38.688	68.903	46.869	-2.227
4700	9.226	80.470	72.042	39.610	68.903	46.390	-2.157
4800	9.232	80.664	72.220	40.533	68.901	45.910	-2.090
4900	9.238	80.854	72.397	41.457	68.899	45.430	-2.026
5000	9.245	81.041	72.575	42.381	68.897	44.953	-1.965
5100	9.251	81.225	72.753	43.306	68.895	44.471	-1.906
5200	9.258	81.404	72.928	44.231	68.893	43.994	-1.849
5300	9.264	81.579	73.100	45.157	68.890	43.515	-1.794
5400	9.270	81.751	73.266	46.084	68.886	43.035	-1.742
5500	9.277	81.924	73.517	47.011	68.883	42.550	-1.691
5600	9.283	82.091	73.531	47.939	68.879	42.070	-1.642
5700	9.290	82.256	73.682	48.868	68.874	41.602	-1.595
5800	9.296	82.417	73.832	49.797	68.870	41.125	-1.550
5900	9.302	82.576	73.978	50.726	68.865	40.644	-1.505
6000	9.308	82.733	74.123	51.656	68.860	40.164	-1.463

December 31, 1962

ΔH_f^o 0 = 73.7 ± 5 kcal. mole⁻¹
 ΔH_f^o 298.15 = 71.9 ± 5 kcal. mole⁻¹
 S_{298.15} = 56.25 ± 0.1 cal. deg.⁻¹ mole⁻¹
 Ground State Configuration 3Σ⁻

Electronic Level and Multiplicity

Σ, cm. ⁻¹	g _i
0	3

ω_e x_e = 4.7 cm.⁻¹

σ = 1

x_e = 1.79 Å

ω_e = 0.00399 cm.⁻¹

B_e = 0.443 cm.⁻¹

Heat of Formation.

E. R. V. Miller and H. B. Dunford, J. Chem. Phys. 35, 1202 (1961) have extrapolated the ground state vibrational levels and obtain D₀ = 67 ± 5 kcal. mole⁻¹ or ΔH_f^o 0 = 73.7 ± 5 kcal. mole⁻¹.

Heat Capacity and Entropy.

Miller and Dunford loc. cit. give all the vibrational and rotational constants, which have been adjusted to the normally occurring isotopic mixture for bromine.

BrN

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o) _{298.15} /T	h _f ^o - H _{298.15} ^o	kcal/mol ΔH _f ^o	ΔG ^o	Log K _p
0	-0.000	INFINITE	-2.785	21.848	21.848	INFINITE
100	8.654	54.420	-1.973	20.785	20.785	45.426
200	10.068	61.162	-1.031	21.203	20.071	21.013
298	10.868	65.347	+0.000	20.630	19.699	14.440
300	10.879	65.414	0.020	19.621	19.700	14.351
400	11.274	71.200	2.263	15.911	21.437	10.435
500	11.774	76.014	6.064	15.911	21.431	8.435
600	12.107	79.377	9.408	15.928	22.774	8.295
700	12.388	81.934	12.133	15.954	23.913	7.466
800	12.621	83.681	14.444	15.986	25.047	6.982
900	12.814	84.728	16.422	16.012	26.181	6.642
1000	12.970	85.126	18.067	16.061	27.305	5.967
1100	13.098	85.134	19.428	16.100	28.426	5.648
1200	13.204	84.178	20.444	16.140	29.546	5.361
1300	13.295	82.668	21.166	16.176	30.666	5.100
1400	13.375	80.728	21.803	16.216	31.786	4.860
1500	13.427	78.511	22.356	16.251	32.883	4.791
1600	13.470	76.019	22.715	16.286	33.961	4.664
1700	13.524	73.254	22.937	16.318	35.001	4.512
1800	13.584	70.254	23.026	16.346	36.000	4.340
1900	13.636	67.044	22.989	16.370	37.000	4.201
2000	13.683	63.644	22.910	16.401	38.000	4.106
2100	13.688	59.709	22.274	16.424	39.503	4.111
2200	13.670	55.345	21.639	16.443	40.600	4.053
2300	13.630	50.530	20.910	16.458	41.600	3.997
2400	13.706	45.256	20.128	16.474	42.796	3.897
2500	13.722	42.095	20.596	16.485	43.893	3.837
2600	13.735	42.634	20.122	16.493	44.989	3.762
2700	13.747	43.152	21.606	16.498	46.086	3.750
2800	13.757	43.650	23.090	16.500	47.183	3.737
2900	13.766	44.136	24.574	16.500	48.277	3.698
3000	13.777	44.603	26.058	16.506	49.372	3.597
3100	13.785	45.054	27.542	16.500	50.470	3.558
3200	13.793	45.498	29.026	16.481	51.565	3.522
3300	13.800	45.936	30.510	16.458	52.659	3.485
3400	13.806	46.370	31.994	16.434	53.753	3.445
3500	13.812	46.779	33.478	16.437	54.855	3.425
3600	13.817	47.118	34.962	16.437	55.954	3.397
3700	13.822	47.497	36.446	16.395	57.051	3.370
3800	13.827	47.816	37.930	16.352	58.148	3.343
3900	13.830	48.129	39.414	16.309	59.245	3.320
4000	13.834	48.515	40.898	16.315	60.349	3.297
4100	13.838	48.917	42.382	16.284	61.450	3.276
4200	13.841	49.320	43.866	16.241	62.551	3.255
4300	13.844	49.725	45.350	16.198	63.652	3.235
4400	13.847	49.894	46.834	16.179	64.761	3.217
4500	13.850	100.204	50.356	16.140	65.867	3.160
4600	13.853	100.510	57.741	16.099	66.973	3.182
4700	13.856	100.816	65.126	16.058	68.079	3.150
4800	13.857	101.099	72.511	16.017	69.185	3.150
4900	13.859	101.385	80.893	15.966	70.292	3.135
5000	13.861	101.665	89.008	15.919	71.404	3.121
5100	13.863	101.946	97.029	15.869	72.509	3.107
5200	13.865	102.220	105.050	15.818	73.614	3.092
5300	13.867	102.473	113.071	15.767	74.737	3.082
5400	13.868	102.712	121.092	15.713	75.867	3.070
5500	13.870	102.987	129.113	15.658	76.964	3.058
5600	13.871	103.237	137.134	15.601	78.075	3.047
5700	13.872	103.482	145.155	15.547	79.186	3.037
5800	13.873	103.723	153.176	15.489	80.317	3.026
5900	13.875	103.961	161.197	15.428	81.428	3.016
6000	13.876	104.194	169.218	15.362	82.547	3.007

Mar. 31, 1962; Dec. 31, 1966

Point Group C_s
S_{298.15} = 85.35 gibbs/mol
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹
1801 (1)
542 (1)
[265] (1)

N-Br = 2.14 ± 0.02 Å
Bond Angle: O-N-Br = 117 ± 3°
Product of the Moments of Inertia: I_AI_BI_C = 5.1631 × 10⁻¹¹⁵ g³ cm⁶

Heat of Formation.

The chemical equilibrium of the reaction 2NO(g) + Br₂(g) = 2NOBr(g) has been studied by Trautz and Dala¹, Blair, Bross and Yost², and Kraus³, respectively. Using the reported equilibrium constants, the enthalpy changes (ΔH_{298.15}) of this reaction are evaluated by both the second and third law methods. Based on the third law ΔH_{298.15} values, the heats of formation for NOBr(g) are derived. The results obtained are presented in the table below. The value of ΔH_{298.15} (NOBr-g) adopted is 19.63 ± 0.2 kcal/mol.

Investigator	No. of Points	Temperature, °K	Second Law Value	Third Law Value	Drift	ΔH _{298.15} kcal/mol
1. Trautz and Dala ¹	*	258.2 - 603.2	-11.11	-11.30	-0.4	19.62
2. Blair et al.	50	296.9 - 502.9	-11.74 ± 0.07	-11.26	1.3 ± 0.2	19.64
3. Kraus	23	264.0 - 290.1	-13.46 ± 0.30	-9.62	-13.7 ± 1.1	20.46

*The data points employed for evaluation are calculated from a given equation.

1. M. Trautz and V. P. Dala, Z. Anorg. Chem. **110**, 1 (1920).
2. C. M. Blair, Jr., P. D. Bross and D. M. Yost, J. Am. Chem. Soc. **56**, 1916 (1934).
3. W. Kraus, Z. Physik. Chem. **A175**, 295 (1936).

Heat Capacity and Entropy.

The molecular structure of NOBr(g) has been determined by electron diffraction by J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **53**, 2029 (1937). The results were confirmed later by T. L. Weatherly and Q. Williams, J. Chem. Phys. **25**, 717 (1956), who studied the microwave spectrum of NOBr(g) in the region 20,000 - 40,000 Mc/sec and analyzed the J = 2-3 transition. The values of bond length and angle adopted are obtained from Ketelaar and Palmer, loc. cit. The infrared absorption spectrum of NOBr(g) has been examined from 400 to 5303 cm⁻¹ by W. O. Burns and H. J. Bernstein, J. Chem. Phys. **18**, 1669 (1950). The authors observed the first two fundamental vibrational frequencies and obtained the third from combination and overtones. These assignments are adopted. The three principal moments of inertia are: I_A = 9.404 × 10⁻⁴⁰, I_B = 2.2965 × 10⁻³⁸ and I_C = 2.5906 × 10⁻³⁸ g cm².

Sodium Bromide (NaBr)

(Crystal) Mol. Wt. = 102.907

T, °K	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	0.000	INFINITE	-	-	2.770	- 84.680	- 84.680	INFINITE
100	8.500	21.420	-	-	1.240	- 84.680	- 84.680	14.491
200	11.590	15.370	-	-	1.176	- 84.680	- 84.680	91.461
298	12.285	20.750	0.000	-	0.000	- 86.380	- 83.476	61.187
300	12.295	20.826	0.023	-	0.023	- 86.386	- 83.477	60.796
400	12.775	25.433	21.739	-	1.278	- 90.595	- 81.693	44.633
500	13.110	27.321	22.176	-	2.573	- 90.482	- 79.479	34.739
600	13.400	28.737	23.240	3.898	-	90.322	- 77.293	28.153
700	13.700	31.825	24.321	5.253	-	90.119	- 75.138	23.458
800	14.000	33.674	25.376	6.638	-	89.877	- 73.014	19.945
900	14.300	35.340	26.392	8.053	-	89.601	- 70.921	17.221
1000	14.500	36.862	27.364	9.498	-	89.286	- 68.861	15.049
1100	14.900	38.268	28.292	10.973	-	88.968	- 66.836	13.278
1200	15.200	39.577	29.179	12.478	-	88.650	- 64.841	11.725
1300	15.500	40.805	30.026	14.013	-	88.332	- 62.877	10.162
1400	15.800	41.965	30.837	15.578	-	88.015	- 60.947	8.629
1500	15.996	43.065	31.617	17.173	-	87.700	- 59.041	7.081
1600	16.400	44.113	32.365	18.798	-	87.387	- 57.162	5.532
1700	16.713	45.117	33.085	20.453	-	87.076	- 55.317	4.006
1800	17.033	46.081	33.781	22.140	-	86.767	- 53.500	2.533
1900	17.362	47.011	34.453	23.860	-	86.460	- 51.713	1.111
2000	17.700	47.910	35.104	25.613	-	86.156	- 49.956	0.000

SODIUM BROMIDE (NaBr),

(CRYSTAL)

MOL. WT. = 102.907

BrNa

$\Delta H_f^0 = -84.68 \pm 0.10 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = -86.38 \pm 0.10 \text{ kcal. mole}^{-1}$
 $\Delta H_m^0 = 6.24 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{298.15} = 51.98 \text{ kcal. mole}^{-1} \text{ to monomer gas}$

$S_{298.15}^0 = 20.75 \pm 0.06 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1020^\circ \text{K.}$

Heat of Formation.

The heat of solution of NaBr(c) in water has been measured by F. A. Askew, E. Bullock, R. T. Smith, R. K. Tinkler, O. Gatty and J. H. Wolfenden, *J. Chem. Soc. 1368* (1934) and W. E. Wallace, *J. Am. Chem. Soc. 71*, 2485 (1949) to be +0.01 and -0.14 kcal. mole⁻¹, respectively. Using $\Delta H_f^{298.15}(\text{Na}^+, \text{aq.}) = -57.39$ and $\Delta H_f^{298.15}(\text{Br}^-, \text{aq.}) = -29.05$ kcal. mole⁻¹, obtained from D. D. Wagman, National Bureau of Standards, private communication, July 2, 1964, the respective value of $\Delta H_f^{298.15}$ for NaBr(c) was found to be -86.5 and -86.45 kcal. mole⁻¹. The adopted value is the average of these two.

Heat Capacity and Entropy.

The low temperature heat capacities (7.21 - 301.63°K.) were measured by T. E. Gardner and A. R. Taylor, Jr., U. S. Bur. Mines RI 6435 (1964). The high temperature enthalpy changes (290 - 645, 290 - 618°K.) were determined by A. Wagner, *Phys. Z. 14*, 5 (1913). Based upon the latter data the high temperature heat capacities were derived. The two sets of C_p data were joined smoothly at 298°K. by graphical method. $S_{298.15}^0$ was obtained from T. E. Gardner and A. R. Taylor, Jr., loc. cit., using $S_{10}^0 = 0.034 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m and ΔH_m^0 were reported by A. S. Dworkin and M. A. Bredig, *J. Phys. Chem. 64*, 269 (1960). The values, $T_m = 1014^\circ \text{K.}$ and $\Delta H_m^0 = 5.52 \text{ kcal. mole}^{-1}$, reported by M. Blanc, *Compt. Rend., 246*, 570 (1958), were not used.

Heat of Sublimation.

The value of ΔH_m^0 at 298.15 was derived from six sets of vapor pressure data by both the second and third law methods. See NaBr(g) table for detail.

SODIUM BROMIDE (NaBr)

(LIQUID)

T, °K.	C _p	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T}$	$\frac{\text{kcal. mole}^{-1}}{H^{\circ} - H_{298}^{\circ}}$	ΔF_f°	Log K _p
0					
100	24.900	24.940	0.000	- 81.105	58.236
200	24.900	24.940	0.000	- 81.105	58.236
298	24.900	24.940	0.000	- 81.105	58.236
300	24.900	24.940	0.000	- 81.105	58.236
400	24.900	24.940	0.000	- 81.105	58.236
500	24.900	24.940	0.000	- 81.105	58.236
600	24.900	24.940	0.000	- 81.105	58.236
700	24.900	24.940	0.000	- 81.105	58.236
800	24.900	24.940	0.000	- 81.105	58.236
900	24.900	24.940	0.000	- 81.105	58.236
1000	24.900	24.940	0.000	- 81.105	58.236
1100	24.900	24.940	0.000	- 81.105	58.236
1200	24.900	24.940	0.000	- 81.105	58.236
1300	24.900	24.940	0.000	- 81.105	58.236
1400	24.900	24.940	0.000	- 81.105	58.236
1500	24.900	24.940	0.000	- 81.105	58.236
1600	24.900	24.940	0.000	- 81.105	58.236
1700	24.900	24.940	0.000	- 81.105	58.236
1800	24.900	24.940	0.000	- 81.105	58.236
1900	24.900	24.940	0.000	- 81.105	58.236
2000	24.900	24.940	0.000	- 81.105	58.236
2100	24.900	24.940	0.000	- 81.105	58.236
2200	24.900	24.940	0.000	- 81.105	58.236
2300	24.900	24.940	0.000	- 81.105	58.236
2400	24.900	24.940	0.000	- 81.105	58.236
2500	24.900	24.940	0.000	- 81.105	58.236

$$S_{298.15}^{\circ} = [24.940] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = [-81.105] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 6.24 \text{ kcal. mole}^{-1}$$

$$T_m = 1020^{\circ} \text{K.}$$

$$\Delta H_v^{\circ} = 38.42 \text{ kcal. mole}^{-1} \text{ to monomer gas}$$

$$T_b = [1720]^{\circ} \text{K. to monomer gas}$$

Heat of Formation.

$\Delta H_f^{\circ} 298.15(1)$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between $H^{\circ} - H_{298.15}^{\circ}$ for crystal and liquid. The equilibrium constant of the reaction $\text{NaBr}(1) + \text{HCl}(g) = \text{NaCl}(1) + \text{HBr}(g)$ has been determined by J. Toguri, H. Flood and T. Forland, Acta Chem. Scand. **17**, 1502 (1963). From the reported data, $\ln K_{900}^{\circ} = -1.19 \pm 0.01$, the heat of reaction ($\Delta H_r^{\circ} 298.15$) was derived to be 2.11 kcal. mole⁻¹. Using $\Delta H_f^{\circ} 298.15$ (HCl, g) = -22.082, $\Delta H_f^{\circ} 298.15$ (NaCl, l) = -92.24 and $\Delta H_f^{\circ} 298.15$ (HBr, g) = -8.70 kcal. mole⁻¹, the value of $\Delta H_f^{\circ} 298.15$ for $\text{NaBr}(1)$ was evaluated to be -81.0 ± 0.5 kcal. mole⁻¹ which is in reasonable agreement with the value adopted. The values of $\Delta H_f^{\circ} 298.15$ for $\text{HCl}(g)$ and $\text{HBr}(g)$ were obtained from D. D. Wagman, National Bureau of Standards, private communication, July 2, 1964.

Heat Capacity and Entropy.

Heat capacity for $\text{NaBr}(1)$ was estimated by comparison with those for $\text{NaCl}(c)$, $\text{AgCl}(c)$ and $\text{AgCl}(l)$. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH_m° were reported by A. S. Dworin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960). The values, $T_m = 1014^{\circ} \text{K.}$ and $\Delta H_m^{\circ} = 5.52 \text{ kcal. mole}^{-1}$, reported by M. Blanc, Compt. Rend., **246**, 570 (1958), were not used.

Vaporization Data.

The boiling point, T_b , was calculated as the temperature at which the value of ΔF_v° becomes zero for the reaction $\text{NaBr}(1) \rightarrow \text{NaBr}(g)$. The difference between ΔH_f° for $\text{NaBr}(l)$ and $\text{NaBr}(g)$ at T_b is the heat of vaporization, ΔH_v° .

Sodium Bromide (NaBr)

(Ideal Gas) Mol. Wt. = 102.907

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(R° H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	7.475	48.724	65.090	-1.637	INFINITE
200	8.395	54.221	58.413	-1.638	78.412
298	8.681	57.628	57.628	-1.639	31.056
300	8.685	57.661	57.628	-1.639	31.145
400	8.833	60.203	57.628	-1.639	30.989
500	8.915	62.183	58.622	-1.639	24.261
600	8.970	63.814	59.356	-1.639	19.084
700	9.010	65.200	60.094	-1.639	17.113
800	9.043	66.405	60.809	-1.639	15.048
900	9.072	67.472	61.491	-1.639	13.049
1000	9.098	68.429	62.138	-1.639	11.289
1100	9.121	69.297	62.750	-1.639	10.482
1200	9.144	70.092	63.329	-1.639	9.722
1300	9.166	70.825	63.878	-1.639	9.011
1400	9.187	71.505	64.399	-1.639	8.342
1500	9.208	72.139	64.894	-1.639	7.713
1600	9.228	72.734	65.365	-1.639	7.123
1700	9.248	73.294	65.816	-1.639	6.573
1800	9.268	73.823	66.246	-1.639	6.063
1900	9.287	74.325	66.658	-1.639	5.593
2000	9.307	74.802	67.053	-1.639	5.163
2100	9.326	75.256	67.433	-1.639	4.773
2200	9.345	75.691	67.799	-1.639	4.423
2300	9.364	76.106	68.151	-1.639	4.113
2400	9.383	76.505	68.491	-1.639	3.843
2500	9.402	76.889	68.819	-1.639	3.613
2600	9.421	77.258	69.137	-1.639	3.423
2700	9.440	77.614	69.444	-1.639	3.273
2800	9.459	77.957	69.742	-1.639	3.163
2900	9.478	78.290	70.031	-1.639	3.083
3000	9.497	78.611	70.312	-1.639	2.983
3100	9.515	78.923	70.585	-1.639	2.913
3200	9.534	79.225	70.850	-1.639	2.863
3300	9.553	79.519	71.108	-1.639	2.823
3400	9.572	79.805	71.360	-1.639	2.793
3500	9.590	80.082	71.605	-1.639	2.773
3600	9.609	80.353	71.844	-1.639	2.763
3700	9.628	80.617	72.078	-1.639	2.763
3800	9.647	80.873	72.306	-1.639	2.773
3900	9.665	81.124	72.529	-1.639	2.793
4000	9.684	81.369	72.747	-1.639	2.823
4100	9.703	81.608	72.960	-1.639	2.863
4200	9.721	81.842	73.169	-1.639	2.913
4300	9.740	82.071	73.373	-1.639	2.963
4400	9.759	82.296	73.573	-1.639	3.013
4500	9.777	82.515	73.770	-1.639	3.063
4600	9.796	82.730	73.962	-1.639	3.113
4700	9.815	82.941	74.151	-1.639	3.163
4800	9.833	83.148	74.336	-1.639	3.213
4900	9.852	83.351	74.518	-1.639	3.263
5000	9.871	83.550	74.697	-1.639	3.313
5100	9.890	83.746	74.872	-1.639	3.363
5200	9.908	83.938	75.045	-1.639	3.413
5300	9.926	84.127	75.214	-1.639	3.463
5400	9.945	84.312	75.381	-1.639	3.513
5500	9.964	84.495	75.545	-1.639	3.563
5600	9.982	84.675	75.707	-1.639	3.613
5700	10.001	84.852	75.865	-1.639	3.663
5800	10.019	85.026	76.022	-1.639	3.713
5900	10.038	85.197	76.176	-1.639	3.763
6000	10.057	85.366	76.328	-1.639	3.813

Sept. 30, 1964

SODIUM BROMIDE (NaBr)

(IDEAL GAS)

BrNa

MOL. WT. = 102.907

$$\Delta H_f^0 = -32.27 \pm 0.50 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 57.628 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = -34.40 \pm 0.50 \text{ kcal. mole}^{-1}$$

Electronic Levels and Quantum Weight

$$\frac{\epsilon_1}{0} = \frac{\epsilon_1}{1}$$

$$\omega_e x_e = 1.50 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$\alpha_e = 0.000939 \text{ cm}^{-1}$$

$$r_e = 2.5020 \pm 0.0001 \text{ \AA}$$

Heat of Formation.

The heat of formation (ΔH_f^0 298.15) was calculated from ΔH_f^0 298.15 and ΔH_f^0 298.15 for NaBr(c). The latter was derived from six sets of corrected vapor pressure data, due to the presence of dimeric species in the vapor, by both the second and third law methods. The results are listed as follows.

Investigator	Reaction	Third Law Value	Second Law Value	ΔH_f^0 298.15 [*] kcal. mole ⁻¹
Niwa ¹	NaBr(c) → NaBr(g)	51.97	50.31	-35.24
Cogin and Kimball ²	NaBr(c) → NaBr(g)	52.26	52.14	-34.18
Mayer and Wintner ³	NaBr(c) → NaBr(g)	52.59	52.59	-33.79**
Ruff and Muggan ⁴	NaBr(l) → NaBr(g)	46.43	47.48	-34.15
Wartenberg and Albrecht ⁵	NaBr(l) → NaBr(g)	46.38	47.54	-34.15
Bloom et al. ⁶	NaBr(l) → NaBr(g)	46.23	51.53	-34.68**

*Based on the average of the second and third law values.

**Only the third law value being used.

1 K. Niwa, J. Pac. Sci., Hokkaido Univ., Ser. III, 2, 201 (1938).

2 G. E. Cogin and G. E. Kimball, J. Chem. Phys. 16, 1035 (1948).

3 J. E. Mayer and I. H. Wintner, J. Chem. Phys., 6, 301 (1938).

4 O. Ruff and S. Muggan, Z. anorg. allgem. Chem., 117, 147 (1921).

5 H. von Wartenberg and P. Albrecht, Z. Electrochem., 27, 162 (1921).

6 H. Bloom, J. O.M. Bodria, N. E. Richards and R. G. Taylor, J. Am. Chem. Soc. 80, 2044 (1958).

The value of ΔH_f^0 298.15 for NaBr(g) adopted is the average value of the six ΔH_f^0 298.15 values listed in the above table. The dissociation energy (D_0^0) was calculated to be 86.28 kcal. mole⁻¹ or 3.74 e.v. which is in good agreement with the values, $D_0^0 = 3.84 \pm 1$ and 3.85 e.v., reported by A. G. Daydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953 and G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, New York, 1950, respectively. According to L. Brewer, private communication, October 23, 1964, Daydon's original reported value, $D_0^0 = 3.8$, is an average of the value of 3.84 e.v. from atomic fluorescence and the value of 3.75 e.v. calculated for Daydon by Brewer from pressure data available at that time.

Heat Capacity and Entropy.

The values of ω_e , $\omega_e x_e$, B_e and α_e were taken from S. A. Rice and W. Klemperer, J. Chem. Phys. 27, 573 (1957). The adopted bond distance (r_e) was reported by A. Honig, M. Mandel, M. L. Stinch and C. H. Townes, Phys. Rev. 96, 629 (1954), which was derived from microwave spectrum. By electron-diffraction method, the Na-Br bond distance was determined as 2.64 ± 0.01 Å by L. R. Maxwell, S. B. Hendricks and V. M. Moseley, Phys. Rev. 52, 968 (1937). The discrepancy may be due to the presence of a large proportion of dimer at the higher pressures used in the electron-diffraction determination. The ground state configuration was reported by G. Herzberg, loc. cit.

BrNa

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _f
0	0.000	INFINITE	-2.272	44.519	INFINITE	
100	9.175	50.995	66.728	44.519	40.487	-39.479
200	8.019	56.241	60.259	44.519	36.217	-38.574
298	8.460	59.537	59.537	43.000	32.298	-23.674
300	8.465	59.589	59.537	42.990	32.232	-23.480
400	8.777	62.007	56.812	38.955	28.548	-16.072
500	8.792	62.007	60.311	38.957	28.568	-11.786
600	8.863	65.616	61.231	38.895	28.589	-8.956
700	8.912	68.986	61.958	38.704	28.219	-6.937
800	8.947	71.719	62.653	38.413	27.568	-5.980
900	8.969	73.821	63.285	38.040	26.640	-5.041
1000	8.989	75.181	63.973	37.608	25.561	-4.162
1100	9.019	76.040	64.577	37.109	24.320	-3.262
1200	9.037	76.182	65.149	36.612	23.009	-2.333
1300	9.069	76.291	65.691	36.123	21.629	-1.409
1400	9.083	76.367	66.204	35.642	20.189	-0.479
1500	9.097	76.434	66.684	35.169	18.689	0.451
1600	9.111	76.486	67.159	34.704	17.129	1.382
1700	9.125	76.525	67.626	34.249	15.509	2.312
1800	9.137	76.556	68.085	33.794	13.829	3.242
1900	9.149	76.580	68.535	33.339	12.089	4.172
2000	9.161	76.606	68.975	32.884	10.289	5.102
2100	9.173	76.633	69.400	32.429	8.429	6.032
2200	9.185	76.661	69.816	31.954	6.509	6.962
2300	9.197	76.689	70.226	31.469	4.589	7.892
2400	9.209	76.718	70.626	30.974	2.669	8.822
2500	9.221	76.748	71.016	30.469	0.749	9.752
2600	9.228	76.778	71.392	29.954	-1.171	10.682
2700	9.232	76.807	71.754	29.429	-3.091	11.612
2800	9.235	76.836	72.106	28.894	-5.011	12.542
2900	9.238	76.865	72.454	28.359	-6.931	13.472
3000	9.240	76.894	72.796	27.824	-8.851	14.402
3100	9.242	76.916	73.132	27.289	-10.771	15.332
3200	9.244	76.938	73.464	26.754	-12.691	16.262
3300	9.246	76.960	73.796	26.219	-14.611	17.192
3400	9.248	76.982	74.122	25.684	-16.531	18.122
3500	9.250	77.004	74.448	25.149	-18.451	19.052
3600	9.252	77.026	74.774	24.614	-20.371	19.982
3700	9.254	77.048	75.100	24.079	-22.291	20.912
3800	9.256	77.070	75.426	23.544	-24.211	21.842
3900	9.258	77.092	75.752	22.999	-26.131	22.772
4000	9.260	77.114	76.078	22.454	-28.051	23.702
4100	9.262	77.136	76.404	21.909	-29.971	24.632
4200	9.264	77.158	76.730	21.364	-31.891	25.562
4300	9.266	77.180	77.056	20.819	-33.811	26.492
4400	9.268	77.202	77.382	20.274	-35.731	27.422
4500	9.270	77.224	77.708	19.729	-37.651	28.352
4600	9.272	77.246	78.034	19.184	-39.571	29.282
4700	9.274	77.268	78.360	18.639	-41.491	30.212
4800	9.276	77.290	78.686	18.094	-43.411	31.142
4900	9.278	77.312	79.012	17.549	-45.331	32.072
5000	9.280	77.334	79.338	16.999	-47.251	33.002
5100	9.282	77.356	79.664	16.454	-49.171	33.932
5200	9.284	77.378	80.000	15.909	-51.091	34.862
5300	9.286	77.400	80.326	15.364	-53.011	35.792
5400	9.288	77.422	80.652	14.819	-54.931	36.722
5500	9.290	77.444	80.978	14.274	-56.851	37.652
5600	9.292	77.466	81.304	13.729	-58.771	38.582
5700	9.294	77.488	81.630	13.184	-60.691	39.512
5800	9.296	77.510	81.956	12.639	-62.611	40.442
5900	9.298	77.532	82.282	12.094	-64.531	41.372
6000	9.300	77.554	82.608	11.549	-66.451	42.302

June 30, 1963; Dec. 31, 1965

Ground State Configuration [$3\sum^-$]
 $S_{298.15}^0 = [59.5]$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 = [45]$ kcal. mole⁻¹
 $\Delta F_f^0 = [45]$ kcal. mole⁻¹

Electronic Levels and Multiplicities

$$\frac{\epsilon_{ij}}{0} \frac{g_i}{[i]}$$

$$\omega_e x_e = [1.5] \text{ cm.}^{-1} \quad \sigma^- = 1$$

$$\alpha_e = [0.0008] \text{ cm.}^{-1} \quad x_e = [2.23] \text{ \AA}$$

$$\omega_e = [400] \text{ cm.}^{-1} \quad B_e = [0.1519] \text{ cm.}^{-1}$$

Heat of Formation.

ΔH_f^0 was estimated as 40.8 kcal. mole⁻¹ by J. S. Gordon, Astrostats International, Livingston, New Jersey, private communication, August 25, 1961. This ΔH_f^0 was changed from the white (α) to red (V) phosphorus reference state.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit.

INTERIM TABLE

Mol. Wt. = 287.13

(Ideal Gas)

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	7.963	55.064	15.449	2.424	15.449	15.449	15.449	INFINITE
200	8.039	61.446	15.420	1.897	15.420	11.577	24.864	-
298	8.082	64.936	15.300	∞	15.069	7.864	8.186	-
300	8.082	64.991	13.288	0.16	13.288	3.922	2.857	-
400	8.006	67.542	9.403	1.796	9.403	1.586	∞	-
500	8.051	69.535	6.594	2.493	6.594	0.181	∞	-
600	8.092	71.170	4.693	3.593	4.693	0.044	∞	-
700	8.096	72.516	3.493	4.494	3.493	0.027	∞	-
800	8.027	73.760	2.842	5.398	2.842	0.001	∞	-
900	8.046	74.825	2.387	6.304	2.387	0.001	∞	-
1000	8.064	75.779	1.947	7.232	1.947	0.001	∞	-
1100	8.084	76.643	1.511	8.186	1.511	0.001	∞	-
1200	8.105	77.425	1.074	9.154	1.074	0.001	∞	-
1300	8.130	78.144	0.632	10.130	0.632	0.001	∞	-
1400	8.158	78.842	0.194	11.114	0.194	0.001	∞	-
1500	8.191	79.475	0.723	12.104	0.723	0.001	∞	-
1600	8.228	80.050	1.265	13.104	1.265	0.001	∞	-
1700	8.269	80.569	1.814	14.114	1.814	0.001	∞	-
1800	8.314	81.031	2.365	15.130	2.365	0.001	∞	-
1900	8.362	81.446	2.914	16.151	2.914	0.001	∞	-
2000	8.413	82.147	3.462	17.174	3.462	0.001	∞	-
2100	8.466	82.608	4.009	18.200	4.009	0.001	∞	-
2200	8.521	83.029	4.556	19.226	4.556	0.001	∞	-
2300	8.576	83.474	5.103	20.251	5.103	0.001	∞	-
2400	8.632	83.883	5.650	21.276	5.650	0.001	∞	-
2500	8.687	84.277	6.197	22.300	6.197	0.001	∞	-
2600	8.742	84.658	6.744	23.324	6.744	0.001	∞	-
2700	8.796	85.027	7.291	24.348	7.291	0.001	∞	-
2800	8.847	85.384	7.838	25.372	7.838	0.001	∞	-
2900	8.898	85.730	8.385	26.396	8.385	0.001	∞	-
3000	8.946	86.067	8.932	27.419	8.932	0.001	∞	-
3100	9.002	86.394	9.479	28.443	9.479	0.001	∞	-
3200	9.056	86.721	10.026	29.467	10.026	0.001	∞	-
3300	9.107	87.021	10.573	30.491	10.573	0.001	∞	-
3400	9.157	87.322	11.119	31.515	11.119	0.001	∞	-
3500	9.205	87.616	11.666	32.539	11.666	0.001	∞	-
3600	9.252	87.903	12.213	33.563	12.213	0.001	∞	-
3700	9.298	88.182	12.760	34.587	12.760	0.001	∞	-
3800	9.343	88.455	13.307	35.611	13.307	0.001	∞	-
3900	9.387	88.722	13.854	36.635	13.854	0.001	∞	-
4000	9.430	88.982	14.401	37.659	14.401	0.001	∞	-
4100	9.472	89.237	14.948	38.683	14.948	0.001	∞	-
4200	9.513	89.486	15.495	39.707	15.495	0.001	∞	-
4300	9.553	89.730	16.042	40.731	16.042	0.001	∞	-
4400	9.593	89.969	16.589	41.755	16.589	0.001	∞	-
4500	9.631	90.203	17.136	42.779	17.136	0.001	∞	-
4600	9.667	90.432	17.683	43.803	17.683	0.001	∞	-
4700	9.702	90.656	18.230	44.827	18.230	0.001	∞	-
4800	9.736	90.876	18.777	45.851	18.777	0.001	∞	-
4900	9.769	91.092	19.324	46.875	19.324	0.001	∞	-
5000	9.800	91.303	19.871	47.900	19.871	0.001	∞	-
5100	9.830	91.511	20.418	48.924	20.418	0.001	∞	-
5200	9.859	91.715	20.965	49.948	20.965	0.001	∞	-
5300	9.887	91.915	21.512	50.972	21.512	0.001	∞	-
5400	9.914	92.112	22.059	51.996	22.059	0.001	∞	-
5500	9.940	92.305	22.606	53.020	22.606	0.001	∞	-
5600	9.965	92.494	23.153	54.044	23.153	0.001	∞	-
5700	9.989	92.681	23.700	55.068	23.700	0.001	∞	-
5800	10.012	92.864	24.247	56.092	24.247	0.001	∞	-
5900	10.034	93.045	24.794	57.116	24.794	0.001	∞	-
6000	10.056	93.222	25.341	58.140	25.341	0.001	∞	-

June 30, 1962

Lead Monobromide (PbBr) (Ideal Gas)

Mol. Wt. = 287.13

 $\Delta H_f^{298.15} = 13.3 \pm 9.2 \text{ kcal. mole}^{-1}$ $S^{298.15} = 64.936 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Ground State Configuration $2\pi_{1/2}$

Electronic Levels and Multiplicities

ϵ , cm. ⁻¹	g_1	g_2
0	1	2
[8000]	2	2

 $\omega_e = 207.5 \text{ cm.}^{-1}$ $\omega_e x_e = 0.50 \text{ cm.}^{-1}$ $B_e = [0.04874] \text{ cm.}^{-1}$ $\sigma = 1$ $\omega_e x_e = [0.00016] \text{ cm.}^{-1}$

Heat of Formation. $\Delta H_f^{298.15}$ was calculated from the dissociation energy of PbBr(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950). B_e and σ_e were estimated by J. S. Gordon, AstroSystems, Inc., private communication, May, 1962. Electronic levels and multiplicities were estimated from those for Pb(g).

(Ideal Gas) GFW = 127.809

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	enthalpy H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	7.000	INFINITE	- 2.375	52.506	52.506	INFINITE
100	7.199	53.119	1.267	52.749	46.272	- 105.502
200	8.466	62.987	1.862	52.508	47.946	- 105.502
298	9.087	62.175	.000	50.800	39.871	- 29.826
300	9.098	62.231	.017	50.789	39.803	- 28.987
400	9.591	67.104	1.932	46.679	34.409	- 15.040
500	10.194	68.943	2.941	46.778	31.924	- 11.828
600	10.333	70.525	3.968	46.672	29.457	- 9.197
700	10.411	71.911	5.005	46.552	27.005	- 7.569
800	10.475	73.242	6.117	46.443	24.587	- 6.041
1000	10.489	75.241	8.144	46.051	19.754	- 3.925
1200	10.500	76.154	9.193	44.897	17.410	- 3.171
1300	10.511	76.975	10.254	44.781	15.847	- 2.583
1400	10.520	77.749	11.329	44.687	14.407	- 2.101
1500	10.529	78.501	12.349	44.505	10.580	- 1.541
1600	10.537	79.182	13.403	44.342	8.325	- 1.137
1700	10.546	79.823	14.460	44.161	6.078	- .781
1800	10.556	80.428	15.528	43.973	3.823	- .467
1900	10.564	81.006	16.606	43.779	1.572	- .186
2000	10.569	81.556	17.642	39.045	- 1.436	.048
2100	10.662	82.066	73.158	38.803	- 2.403	.250
2200	10.684	82.563	73.574	38.562	- 4.361	.433
2300	10.698	83.049	73.964	38.320	- 6.319	.590
2400	10.707	83.498	74.332	38.083	- 8.260	.720
2500	10.717	83.932	74.737	37.850	- 10.168	.889
2600	10.766	84.334	75.098	37.616	- 12.083	1.016
2700	10.784	84.761	75.449	37.382	- 13.990	1.132
2800	10.801	85.133	75.793	37.148	- 15.897	1.240
2900	10.814	85.533	76.118	36.920	- 17.776	1.340
3000	10.831	85.900	76.438	36.690	- 19.659	1.432
3100	10.845	86.255	76.749	36.461	- 21.532	1.518
3200	10.858	86.599	77.051	36.233	- 23.402	1.598
3300	10.870	86.933	77.343	36.006	- 25.269	1.673
3400	10.881	87.258	77.633	35.779	- 27.114	1.743
3500	10.892	87.574	77.912	35.553	- 28.961	1.808
3600	10.902	87.881	78.185	- 66.299	- 30.538	1.854
3700	10.911	88.150	78.451	- 66.466	- 32.402	1.898
3800	10.919	88.419	78.716	- 66.633	- 34.263	1.941
3900	10.929	88.755	78.965	- 66.929	- 36.123	1.983
4000	10.937	89.031	79.213	- 67.164	- 38.000	2.025
4100	10.945	89.302	79.456	- 67.412	- 40.000	2.067
4200	10.952	89.563	79.696	- 67.681	- 42.000	2.109
4300	10.959	89.823	79.932	- 67.961	- 44.000	2.151
4400	10.967	90.075	80.154	- 68.225	- 46.000	2.193
4500	10.975	90.322	80.377	- 68.518	- 48.000	2.235
4600	10.982	90.563	80.596	- 68.821	- 50.000	2.277
4700	10.989	90.810	80.810	- 69.133	- 52.000	2.319
4800	10.997	91.031	81.010	- 69.448	- 54.000	2.361
4900	11.004	91.256	81.227	- 69.787	- 56.000	2.403
5000	11.012	91.480	81.430	- 70.125	- 58.000	2.445
5100	11.020	91.698	81.629	- 70.472	- 60.000	2.487
5200	11.026	91.912	81.817	- 70.829	- 62.000	2.529
5300	11.032	92.122	82.007	- 71.186	- 64.000	2.571
5400	11.038	92.329	82.206	- 71.555	- 66.000	2.613
5500	11.042	92.531	82.392	- 71.927	- 68.000	2.655
5600	11.041	92.731	82.575	- 72.307	- 70.000	2.697
5700	11.039	92.919	82.752	- 72.687	- 72.000	2.739
5800	11.037	93.109	82.929	- 73.067	- 74.000	2.781
5900	11.039	93.309	83.106	- 73.470	- 76.000	2.823
6000	11.038	93.495	83.278	- 73.866	- 78.000	2.865

Dec. 31, 1961; June 30, 1964; Sept. 30, 1964; June 30, 1968

TITANIUM MONOBROMIDE (TiBr)

(IDEAL GAS)

GFW = 127.809

Ground State Configuration [Σ]
 $S^\circ_{298.15} = 62.18 \pm 2.0$ gibbs/mol
 $\Delta H^\circ_{298.15} = [52.5 \pm 10.0]$ kcal/mol
 $\Delta H^\circ_{298.15} = [50.8 \pm 10.0]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

$\omega_e = [295]$ cm⁻¹
 $B_e = [0.0904]$ cm⁻¹
 $\omega_e x_e = [2.21]$ cm⁻¹
 $\omega_e = [0.00067]$ cm⁻¹
 $\sigma = 1$
 $r_e = [2.5]$ Å

Heat of Formation

The heat of formation, ΔH°_{298} , of TiBr (g) is calculated from the dissociation energy, D°_0 , which is estimated as 104 kcal/mol. This estimate is obtained from the relation $D(TiBr_4) < D^\circ(TiBr) < D(TiBr_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF₂(g) by Zubov and Margrave (1).

Heat Capacity and Entropy

The vibrational frequency, ω_e , and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The internuclear distance is estimated from Guggenheimer's relation (2). B_e is calculated from r_e . The ground state term and electronic levels are estimated from the ground state multiplet of Ti (3). ω_e is estimated from the Morse potential function.

References

1. K. F. Zubov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. K. M. Guggenheimer, Proc. Phys. Soc. **58**, 456 (1946).
3. C. E. Moore, U. S. Natl. Bur. Std., Circ. 487, 1949.

Tungsten Monobromide (WBr)

(Ideal Gas) GFW = 263.759

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^o}$	$-(G^o - H^o_{298})/T$	H ^o - H ^o ₂₉₈	kcal/mol ΔH^o	ΔG^o	Log K _p
0	.000	INFINITE	INFINITE	2.324	181.894	181.894	INFINITE
100	7.389	56.323	72.519	1.620	182.109	182.109	-300.178
200	8.268	61.268	65.119	.861	182.492	182.492	-414.668
300	8.312	65.130	60.130	.000	183.100	183.493	-94.144
400	8.616	65.183	65.130	.016	180.088	125.361	-93.511
500	8.767	67.685	65.670	.686	136.249	125.230	-68.423
600	8.946	69.651	66.117	1.767	136.088	122.493	-53.542
700	8.995	71.268	66.895	2.684	135.920	119.790	-43.634
800	8.931	72.642	67.577	3.544	135.744	117.114	-36.565
900	8.761	73.837	68.287	4.440	135.558	114.466	-31.271
1000	8.592	74.894	68.963	5.334	135.364	111.942	-27.159
1100	8.025	75.943	69.604	6.239	135.161	109.240	-23.874
1200	9.062	76.705	70.211	7.143	134.950	106.557	-21.191
1300	9.102	77.495	70.786	8.051	134.732	104.094	-18.950
1400	9.144	78.225	71.330	8.963	134.506	101.552	-17.072
1500	9.189	78.905	71.847	9.880	134.272	99.024	-15.458
1600	9.234	79.540	72.339	10.801	134.032	96.516	-14.062
1700	9.279	80.137	72.808	11.727	133.784	94.024	-12.843
1800	9.324	80.701	73.256	12.657	133.528	91.564	-11.769
1900	9.369	81.236	73.685	13.592	133.265	89.082	-10.816
2000	9.413	81.743	74.096	14.531	132.995	86.637	-9.966
2100	9.458	82.227	74.490	15.474	132.717	84.205	-9.201
2200	9.503	82.690	74.870	16.422	132.431	81.785	-8.511
2300	9.549	83.133	75.235	17.375	132.136	79.378	-7.885
2400	9.596	83.558	75.588	18.332	131.835	76.989	-7.316
2500	9.646	83.968	75.929	19.294	131.526	74.611	-6.794
2600	9.698	84.363	76.258	20.261	131.210	72.245	-6.316
2700	9.753	84.744	76.577	21.234	130.886	69.894	-5.875
2800	9.811	85.113	76.887	22.212	130.551	67.554	-5.460
2900	9.872	85.471	77.187	23.196	130.195	65.229	-5.061
3000	9.937	85.819	77.478	24.187	129.809	62.911	-4.741
3100	10.005	86.157	77.762	25.184	129.388	60.514	-4.416
3200	10.077	86.484	78.038	26.184	128.920	58.328	-4.112
3300	10.151	86.807	78.307	27.199	128.400	56.059	-3.829
3400	10.228	87.121	78.570	28.218	127.821	53.805	-3.563
3500	10.307	87.427	78.826	29.245	127.175	51.574	-3.315
3600	10.388	87.727	79.076	30.280	126.448	49.362	-3.082
3700	10.471	88.021	79.320	31.322	125.614	47.168	-2.863
3800	10.554	88.309	79.559	32.374	124.644	45.008	-2.661
3900	10.638	88.591	79.793	33.431	123.544	42.889	-2.467
4000	10.722	88.869	80.022	34.501	122.308	40.812	-2.280
4100	10.808	89.141	80.247	35.578	120.942	38.781	-2.100
4200	10.898	89.409	80.467	36.662	119.444	36.793	-1.933
4300	10.969	89.673	80.683	37.755	117.816	34.845	-1.787
4400	11.049	89.932	80.895	38.856	116.056	32.946	-1.650
4500	11.127	90.186	81.104	39.965	114.169	31.096	-1.520
4600	11.202	90.437	81.308	41.081	112.156	29.293	-1.395
4700	11.275	90.684	81.509	42.205	110.009	27.533	-1.278
4800	11.345	90.928	81.707	43.336	107.736	25.816	-1.163
4900	11.411	91.167	81.902	44.474	105.340	24.142	-1.050
5000	11.475	91.403	82.093	45.614	102.821	22.611	-0.938
5100	11.535	91.636	82.282	46.769	100.176	21.224	-0.828
5200	11.592	91.865	82.467	47.925	97.408	19.981	-0.720
5300	11.645	92.090	82.650	49.087	94.526	18.775	-0.615
5400	11.695	92.312	82.831	50.254	91.534	17.606	-0.514
5500	11.741	92.531	83.008	51.426	88.434	16.472	-0.415
5600	11.783	92.747	83.183	52.602	85.221	15.372	-0.318
5700	11.822	92.960	83.356	53.783	81.904	14.296	-0.224
5800	11.857	93.170	83.526	54.966	78.480	13.244	-0.134
5900	11.889	93.376	83.694	56.154	74.952	12.214	-0.048
6000	11.917	93.560	83.860	57.344	71.320	11.204	-0.066
6100	11.943	93.780	84.024	58.537	67.584	10.214	-0.189

June 30, 1967

TUNGSTEN MONOBROMIDE (WBr)

(IDEAL GAS)

GFW = 263.759

Ground State Configuration [2_g] $\Delta H^o_{298.15} = [141.9 \pm 20] \text{ kcal/mol}$ $S^o_{298.15} = [65.1] \text{ gibbs/mol}$ $\Delta H^o_{298.15} = [140.1 \pm 20] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

E_i , cm ⁻¹	g_i
0	[4]
[5000]	[2]
[15000]	[20]

 $\omega_e X_e = [0.80] \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = [321.4] \text{ cm}^{-1}$ $\alpha_e = [0.00015] \text{ cm}^{-1}$ $r_e = [2.40] \text{ \AA}$

Heat of Formation

The heat of formation, $\Delta H^o_{298}(\text{WBr}, g) = 140.1 \text{ kcal/mol}$, is calculated from the bond dissociation energy.

$D_{298}(\text{W-Br}) = 90 \pm 20 \text{ kcal/mol}$. This value of D_{298} is estimated to be slightly higher than the average bond dissociation energy of $\text{WBr}_2(g)$, by analogy with the WCl_2 system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $\text{WBr}_2(g)$. This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 486 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D_0^* + 0.5 \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is $53.27 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for $\text{WF}(g)$. See $\text{WF}(g)$ table (March 31, 1967) for details.

GTW = 171.129

(IDEAL GAS)

ZIRCONIUM MONOBROMIDE (ZrBr₄)

Zirconium Monobromide (ZrBr)

(Ideal Gas) GTW = 171.129

Ground State Configuration [4f²]S_{298.15} = [63.4 ± 2] gibbs/mol $\Delta H_f^\circ = [73.9 \pm 10]$ kcal/mol $\Delta H_f^\circ_{298.15} = [72 \pm 10]$ kcal/mol

Electronic Levels and Quantum Heights

ϵ_i , cm ⁻¹	$\frac{g_i}{\epsilon_i}$
0	[4]
[3000]	[4]
[8000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

 $\omega_e = [317]$ cm⁻¹ $\omega_e x_e = [0.69]$ cm⁻¹ $\sigma = 1$ $B_e = [0.065]$ cm⁻¹ $r_e = [0.00018]$ cm⁻¹ $r = [2.47]$ Å

Heat of Formation

The heat of formation, $\Delta H_f^\circ(\text{ZrBr}, g) = 72$ kcal/mol, is derived from the estimated bond dissociation energy, $D_{298}^\circ(\text{Zr-Br}) = 103.5 \pm 10$ kcal/mol. The value of $D_{298}^\circ(\text{Zr-Br})$ is calculated from the relation $D_{298}^\circ(\text{Zr-Br})/n_{298}^\circ(\text{Ti-Br}) = D_{298}^\circ(\text{Zr-Br}_4)/n_{298}^\circ(\text{Ti-Br}_4)$ where the average bond dissociation energies, $D_{298}^\circ(\text{Zr-Br}_4) = 102.2$ kcal/mol, $D_{298}^\circ(\text{Ti-Br}_4) = 87.9$ kcal/mol and $D_{298}^\circ(\text{Ti-Cl}) = 89.0$ kcal/mol, all calculated from JANAF ΔH_f° for $\text{ZrBr}_4(g)$, $\text{TiBr}_4(g)$, $\text{TiCl}_4(g)$, $\text{Zr}(g)$, $\text{Ti}(g)$ and $\text{Br}(g)$.

Heat Capacity and Entropy

The bond distance is assumed to be the same as that in $\text{ZrBr}_4(g)$, which was estimated as 2.47 Å by Godnev, Aleksandrova and Rikina, Optics and Spectroscopy, 1, 172 (1959). The estimated bond distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 436 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4 (D_0 + 0.5 \omega_e) = 0.0021$. The rotational constant B_e is calculated from the estimated bond distance. The value of ω_e is calculated from the Morse potential function. The moment of inertia is 42.1488×10^{-39} g cm².

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952. The electronic levels and quantum weights are estimated to be the same as those of $\text{Zr}(g)$.

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔG°	Log K _p
0	7.000	INFINITE	2.328	73.923	INFINITE	
100	7.404	70.863	1.622	66.827	66.827	1.776
200	7.762	68.432	1.000	61.286	61.286	1.377
298	8.020	63.443		73.000	61.286	0.923
300	8.024	63.443		71.988	61.220	0.924
400	8.276	66.000	0.16	58.416	58.416	0.734
500	8.475	67.969	0.430	51.911	51.911	0.561
600	8.624	69.596	0.650	47.427	47.427	0.401
700	8.743	70.987	0.895	44.806	44.806	0.261
800	8.835	72.209	1.160	43.401	43.401	0.136
900	8.902	73.302	1.440	42.804	42.804	0.024
1000	8.949	74.295	1.720	42.856	42.856	0.000
1100	8.976	75.206	2.000	42.856	42.856	0.000
1200	8.985	76.049	2.270	42.856	42.856	0.000
1300	8.985	76.834	2.540	42.856	42.856	0.000
1400	8.976	77.569	2.800	42.856	42.856	0.000
1500	8.958	78.260	3.050	42.856	42.856	0.000
1600	8.932	78.911	3.290	42.856	42.856	0.000
1700	8.898	79.528	3.520	42.856	42.856	0.000
1800	8.857	80.113	3.740	42.856	42.856	0.000
1900	8.809	80.669	3.950	42.856	42.856	0.000
2000	8.756	81.199	4.150	42.856	42.856	0.000
2100	8.700	81.704	4.340	42.856	42.856	0.000
2200	8.640	82.188	4.520	42.856	42.856	0.000
2300	8.577	82.651	4.690	42.856	42.856	0.000
2400	8.511	83.095	4.850	42.856	42.856	0.000
2500	8.442	83.522	5.000	42.856	42.856	0.000
2600	8.370	83.932	5.140	42.856	42.856	0.000
2700	8.296	84.327	5.270	42.856	42.856	0.000
2800	8.219	84.709	5.390	42.856	42.856	0.000
2900	8.140	85.077	5.500	42.856	42.856	0.000
3000	8.058	85.432	5.600	42.856	42.856	0.000
3100	7.973	85.777	5.690	42.856	42.856	0.000
3200	7.886	86.110	5.770	42.856	42.856	0.000
3300	7.797	86.433	5.850	42.856	42.856	0.000
3400	7.706	86.747	5.920	42.856	42.856	0.000
3500	7.613	87.051	5.990	42.856	42.856	0.000
3600	7.518	87.347	6.050	42.856	42.856	0.000
3700	7.421	87.635	6.110	42.856	42.856	0.000
3800	7.322	87.916	6.160	42.856	42.856	0.000
3900	7.221	88.191	6.210	42.856	42.856	0.000
4000	7.118	88.455	6.250	42.856	42.856	0.000
4100	7.013	88.715	6.290	42.856	42.856	0.000
4200	6.906	88.969	6.330	42.856	42.856	0.000
4300	6.797	89.219	6.370	42.856	42.856	0.000
4400	6.686	89.466	6.410	42.856	42.856	0.000
4500	6.573	89.709	6.450	42.856	42.856	0.000
4600	6.458	89.947	6.490	42.856	42.856	0.000
4700	6.342	90.179	6.530	42.856	42.856	0.000
4800	6.224	90.406	6.570	42.856	42.856	0.000
4900	6.105	90.629	6.610	42.856	42.856	0.000
5000	5.984	90.848	6.650	42.856	42.856	0.000
5100	5.861	91.064	6.690	42.856	42.856	0.000
5200	5.736	91.276	6.730	42.856	42.856	0.000
5300	5.610	91.484	6.770	42.856	42.856	0.000
5400	5.483	91.688	6.810	42.856	42.856	0.000
5500	5.355	91.888	6.850	42.856	42.856	0.000
5600	5.226	92.084	6.890	42.856	42.856	0.000
5700	5.096	92.276	6.930	42.856	42.856	0.000
5800	4.964	92.464	6.970	42.856	42.856	0.000
5900	4.831	92.648	7.010	42.856	42.856	0.000
6000	4.697	92.828	7.050	42.856	42.856	0.000

Sept. 30, 1984; June 30, 1970

Tungsten Monobromide (WBr)

(Ideal Gas) GFW = 263.759

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0	7.300	56.000	INFINITE	-2.324	141.894	141.894	INFINITE
100	8.268	61.754	65.909	-1.830	140.432	132.480	14.990
200	8.512	65.130	65.130	-1.009	140.100	129.433	94.144
300	8.616	65.183	65.130	.016	140.088	129.361	93.511
400	8.767	67.685	65.470	.884	136.249	125.230	68.423
500	8.946	69.651	66.117	1.767	136.088	124.493	53.542
600	9.095	71.268	66.845	2.654	135.920	119.790	43.634
700	9.231	72.642	67.577	3.544	135.744	117.116	36.565
800	9.361	73.837	68.287	4.440	135.558	114.466	31.271
900	9.482	74.894	68.983	5.334	135.364	111.842	27.159
1000	9.605	75.843	69.664	6.239	135.161	109.240	23.674
1100	9.662	76.705	70.211	7.143	134.950	106.557	21.191
1200	9.710	77.495	70.736	8.051	134.732	104.995	18.958
1300	9.754	78.225	71.330	8.963	134.506	103.552	17.072
1400	9.795	78.905	71.887	9.880	134.272	102.224	15.488
1500	9.834	79.540	72.339	10.801	134.032	100.916	14.062
1600	9.870	80.137	72.808	11.727	133.784	99.624	12.893
1700	9.904	80.701	73.256	12.657	133.528	98.346	11.769
1800	9.936	81.236	73.685	13.592	133.265	97.082	10.616
1900	9.967	81.743	74.096	14.531	132.995	95.837	9.466
2000	9.996	82.227	74.490	15.474	132.717	94.605	8.320
2100	9.953	82.690	74.870	16.422	132.431	93.385	7.185
2200	9.949	83.133	75.235	17.375	132.136	92.178	6.065
2300	9.956	83.558	75.588	18.332	131.835	90.989	4.964
2400	9.964	83.968	75.929	19.294	131.526	89.811	3.881
2500	9.968	84.363	76.258	20.261	131.210	88.645	2.816
2600	9.973	84.744	76.577	21.234	130.886	87.494	1.775
2700	9.981	85.113	76.887	22.212	130.551	86.355	0.755
2800	9.987	85.471	77.187	23.196	130.215	85.229	-0.261
2900	9.993	85.819	77.498	24.187	129.879	84.111	-1.271
3000	10.000	86.157	77.762	25.184	129.544	83.001	-2.311
3100	10.007	86.486	78.038	26.184	129.220	81.901	-3.381
3200	10.015	86.807	78.307	27.190	128.897	80.811	-4.481
3300	10.028	87.121	78.570	28.218	128.571	79.731	-5.611
3400	10.037	87.427	78.826	29.245	128.245	78.661	-6.771
3500	10.048	87.727	79.076	30.280	127.919	77.611	-7.961
3600	10.054	88.021	79.320	31.322	127.593	76.571	-9.181
3700	10.054	88.309	79.559	32.374	127.267	75.541	-10.431
3800	10.058	88.591	79.793	33.433	126.941	74.521	-11.711
3900	10.062	88.869	80.022	34.501	126.615	73.511	-13.021
4000	10.065	89.141	80.247	35.576	126.289	72.511	-14.361
4100	10.068	89.409	80.467	36.662	125.963	71.521	-15.731
4200	10.069	89.673	80.683	37.755	125.637	70.541	-17.131
4300	10.069	89.932	80.895	38.856	125.311	69.571	-18.561
4400	10.069	90.186	81.104	39.965	124.985	68.611	-20.021
4500	10.069	90.437	81.308	41.081	124.659	67.661	-21.511
4600	10.069	90.684	81.509	42.205	124.333	66.721	-23.021
4700	10.069	90.928	81.707	43.336	124.007	65.791	-24.551
4800	10.069	91.167	81.902	44.474	123.681	64.871	-26.101
4900	10.069	91.403	82.093	45.614	123.355	63.961	-27.671
5000	10.069	91.638	82.282	46.760	123.029	63.061	-29.261
5100	10.069	91.865	82.467	47.925	122.703	62.171	-30.871
5200	10.069	92.090	82.650	49.087	122.377	61.291	-32.501
5300	10.069	92.312	82.831	50.254	122.051	60.421	-34.151
5400	10.069	92.531	83.008	51.426	121.725	59.561	-35.821
5500	10.069	92.747	83.183	52.602	121.400	58.711	-37.511
5600	10.069	92.960	83.356	53.783	121.074	57.871	-39.221
5700	10.069	93.170	83.526	54.966	120.748	57.041	-40.951
5800	10.069	93.376	83.694	56.154	120.422	56.221	-42.701
5900	10.069	93.580	83.860	57.344	120.096	55.411	-44.471
6000	10.069	93.780	84.024	58.537	119.770	54.611	-46.261

June 30, 1967

TUNGSTEN MONOBROMIDE (WBr)

(IDEAL GAS)

GFW = 263.759

Ground State Configuration [2Δ]

 $\Delta H_f^o = [141.9 \pm 20] \text{ kcal/mol}$ $S_{298.15}^o = [65.1] \text{ gibbs/mol}$ $\Delta H_f^o = [141.9 \pm 20] \text{ kcal/mol}$ $\Delta H_f^o = [140.1 \pm 20] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	S_i
0	[4]
[5000]	[2]
[15000]	[20]

 $\sigma = 1$ $r_e = [2.40] \text{ Å}$ $\omega_e = [321.4] \text{ cm}^{-1}$ $\omega_e x_e = [0.80] \text{ cm}^{-1}$ $\omega_e = [0.00015] \text{ cm}^{-1}$

Heat of Formation

The heat of formation, $\Delta H_f^o(\text{WBr}, g)$, is calculated from the bond dissociation energy, $D_{298}^o(\text{W-Br}) = 90 \pm 20 \text{ kcal/mol}$. This value of D_{298}^o is estimated to be slightly higher than the average bond dissociation energy of $\text{WBr}_2(g)$, by analogy with the WCl_4 system.The bond distance is estimated to be the same as that in $\text{WBr}_2(g)$. This distance is then used with Guggenheim's relation for polar molecules to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheim, Proc. Phys. Soc. (London) 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4D_e^o + 0.5 \omega_e = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of ω_e is calculated from the Morse potential function. The moment of inertia is $53.27 \times 10^{-39} \text{ g cm}^2$.The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for $\text{WF}_6(g)$. See WF(g) table (March 31, 1967) for details.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $\text{WBr}_2(g)$. This distance is then used with Guggenheim's relation for polar molecules to calculate the fundamental vibrational frequency, ω_e (K. M. Guggenheim, Proc. Phys. Soc. (London) 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4D_e^o + 0.5 \omega_e = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of ω_e is calculated from the Morse potential function. The moment of inertia is $53.27 \times 10^{-39} \text{ g cm}^2$.The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for $\text{WF}_6(g)$. See WF(g) table (March 31, 1967) for details.

GFW = 171.129

(IDEAL GAS)

ZIRCONIUM MONOBROMIDE (ZrBr)

Zirconium Monobromide (ZrBr)

(Ideal Gas) GFW = 171.129

Ground State Configuration $[4f^2]$ $\Delta H_f^\circ = [73.9 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = [63.4 \pm 2] \text{ gibbs/mol}$ $\Delta H_f^\circ = [73.9 \pm 10] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

t_i, cm^{-1}	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

 $\omega_e = [317] \text{ cm}^{-1}$ $\omega_e x_e = [0.69] \text{ cm}^{-1}$ $\sigma = 1$ $B_e = [0.065] \text{ cm}^{-1}$ $\omega_e = [0.00018] \text{ cm}^{-1}$ $r = [2.47] \text{ \AA}$

Heat of Formation

The heat of formation, $\Delta H_f^\circ(\text{ZrBr}, g) = 72 \text{ kcal/mol}$, is derived from the estimated bond dissociation energy, $D_{298}^\circ(\text{Zr-Br}) = 103.5 \pm 10 \text{ kcal/mol}$. The value of $D_{298}^\circ(\text{Zr-Br})$ is calculated from the relation $D_{298}^\circ(\text{Zr-Br})/D_{298}^\circ(\text{Ti-Br}) = D_{298}^\circ(\text{Zr-Br})/D_{298}^\circ(\text{Ti-Br})$ where the average bond dissociation energies, $D_{298}^\circ(\text{Zr-Br}) = 102.2 \text{ kcal/mol}$, $D_{298}^\circ(\text{Ti-Br}) = 87.9 \text{ kcal/mol}$ and $D_{298}^\circ(\text{Ti-Cl}) = 89.0 \text{ kcal/mol}$, all calculated from JANAF ΔH_f° for $\text{ZrBr}_2(g)$, $\text{TiBr}_2(g)$, $\text{TiCl}_2(g)$, $\text{Zr}(g)$, $\text{Ti}(g)$ and $\text{Br}(g)$.

Heat Capacity and Entropy

The bond distance is assumed to be the same as that in $\text{ZrBr}_2(g)$, which was estimated as 2.47 \AA by Godnev, Aleksandrova and Rignia, Optics and Spectroscopy, 1, 172 (1959). The estimated bond distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 416 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4 (D_0 + 0.5 \omega_e) = 0.0021$. The rotational constant B_e is calculated from the estimated bond distance. The value of ω_e is calculated from the Morse potential function. The moment of inertia is $42.1488 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952. The electronic levels and quantum weights are estimated to be the same as those of $\text{ZrF}(g)$.

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	2.328	73.923	73.923	INFINITE
100	7.404	54.620	70.843	1.422	74.082	69.599	152.104
200	8.282	60.063	74.222	0.832	74.261	65.297	71.277
298	8.650	63.443	76.442	0.000	74.000	61.286	44.253
300	8.624	63.496	76.493	-0.016	71.988	61.220	44.598
400	8.776	66.000	78.743	0.887	68.116	58.414	31.916
500	8.875	67.969	80.430	1.769	67.906	56.011	24.442
600	8.973	69.594	81.640	2.462	67.427	53.454	19.543
700	9.066	70.987	82.495	3.165	67.027	51.335	16.028
800	9.215	72.209	83.009	4.000	67.161	49.055	13.401
900	9.353	73.302	83.293	5.004	66.874	46.808	11.367
1000	9.482	74.295	83.565	6.250	66.582	44.595	9.746
1100	9.626	75.204	83.826	7.304	66.270	42.411	8.429
1200	9.751	76.069	84.075	8.275	65.991	40.307	7.341
1300	9.865	76.834	84.314	9.256	65.725	38.249	6.430
1400	9.968	77.569	84.544	10.248	65.479	36.204	5.652
1500	10.058	78.260	84.760	11.249	65.251	34.170	4.979
1600	10.136	78.911	84.961	12.259	65.048	32.147	4.391
1700	10.203	79.528	85.148	13.276	64.818	30.136	3.874
1800	10.260	80.113	85.319	14.299	64.600	28.134	3.416
1900	10.308	80.669	85.472	15.328	64.371	26.144	3.007
2000	10.348	81.199	85.618	16.360	64.165	24.163	2.640
2100	10.380	81.704	85.750	17.397	63.871	22.192	2.310
2200	10.407	82.188	85.868	18.436	63.596	20.206	2.027
2300	10.428	82.651	85.974	19.478	63.339	18.693	1.776
2400	10.446	83.095	86.069	20.522	63.094	16.987	1.547
2500	10.459	83.522	86.155	21.567	62.861	15.290	1.337
2600	10.470	83.932	86.235	22.614	62.639	13.602	1.143
2700	10.479	84.327	86.304	23.661	62.422	11.921	0.945
2800	10.485	84.709	86.364	24.709	62.210	10.249	0.800
2900	10.491	85.077	86.415	25.757	62.003	8.588	0.687
3000	10.495	85.432	86.457	26.807	61.794	6.926	0.595
3100	10.498	85.777	86.490	27.857	61.591	5.276	0.527
3200	10.501	86.110	86.513	28.907	61.394	3.633	0.484
3300	10.504	86.433	86.527	29.957	61.202	1.995	0.432
3400	10.506	86.747	86.537	31.008	61.014	0.364	0.379
3500	10.508	87.051	86.542	32.058	60.831	-1.259	0.322
3600	10.511	87.347	86.548	33.109	60.652	-2.877	0.265
3700	10.513	87.635	86.554	34.161	60.478	-4.490	0.205
3800	10.516	87.916	86.559	35.212	60.308	-6.103	0.145
3900	10.519	88.189	86.564	36.264	60.141	-7.716	0.082
4000	10.522	88.455	86.568	37.316	59.978	-9.329	0.014
4100	10.525	88.715	86.572	38.368	59.818	-10.942	0.000
4200	10.529	88.969	86.576	39.421	59.661	-12.555	0.000
4300	10.533	89.217	86.580	40.474	59.506	-14.168	0.000
4400	10.537	89.459	86.583	41.527	59.353	-15.781	0.000
4500	10.542	89.698	86.586	42.581	59.202	-17.394	0.000
4600	10.546	89.927	86.589	43.636	59.052	-19.007	0.000
4700	10.552	90.154	86.592	44.691	58.903	-20.620	0.000
4800	10.557	90.377	86.594	45.746	58.756	-22.233	0.000
4900	10.563	90.594	86.596	46.801	58.611	-23.846	0.000
5000	10.568	90.808	86.598	47.856	58.468	-25.459	0.000
5100	10.574	91.017	86.600	48.911	58.326	-27.072	0.000
5200	10.581	91.222	86.602	49.966	58.185	-28.685	0.000
5300	10.587	91.424	86.604	51.021	58.045	-30.298	0.000
5400	10.593	91.622	86.606	52.076	57.906	-31.911	0.000
5500	10.600	91.816	86.608	53.131	57.768	-33.524	0.000
5600	10.607	92.008	86.610	54.186	57.631	-35.137	0.000
5700	10.614	92.195	86.612	55.241	57.495	-36.750	0.000
5800	10.620	92.380	86.614	56.296	57.360	-38.363	0.000
5900	10.627	92.562	86.616	57.351	57.225	-40.000	0.000
6000	10.634	92.740	86.618	58.406	57.090	-41.637	0.000

Sept. 30, 1964; June 30, 1970

Bromine (Br₂)

(Reference State) Mol. Wt. = 159.832

T, K.	C _p ^a	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S^\circ}$	$-(F^\circ - H^\circ_{298})/T$	$\frac{\text{kcal. mole}^{-1}}{\Delta H^\circ_f}$	ΔF°_f	Log K _p
0	.000	.000	INFINITE	5.859	.000	.000
100	10.419	12.670	64.760	5.191	.000	.000
200	12.851	20.498	40.998	4.020	.000	.000
298	16.090	36.384	36.384	.000	.000	.000
300	16.077	36.496	36.384	.033	.000	.000
400	8.775	61.203	40.520	8.273	.000	.000
500	8.857	63.172	44.860	9.156	.000	.000
600	8.898	64.791	48.051	10.044	.000	.000
700	8.894	67.167	50.943	10.937	.000	.000
800	8.970	67.363	52.573	11.833	.000	.000
900	8.992	68.421	54.276	12.731	.000	.000
1000	9.011	69.370	55.739	13.631	.000	.000
1100	9.027	70.229	57.018	14.533	.000	.000
1200	9.052	71.745	58.152	15.436	.000	.000
1300	9.056	71.740	59.169	16.341	.000	.000
1400	9.069	72.411	60.092	17.247	.000	.000
1500	9.082	73.037	60.934	18.155	.000	.000
1600	9.094	73.424	61.700	19.064	.000	.000
1700	9.106	74.574	62.426	19.974	.000	.000
1800	9.118	74.696	63.084	20.885	.000	.000
1900	9.128	75.190	63.717	21.797	.000	.000
2000	9.141	75.658	64.303	22.711	.000	.000
2100	9.152	76.104	64.854	23.625	.000	.000
2200	9.163	76.530	65.375	24.541	.000	.000
2300	9.174	76.938	65.869	25.456	.000	.000
2400	9.185	77.329	66.339	26.376	.000	.000
2500	9.196	77.704	66.786	27.295	.000	.000
2600	9.206	78.065	67.213	28.215	.000	.000
2700	9.217	78.422	67.621	29.135	.000	.000
2800	9.228	78.748	68.013	30.048	.000	.000
2900	9.238	79.072	68.388	30.962	.000	.000
3000	9.249	79.385	68.750	31.906	.000	.000
3100	9.260	79.689	69.098	32.832	.000	.000
3200	9.270	79.983	69.433	33.756	.000	.000
3300	9.281	80.268	69.757	34.666	.000	.000
3400	9.291	80.545	70.071	35.614	.000	.000
3500	9.302	80.815	70.374	36.544	.000	.000
3600	9.312	81.077	70.667	37.467	.000	.000
3700	9.323	81.332	70.952	38.406	.000	.000
3800	9.333	81.581	71.229	39.339	.000	.000
3900	9.344	81.824	71.497	40.273	.000	.000
4000	9.354	82.060	71.758	41.208	.000	.000
4100	9.365	82.291	72.012	42.144	.000	.000
4200	9.375	82.517	72.260	43.081	.000	.000
4300	9.386	82.738	72.501	44.019	.000	.000
4400	9.396	82.954	72.736	44.958	.000	.000
4500	9.406	83.165	72.965	45.898	.000	.000
4600	9.417	83.372	73.189	46.839	.000	.000
4700	9.427	83.575	73.408	47.781	.000	.000
4800	9.438	83.773	73.622	48.725	.000	.000
4900	9.448	83.968	73.831	49.669	.000	.000
5000	9.458	84.159	74.036	50.614	.000	.000
5100	9.469	84.346	74.236	51.561	.000	.000
5200	9.479	84.530	74.432	52.508	.000	.000
5300	9.490	84.711	74.625	53.456	.000	.000
5400	9.500	84.888	74.813	54.406	.000	.000
5500	9.510	85.063	74.998	55.356	.000	.000
5600	9.521	85.234	75.179	56.308	.000	.000
5700	9.531	85.403	75.357	57.261	.000	.000
5800	9.542	85.569	75.532	58.214	.000	.000
5900	9.552	85.732	75.703	59.169	.000	.000
6000	9.562	85.892	75.872	60.125	.000	.000

September 30, 1961

Br₂

MOL. WT. = 159.832

(REFERENCE STATE)

0°K to 285.90°K Crystal
 285.90°K to 332.82°K Liquid
 332.82°K to 6000°K Ideal Diatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal and Liquid.

Low temperature thermal data have been adopted from the work of D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. **80**, 4129 (1958)]. References to older work are given by Hildenbrand, et al., and are not given any weight here.

Heat of Melting and Melting Point.

Hildenbrand, et al., (loc. cit.) report $T_m = 285.90^\circ\text{K}$ and $\Delta H_m = 2.527 \text{ kcal. mole}^{-1}$.

Heat of Sublimation, Ideal Gas Functions.

See ideal gas tables for details.

T, °K.	cal. mole ⁻¹ deg. ⁻¹		-(F°-H° ₂₉₈)/T		H°-H° ₂₉₈		kcal. mole ⁻¹		Log K _P
	C _p ^o	S°			H°-H° ₂₉₈	ΔH _f ^o	ΔH _f ^o	ΔF _f ^o	
0									
100									
200									
298	18.090	36.384	36.384		.000	.000	.000	.000	.000
300	18.077	36.406	36.384		.033	.000	.000	.000	.000
400	18.060	41.676	37.091		1.834	- 6.439	1.372	- .789	.000
500	18.000	45.692	38.425		3.634	- 5.522	3.216	- 1.406	.000
600	18.000	48.974	39.918		5.434	- 4.610	4.680	- 1.777	.000
700	18.000	51.749	41.415		7.234	- 3.703	6.390	- 1.995	.000
800	18.000	54.153	42.860		9.034	- 2.799	7.769	- 2.122	.000
900	18.000	56.273	44.235		10.834	- 1.897	9.036	- 2.194	.000
1000	18.000	58.169	45.535		12.634	- .997	10.204	- 2.230	.000

BROMINE (Br₂)

(LIQUID)

MOL. WT. = 159.832

ΔH_f^o 298 = 0

ΔH_m^o = 2.527 kcal. mole⁻¹

ΔH_v^o = 7.084 kcal. mole⁻¹

T_m = 265.90°K.

T_b = 332.62°K.

Heat of Formation.

The heat of formation at 298.15°K is zero by definition.

Heat Capacity.

The liquid heat capacity data of D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. 80, 4129 (1958)] were extrapolated to a constant value of 18.0 cal. mole⁻¹ deg.⁻¹

Entropy.

The entropy is that given by Hildenbrand, et al., (loc. cit.) for liquid bromine at 298.15°K.

Vaporization.

See ideal gas tables for details.

Bromine, Diatomic (Br₂)

(Ideal Gas) Mol. Wt. = 159.832

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	7.000	INFINITE	2.324	10.922	INFINITE	
100	6.385	58.000	1.650	10.922	3.721	15.669
200	6.265	58.070	1.056	10.922	3.721	15.669
298	6.616	58.647	.000	7.387	3.749	4.549
300	6.620	58.704	.016	7.376	3.750	4.549
400	6.775	61.204	58.987	.000	.000	.000
500	6.857	63.171	1.789	.000	.000	.000
600	6.908	64.791	60.363	.000	.000	.000
700	6.944	66.167	61.096	.000	.000	.000
800	6.970	67.363	61.806	.000	.000	.000
900	6.992	68.421	62.484	.000	.000	.000
1000	7.011	69.369	63.126	.000	.000	.000
1100	7.027	70.229	63.733	.000	.000	.000
1200	7.042	71.015	64.307	.000	.000	.000
1300	7.056	71.739	64.852	.000	.000	.000
1400	7.069	72.411	65.368	.000	.000	.000
1500	7.082	73.037	65.859	.000	.000	.000
1600	7.094	73.624	66.326	.000	.000	.000
1700	7.106	74.175	66.771	.000	.000	.000
1800	7.118	74.696	67.197	.000	.000	.000
1900	7.129	75.190	67.605	.000	.000	.000
2000	7.141	75.656	67.996	.000	.000	.000
2100	7.152	76.104	68.372	.000	.000	.000
2200	7.163	76.530	68.733	.000	.000	.000
2300	7.174	76.938	69.081	.000	.000	.000
2400	7.185	77.329	69.416	.000	.000	.000
2500	7.196	77.704	69.740	.000	.000	.000
2600	7.206	78.065	70.054	.000	.000	.000
2700	7.217	78.412	70.357	.000	.000	.000
2800	7.228	78.748	70.651	.000	.000	.000
2900	7.238	79.072	70.935	.000	.000	.000
3000	7.249	79.385	71.212	.000	.000	.000
3100	7.260	79.688	71.480	.000	.000	.000
3200	7.270	79.983	71.742	.000	.000	.000
3300	7.281	80.268	71.996	.000	.000	.000
3400	7.291	80.545	72.243	.000	.000	.000
3500	7.302	80.815	72.484	.000	.000	.000
3600	7.312	81.077	72.719	.000	.000	.000
3700	7.323	81.332	72.949	.000	.000	.000
3800	7.333	81.581	73.172	.000	.000	.000
3900	7.344	81.823	73.391	.000	.000	.000
4000	7.354	82.060	73.605	.000	.000	.000
4100	7.365	82.291	73.814	.000	.000	.000
4200	7.375	82.517	74.019	.000	.000	.000
4300	7.386	82.738	74.219	.000	.000	.000
4400	7.396	82.954	74.415	.000	.000	.000
4500	7.406	83.165	74.607	.000	.000	.000
4600	7.417	83.372	74.795	.000	.000	.000
4700	7.427	83.574	74.980	.000	.000	.000
4800	7.438	83.773	75.161	.000	.000	.000
4900	7.448	83.968	75.339	.000	.000	.000
5000	7.458	84.159	75.513	.000	.000	.000
5100	7.469	84.346	75.685	.000	.000	.000
5200	7.479	84.530	75.853	.000	.000	.000
5300	7.490	84.711	76.018	.000	.000	.000
5400	7.500	84.888	76.181	.000	.000	.000
5500	7.510	85.063	76.341	.000	.000	.000
5600	7.521	85.234	76.498	.000	.000	.000
5700	7.531	85.403	76.653	.000	.000	.000
5800	7.542	85.569	76.805	.000	.000	.000
5900	7.552	85.732	76.955	.000	.000	.000
6000	7.562	85.892	77.103	.000	.000	.000

BROMINE, DIATOMIC (Br₂) (IDEAL GAS)

ΔH_f[°] = 10.922 ± .030 kcal. mole⁻¹
 Ground State = ¹Σ_g⁺
 ΔH_f[°] 298 = 7.387 kcal. mole⁻¹
 S₂₉₈[°] = 58.647 cal. deg.⁻¹ mole⁻¹

ΔG_f[°] = 1.070 cal. mole⁻¹
 ΔG_f[°] 298 = 0.000275 cal. mole⁻¹
 σ = 2

Thermodynamic Functions.

Spectroscopic data listed by O. Herzberg [Spectra of Diatomic Molecules, D. Van Nostrand Company, New York, 1950] have been adjusted to the isotopic mixture (50.52% Br-79, 49.48% Br-81). The calculated functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards **55**, 147 (1955)] who used the same spectroscopic data.

Heat of Formation.

The heat of vaporization at 298.15°K was reported by D. L. Hildenbrand, W. R. Kramer, R. A. McDonald, and D. R. Stull [J. Am. Chem. Soc. **80**, 4129 (1958)] as 7.387 ± .027 kcal. mole⁻¹, which calculates to 10.922 kcal. mole⁻¹ at 0°K. Vapor pressure data from the literature and the above adopted thermodynamic functions for liquid and gas were used to calculate ΔH_f[°] as follows:

Liquid range

Fischer and Bingle¹ (298° to 389°K) 10.905 ± .019
 Ramsay and Young² (265° to 329°K) 10.924 ± .008
 Scheffer and Voogd³ (270° to 362°K) 10.906 ± .018

Solid range

Frey and Gregory⁴ (177° to 195°K) 10.941 ± .029
 Henglein, Rosenberg, and Muchlinski⁵ (177° to 241°K) 10.912 ± .034
 Ramsay and Young² (258° to 262°K) 10.966 ± .014
 Scheffer and Voogd³ (253° to 264°K) 10.961 ± .014

For the liquid range, the data of Fischer and Bingle as well as that of Scheffer and Voogd show a decided decrease with increasing temperature, starting at about 10.94 and decreasing to 10.87 kcal. mole⁻¹. The data of Ramsay and Young show only a small trend with temperature and are in good agreement with the calorimetric value. For the solid range, the data are too scattered to be conclusive. The calorimetric value, as supported by Ramsay and Young, is adopted as the heat of formation of the ideal gas.

References to Vapor Pressure Data

- (1) J. Fischer and J. Bingle, J. Am. Chem. Soc. **77**, 6511 (1955).
- (2) J. Ramsay and J. Young, J. Chem. Soc. **43**, 453 (1896).
- (3) F. E. C. Scheffer and M. Voogd, Rec. trav. chim. **45**, 214 (1926).
- (4) M. B. Frey and N. W. Gregory, J. Am. Chem. Soc. **82**, 1068 (1960).
- (5) F. A. Henglein, G. von Rosenberg, and A. Muchlinski, Z. Physik. **11**, 1 (1922).



Iron Dibromide (FeBr₂)
(Crystal) GFW = 215.665

IRON DIBROMIDE (FeBr₂)

(CRYSTAL)

GFW = 215.665

T, °K	Cp	gkcal/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100						
200						
298	19.176	33.620	13.620	+0.00	- 56.729	41.584
300	19.186	33.739	13.739	- 0.035	- 56.712	41.314
400	19.718	39.331	34.379	- 1.981	- 66.429	29.687
500	20.250	43.788	38.830	- 3.979	- 65.089	22.451
600	20.782	47.527	42.576	- 6.031	- 65.555	17.658
700	21.314	50.864	45.913	- 8.033	- 65.033	14.290
800	21.846	53.809	48.858	- 10.035	- 64.511	11.750
900	22.378	56.409	51.458	- 12.609	- 64.301	9.773
1000	22.910	58.784	53.833	- 14.869	- 64.084	8.214
1100	23.442	61.003	55.979	- 17.167	- 64.053	6.840
1200	23.974	63.009	57.985	- 19.501	- 63.929	5.683
1300	24.506	64.784	59.760	- 21.981	- 63.053	4.994
1400	25.038	66.841	61.817	- 24.459	- 62.320	4.242
1500	25.570	68.586	63.562	- 26.989	- 61.551	3.597

ΔHf° = Unknown

ΔH°_{298.15} = -59.5 ± 0.5 kcal/mol

ΔHt° = 0.1 kcal/mol

ΔHe° = [12 ± 3] kcal/mol

ΔHs°_{298.15} (to monomer) = [49.6] kcal/mol

ΔHs°_{298.15} (to dimer) = [58.5] kcal/mol

Heat of Formation.

The heats of solution of Fe(c), Br₂(l) and FeBr₂(c) in Br₂-KBr aqueous solution were measured by use of ice calorimeter by (1) W. Heber and A. Woerner, Z. Elektrochem. 40, 287 (1934). From the results obtained the heat of formation for FeBr₂(c) was reported to be -59.87 kcal/mol.

The heats of solution of FeBr₂(c) in water were determined by (2) J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952) and (3) P. Paoletti, Trans. Faraday Soc. 51, 219 (1955), to be -20.1 ± 0.4 and -20.08 ± 0.08 kcal/mol, respectively. Using ΔHf°_{298.15} = -29.05 and -21.3 kcal/mol for Br⁻(aq) and Fe²⁺(aq), the corresponding heats of formation for FeBr₂(c) were calculated as -59.3 and -59.34 kcal/mol. The value of ΔHf°_{298.15} (Br⁻, aq) was taken from "Selected Values of Chemical Thermodynamic Properties," Part I, Technical Note 270-1, by D. D. Wagman, W. H. Evans, I. Halow, Y. B. Farkner, S. M. Bailey and R. H. Schumm, National Bureau of Standards, 1965. The value of ΔHf°_{298.15} (Fe²⁺, aq) was derived from heats of solution and formation for FeCl₂(c) using ΔHf°_{298.15}(Cl⁻, aq) = -39.562 kcal/mol from the same source as ΔHf°_{298.15} (Br⁻, aq)

The value of ΔHf°_{298.15} (FeBr₂, c) adopted is -59.5 ± 0.5 kcal/mol.

Heat Capacity and Entropy.

The heat capacities, 323-633°K, were measured by N. W. Gregory and H. E. O'Neal, J. Am. Chem. Soc. 81, 2649 (1959). Those for temperatures below 323°K and above 633°K were estimated by linear extrapolation. Low temperature heat capacities, 12-110°K, were reported by G. Miljutin and N. Nachimowitsch, Phys. Trans. Ukrain. Acad. Sci. 9, 71 (1940). However, these data are inadequate for obtaining an accurate entropy at 298°K. The adopted S°_{298.15} value was reported by N. W. Gregory and R. O. McLaren, J. Phys. Chem. 59, 110 (1955). It was obtained from E. F. Westrum, Jr., University of Michigan, Ann Arbor, Michigan, by private communication. A magnetic transition at 11°K was reported by H. Bizette, C. Terrier, and B. Tsal, Compt. rend. 245, 507 (1957).

Transition Data.

Tt and ΔHt° were taken from N. W. Gregory and H. E. O'Neal, loc. cit.

Melting Data.

Tm adopted was reported by R. O. McLaren and N. W. Gregory, J. Phys. Chem. 59, 184 (1955). The value was calculated from the vapor pressure equations and is slightly above the previously reported value, 684°C (957°K), by A. Ferrari, A. Celeri and F. Giorgi, Atti accad. Nazl. Lincei 9, 782, 1134 (1929). However, it agrees well with 962 ± 2°K obtained by the differential thermocouple cooling curve analysis by the same authors. The ΔHm° value was estimated from the vapor pressure data in order to obtain good agreement between the second and third law heats of vaporization. See the FeBr₂(g) table for details.

Heat of Sublimation.

ΔHs°_{298.15} (to monomer) is calculated as the difference between ΔHf°_{298.15} for FeBr₂(g) and FeBr₂(c). ΔHs°_{298.15} (to dimer) is calculated as the difference between those for Fe₂Br₄(g) and 2 FeBr₂(c).

Sept. 30, 1966





Iron Dibromide (FeBr₂)

(Liquid) GFW = 215.665

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	25.500	40.483	40.483	0.000	-50.431	-49.706	36.436
300	25.500	40.541	40.483	0.047	-50.428	-49.702	36.208
400	25.500	40.677	40.483	2.957	-50.744	-48.108	26.285
500	25.500	53.667	43.372	5.147	-55.752	-46.065	20.135
600	25.500	56.316	45.487	7.697	-54.820	-44.217	16.106
700	25.500	62.247	47.608	10.267	-53.952	-42.519	13.215
800	25.500	65.652	49.655	15.497	-52.480	-39.454	9.581
900	25.500	67.342	51.645	17.867	-51.597	-38.035	8.313
1000	25.500	73.772	55.184	20.447	-51.724	-36.647	7.281
1100	25.500	75.991	56.827	22.597	-51.750	-35.259	6.479
1200	25.500	78.922	58.853	25.413	-51.613	-32.776	5.117
1300	25.500	81.681	61.250	28.097	-49.613	-32.776	4.804
1400	25.500	83.327	62.579	30.667	-48.824	-31.602	4.163
1500	25.500	84.873	63.845	33.197	-48.052	-30.479	3.142
1600	25.500	86.705	65.071	35.767	-47.597	-29.368	2.837
1700	25.500	88.017	66.319	40.687	-46.978	-27.146	2.837
1800	25.500			43.397	-49.398	-25.962	

IRON DIBROMIDE (FeBr₂)

(LIQUID)

GFW = 215.665

$$\Delta H_f^{298.15} = [-50.431] \text{ kcal/mol}$$

$$\Delta H_m = [12 + 3] \text{ kcal/mol}$$

$$\Delta H_v = [29.4] \text{ kcal/mol}$$

$$S_{298.15}^{298.15} = [40.483] \text{ gibbs/mol}$$

$$T_m = 964^\circ\text{K}$$

$$T_b = [1207]^\circ\text{K}$$

Heat of Formation.

The value of $\Delta H_f^{298.15}$ (l) was obtained from $\Delta H_f^{298.15}$ (c) by adding ΔH_m° and the difference between H_m° and $H_{298.15}^\circ$ for FeBr₂(c) and FeBr₂(l).

Heat Capacity and Entropy.

The heat capacity was assumed to be constant in the temperature range from 298.15 to 2000°K and was estimated on the basis of 8.5 gibbs/g-atom. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See FeBr₂(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the total pressure of FeBr₂(g) and Fe₂Br₃(g) over FeBr₂(l) equals one atmosphere. Based on the vapor composition and the values of ΔH_v° for both the monomer and dimer at T_b, the heat of vaporization is derived.



Iron Dibromide (FeBr₂)
(Ideal Gas) GFW = 215.665



OPW = 215.665

(IDEAL GAS)

IRON DIBROMIDE (FeBr₂)

Point Group [D_{2h}]
S_{298.15} = [80.6] gibbs/mol
ΔH_{f,0}^o = [-6.8 ± 0.5] kcal/mol
ΔH_{f,298.15}^o = [-9.9 ± 0.5] kcal/mol

Electronic Levels and Quantum Weights

ε _i , cm ⁻¹	g _i
-----------------------------------	----------------

0	[10]
[4450]	[10]
[6900]	[5]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹

Bond Distances: Fe-Br = [2.24] Å

Bond Angles: Br-Fe-Br = [180]^o

Rotational Constant: B₀ = [0.02102] cm⁻¹

Heat of Formation.

The vapor pressures of FeBr₂(c) and FeBr₂(l) have been measured in the temperature range from 623.15 to 982.15^oK by several investigators. Using the reported data the corresponding enthalpy changes (ΔH^o) for the reactions (A) FeBr₂(c) = FeBr₂(g) and (B) FeBr₂(l) = FeBr₂(g) were evaluated by both the second and third law methods. The results obtained are presented in the following table. The values of ΔH_{f,298.15}^o for FeBr₂(g) are calculated based on the third law values for ΔH_{f,298.15}^o. The value of ΔH_{f,298.15}^o for FeBr₂(g) adopted is -9.9 ± 0.5 kcal/mol.

Reference	Reaction	Temperature, ^o K	Method	ΔH _{f,298.15} ^o , kcal/mol	Drift	ΔH _{f,298.15} ^o , kcal/mol
1	(A)	673.15- 982.15	Transpiration	50.04	- 0.75	- 9.94
1	(A)	823.15- 718.15	Effusion	49.21	+ 1.37	- 9.36
1	(A)	873.15- 962.15	Diaphragm	59.20	-10.09	- 9.65
2	(A)	870.0 - 740.0	Torsion - Effusion	49.11	+ 0.71	- 9.91
1	(B)	982.15-1182.15	Diaphragm	39.77	+ 0.93	- 9.59

1. R. O. MacLaren and N. W. Gregory, J. Phys. Chem. **59**, 184 (1955).
2. R. J. Sime and N. W. Gregory, J. Phys. Chem. **64**, 86 (1960).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The electronic levels and quantum weights were estimated by comparison with those for FeCl₂(g) reported by C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966). The bond distance was estimated by L. Brewer, O. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963). The vibrational frequencies were estimated in order to obtain good agreement between the second and third law heats of sublimation and vaporization. The moment of inertia is 1.53146 x 10⁻³⁷ g cm².

Sept. 30, 1966



T, ^o K	Cp ^o	gibbs/mol S ^o - (G ^o - H _{298.15} ^o)/T	kcal/mol H ^o - H _{298.15} ^o	ΔH ^o	ΔG ^o	Log Kp
0	+0.00	INFINITE	- 3.829	- 6.795	- 6.795	INFINITE
100	12.721	65.559	2.760	- 6.497	- 11.619	25.394
200	14.081	74.890	1.406	- 6.736	- 16.674	18.220
298	14.446	80.604	+0.00	- 9.900	- 21.138	15.494
300	14.450	80.604	- 0.077	- 9.917	- 21.206	15.460
400	14.669	86.891	1.466	- 17.332	- 23.454	12.814
500	14.752	88.174	2.259	- 17.410	- 24.977	10.917
600	14.802	90.869	4.436	- 17.550	- 26.479	9.645
700	14.842	93.153	7.918	- 17.750	- 27.952	8.727
800	14.874	95.064	11.686	- 18.000	- 29.300	8.048
900	14.939	96.894	15.895	- 18.411	- 30.700	7.477
1000	15.004	98.472	18.079	- 18.970	- 32.138	7.024
1100	15.080	99.905	18.090	- 19.743	- 33.413	6.639
1200	15.164	101.251	18.047	- 20.797	- 34.637	6.309
1300	15.254	102.526	18.000	- 22.080	- 35.800	6.024
1400	15.344	103.752	18.015	- 23.563	- 36.963	5.775
1500	15.435	104.933	18.049	- 25.242	- 38.114	5.558
1600	15.523	106.062	18.046	- 27.172	- 39.287	5.366
1700	15.609	107.146	18.047	- 29.360	- 40.467	5.195
1800	15.695	108.180	18.047	- 31.700	- 41.646	5.040
1900	15.771	109.179	18.047	- 34.199	- 42.824	4.875
2000	15.812	109.129	18.047	- 36.847	- 44.003	4.724
2100	15.865	109.902	18.047	- 39.643	- 45.182	4.586
2200	15.928	110.549	18.047	- 42.586	- 46.361	4.458
2300	15.998	111.074	18.047	- 45.686	- 47.540	4.337
2400	16.062	111.482	18.047	- 48.943	- 48.719	4.222
2500	16.120	111.774	18.047	- 52.358	- 49.898	4.117
2600	16.172	111.956	18.047	- 55.930	- 51.077	4.031
2700	16.219	112.029	18.047	- 59.660	- 52.256	3.955
2800	16.261	112.094	18.047	- 63.550	- 53.435	3.889
2900	16.298	112.152	18.047	- 67.599	- 54.614	3.833
3000	16.330	112.204	18.047	- 71.808	- 55.793	3.786
3100	16.356	112.252	18.047	- 76.177	- 56.972	3.747
3200	16.377	112.296	18.047	- 80.706	- 58.151	3.714
3300	16.393	112.336	18.047	- 85.395	- 59.330	3.686
3400	16.405	112.372	18.047	- 90.244	- 60.509	3.662
3500	16.413	112.404	18.047	- 95.253	- 61.688	3.641
3600	16.417	112.432	18.047	- 100.422	- 62.867	3.622
3700	16.418	112.456	18.047	- 105.751	- 64.046	3.606
3800	16.416	112.476	18.047	- 111.240	- 65.225	3.593
3900	16.411	112.492	18.047	- 116.889	- 66.404	3.582
4000	16.403	112.504	18.047	- 122.698	- 67.583	3.572
4100	16.392	112.512	18.047	- 128.667	- 68.762	3.563
4200	16.378	112.516	18.047	- 134.796	- 69.941	3.555
4300	16.361	112.516	18.047	- 141.085	- 71.120	3.548
4400	16.341	112.512	18.047	- 147.534	- 72.300	3.542
4500	16.318	112.504	18.047	- 154.143	- 73.479	3.537
4600	16.292	112.492	18.047	- 160.912	- 74.658	3.533
4700	16.263	112.476	18.047	- 167.841	- 75.837	3.530
4800	16.231	112.456	18.047	- 174.930	- 77.016	3.527
4900	16.196	112.432	18.047	- 182.179	- 78.195	3.524
5000	16.159	112.404	18.047	- 189.588	- 79.374	3.521
5100	16.119	112.372	18.047	- 197.157	- 80.553	3.518
5200	16.076	112.336	18.047	- 204.886	- 81.732	3.515
5300	16.030	112.296	18.047	- 212.775	- 82.911	3.512
5400	15.981	112.252	18.047	- 220.824	- 84.090	3.509
5500	15.929	112.204	18.047	- 229.033	- 85.269	3.506
5600	15.874	112.152	18.047	- 237.392	- 86.448	3.503
5700	15.816	112.094	18.047	- 245.911	- 87.627	3.500
5800	15.755	112.029	18.047	- 254.590	- 88.806	3.497
5900	15.691	111.956	18.047	- 263.429	- 89.985	3.494
6000	15.614	111.874	18.047	- 272.428	- 91.164	3.491

Mercury Dibromide (HgBr₂)

INTERIM TABLE

(Crystal) Mol. Wt. = 360.442

T, °K.	C _p ^o	$\int_0^T C_p^o dT$ cal. mole ⁻¹ deg. ⁻¹	$\int_0^T C_p^o dT$ S ^o	$-(F^o - H_{298}^o)/T$	ΔH_f^o kcal. mole ⁻¹	ΔF_f^o	Log K _p
0							
100							
200							
298	18.000	40.706	40.706	.000	40.500	36.371	26.659
300	18.013	40.817	40.706	.033	40.512	36.385	26.674
400	18.714	40.095	40.491	1.070	40.577	36.437	26.706
500	19.418	50.347	42.794	3.776	47.205	30.007	13.116
600	20.114	53.648	44.361	5.752	46.766	26.509	9.682
700	20.814	57.101	45.960	7.799	46.287	21.717	6.760
800	21.514	60.614	47.214	9.812	45.771	16.886	4.244
900	22.214	64.201	48.034	12.002	45.221	10.886	2.644
1000	22.914	67.877	50.519	14.358	44.542	5.613	1.227
1100	23.614	71.604	51.926	16.864	43.745	.428	.085
1200	24.314	75.379	53.276	19.501	42.826	4.670	.850
1300	25.014	79.204	54.581	22.261	41.789	10.693	1.629
1400	25.714	83.079	55.841	25.134	40.639	16.454	2.414
1500	26.414	86.904	57.056	28.099	39.386	21.954	3.204

Br₂Hg

MERCURY DIBROMIDE (HgBr₂) (crystal)

Mol. Wt. = 360.442
 ΔH_f^o 298.15 = -40.500 ± 0.5 kcal. mole⁻¹
 $S_{298.15}^o$ = [40.706] ± 1.5 cal. deg. ⁻¹ mole⁻¹
 T_m = 514°K
 ΔH_m = 4.280 ± 0.08 kcal. mole⁻¹

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1962).

Heat Capacity and Entropy. C_p was assumed to be a linear function of temperature and was fitted to the data of M. Guinchant, Comp. Rend. 145, 320 (1907) and G. J. Janz and J. Goodkin, J. Phys. Chem. 63, 1975 (1959). The entropy was estimated by adjusting its value until the melting, sublimation and vaporization data were in agreement.

Melting. T_m was taken from National Bureau of Standards (U.S.) Circular 500 (loc. cit.). ΔH_m was given by G. J. Janz and J. Goodkin (loc. cit.).

Br₂Hg

INTERIM TABLE

(Liquid) Mol. Wt. = 360.442

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _f
0						
100						
200						
298	16,000	46,797	.000	37,158	34,885	25.541
300	16,013	46,908	.033	37,170	34,830	25.372
400	24,400	51,091	2,205	43,659	32,408	17,816
500	24,400	56,536	4,645	42,994	29,891	13,065
600	24,400	62,984	7,085	42,091	27,356	9,964
700	24,400	69,432	9,525	39,712	24,826	7,370
800	24,400	75,880	11,965	37,172	22,296	5,170
900	24,400	82,328	14,405	34,126	19,562	3,541
1000	24,400	88,776	16,845	31,083	16,736	2,263
1100	24,400	95,224	19,285	28,042	13,902	1,236
1200	24,400	101,672	21,725	25,002	11,068	.632
1300	24,400	108,120	24,165	21,962	8,234	.192
1400	24,400	114,568	26,605	18,926	5,397	-.1678
1500	24,400	121,016	29,045	15,891	2,561	-.7367

March 31, 1962

MERCURY DIBROMIDE (HgBr₂)

(Liquid)

Mol. Wt. = 360.442

ΔH_f° 298.15 = -37.158 ± 0.58 kcal. mole⁻¹S° 298.15 = (46.797) ± 1.5 cal. deg.⁻¹ mole⁻¹T_m = 514°KΔH_m = 4.280 ± 0.08 kcal. mole⁻¹T_b = 592°KΔH_v = 14.148 ± 0.25 kcal. mole⁻¹Heat of Formation. Calculated from ΔH_f°(c).

Heat Capacity and Entropy. C_p obtained from the data of G. J. Janz and J. Goodkin, *J. Phys. Chem.* **53**, 1975 (1959) in the range 507-544°K, it was assumed constant above and below this value.

A glass type transition was assumed at 343°K below which the heat capacity was equal to that of the crystal. The entropy was obtained from S°(c), the entropy of fusion and the estimated heat capacity.

Melting and Vaporization. T_m and T_b were taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952). ΔH_m was given by G. J. Janz and J. Goodkin (loc. cit.) and ΔH_v was obtained from the data of E. B. R. Pridoux, *J. Chem. Soc. (London)* **97**, 2032 (1910) and F. M. G. Johnson, *J. Amer. Chem. Soc.* **33**, 777 (1911).

Mercury Dibromide (HgBr₂)

(Ideal Gas) Mol. Wt. = 360.442

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	12.900	41.900	IMFIMIF	2.742	16.074	16.074	IMFIMIF
200	12.240	41.740	10.000	1.156	16.156	16.156	10.000
300	12.000	41.500	10.000	1.156	16.156	16.156	10.000
400	11.716	41.216	10.000	1.156	16.156	16.156	10.000
500	11.412	40.912	10.000	1.156	16.156	16.156	10.000
600	11.088	40.588	10.000	1.156	16.156	16.156	10.000
700	10.744	40.244	10.000	1.156	16.156	16.156	10.000
800	10.380	39.880	10.000	1.156	16.156	16.156	10.000
900	10.000	39.500	10.000	1.156	16.156	16.156	10.000
1000	9.612	39.112	10.000	1.156	16.156	16.156	10.000
1100	9.216	38.716	10.000	1.156	16.156	16.156	10.000
1200	8.812	38.312	10.000	1.156	16.156	16.156	10.000
1300	8.400	37.900	10.000	1.156	16.156	16.156	10.000
1400	7.980	37.480	10.000	1.156	16.156	16.156	10.000
1500	7.552	37.052	10.000	1.156	16.156	16.156	10.000
1600	7.116	36.616	10.000	1.156	16.156	16.156	10.000
1700	6.672	36.172	10.000	1.156	16.156	16.156	10.000
1800	6.220	35.720	10.000	1.156	16.156	16.156	10.000
1900	5.760	35.260	10.000	1.156	16.156	16.156	10.000
2000	5.292	34.792	10.000	1.156	16.156	16.156	10.000
2100	4.816	34.316	10.000	1.156	16.156	16.156	10.000
2200	4.332	33.832	10.000	1.156	16.156	16.156	10.000
2300	3.840	33.340	10.000	1.156	16.156	16.156	10.000
2400	3.340	32.840	10.000	1.156	16.156	16.156	10.000
2500	2.832	32.332	10.000	1.156	16.156	16.156	10.000
2600	2.316	31.816	10.000	1.156	16.156	16.156	10.000
2700	1.792	31.292	10.000	1.156	16.156	16.156	10.000
2800	1.260	30.760	10.000	1.156	16.156	16.156	10.000
2900	0.720	30.220	10.000	1.156	16.156	16.156	10.000
3000	0.176	29.676	10.000	1.156	16.156	16.156	10.000
3100	-0.368	29.132	10.000	1.156	16.156	16.156	10.000
3200	-0.904	28.588	10.000	1.156	16.156	16.156	10.000
3300	-1.432	28.044	10.000	1.156	16.156	16.156	10.000
3400	-1.952	27.500	10.000	1.156	16.156	16.156	10.000
3500	-2.464	26.956	10.000	1.156	16.156	16.156	10.000
3600	-2.968	26.412	10.000	1.156	16.156	16.156	10.000
3700	-3.464	25.868	10.000	1.156	16.156	16.156	10.000
3800	-3.952	25.324	10.000	1.156	16.156	16.156	10.000
3900	-4.432	24.780	10.000	1.156	16.156	16.156	10.000
4000	-4.904	24.236	10.000	1.156	16.156	16.156	10.000
4100	-5.368	23.692	10.000	1.156	16.156	16.156	10.000
4200	-5.824	23.148	10.000	1.156	16.156	16.156	10.000
4300	-6.272	22.604	10.000	1.156	16.156	16.156	10.000
4400	-6.712	22.060	10.000	1.156	16.156	16.156	10.000
4500	-7.144	21.516	10.000	1.156	16.156	16.156	10.000
4600	-7.568	20.972	10.000	1.156	16.156	16.156	10.000
4700	-7.984	20.428	10.000	1.156	16.156	16.156	10.000
4800	-8.392	19.884	10.000	1.156	16.156	16.156	10.000
4900	-8.792	19.340	10.000	1.156	16.156	16.156	10.000
5000	-9.184	18.796	10.000	1.156	16.156	16.156	10.000
5100	-9.568	18.252	10.000	1.156	16.156	16.156	10.000
5200	-9.944	17.708	10.000	1.156	16.156	16.156	10.000
5300	-10.312	17.164	10.000	1.156	16.156	16.156	10.000
5400	-10.672	16.620	10.000	1.156	16.156	16.156	10.000
5500	-11.024	16.076	10.000	1.156	16.156	16.156	10.000
5600	-11.368	15.532	10.000	1.156	16.156	16.156	10.000
5700	-11.704	14.988	10.000	1.156	16.156	16.156	10.000
5800	-12.032	14.444	10.000	1.156	16.156	16.156	10.000
5900	-12.352	13.896	10.000	1.156	16.156	16.156	10.000
6000	-12.664	13.352	10.000	1.156	16.156	16.156	10.000

March 31, 1962



MERCURY DIBROMIDE (HgBr₂) (Ideal Gas)

Mol. Wt. = 360.442
 ΔH_f^0 298.15 = -20.424 ± 2.0 kcal. mole⁻¹
 ΔF_f^0 298.15 = 76.511 cal. deg.⁻¹ mole⁻¹
 Point group = D_{2h}

Vibrational Levels and Multiplicities

Ω, cm.⁻¹
 $\left\{ \begin{matrix} 225 \\ 41 \\ 293 \end{matrix} \right\}$
 $\left\{ \begin{matrix} 1 \\ 2 \\ 1 \end{matrix} \right\}$

Hg-Br distance = 2.41 Å
 Moment of Inertia = 154.12 X 10⁻³⁹ g. cm.²
 σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952, was combined with the 3rd law heat of sublimation at 298°K from the data of K. Naka and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III 2, 163 (1938) and P. M. O. Johnson, J. Amer. Chem. Soc. 53, 777 (1931).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The bond length is an average of the values given by H. Braune and S. Knoke, Zeits. phys. Chemie B23, 163 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. Jones and L. E. Sutton, Trans. Farad. Soc. 33, 852 (1937) and P. A. Akishin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. 33, 20 (1959).



T, °K.	cal. mole ⁻¹ deg ⁻¹		kcal. mole ⁻¹		Log K _p
	C _p ^o	S ^o - (F ^o - H _{298^o)/T}	H ^o - H _{298^o}	ΔF ^o	
0					
100					
200					
298	25.000	32.283	0.000	48.800	42.705
300	25.025	32.438	.046	48.811	42.666
400	26.200	39.805	2.610	53.809	39.158
500	27.020	45.744	5.273	58.333	35.049
600	27.430	50.726	8.007	62.785	31.044
700	28.000	55.025	10.764	67.242	27.292
800	28.470	58.789	13.423	71.734	23.892
900	28.780	62.171	16.066	76.329	20.794
1000	29.050	65.217	18.737	81.032	17.933
1100	29.293	67.987	21.429	85.843	15.307
1200	29.510	70.556	24.135	90.761	12.911
1300	29.687	72.924	26.859	95.786	10.749
1400	29.910	75.132	29.603	100.925	8.823
1500	30.180	77.203	32.378	106.176	7.109

March 31, 1962

MERCURY MONOBROMIDE, DIMERIC (Hg₂Br₂) (Crystal)

Mol. Wt. = 561.052

ΔH_f^o 298.15 = -48.800 ± 0.2 kcal. mole⁻¹

S_{298.15}^o = 52.283 ± 0.75 cal. deg. ⁻¹ mole⁻¹

T_{sub} = 666°K (decomp.)

Heat of Formation. The average of the values obtained from the cell measurements of T. W. Dakin and D. T. Ewing, *J. Am. Chem. Soc.* 62, 2280 (1940) and those of P. Iahikawa and Y. Ueda, *J. Chem. Soc. Japan* 51, 59 (1930) was adopted.

Heat Capacity and Entropy. The heat capacity was estimated by analogy with mercurous chloride. The entropy of formation was obtained from the free energy and heat of formation data listed under heat of formation.

Sublimation. The vapor pressure over mercurous bromide reaches one atmosphere at 666°K according to G. Jung and W. Ziegler *Zeits. f. physik. Chem.* A150, 138 (1930). At this point the vapor is dissociated into Hg(g) and HgBr₂(g).

Potassium Bromide, Dimeric (K_2Br_2)
(Ideal Gas) $GF^\circ = 238.022$



T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	0.000	-124.977	-124.977	INFINITE
100	17.165	49.000	124.977	5.922	-124.977	-124.977	16.237
200	19.165	82.165	91.681	1.903	-125.765	-132.905	145.231
298	19.546	85.902	85.902	0.000	-129.200	-135.939	99.646
300	19.550	86.023	86.023	0.036	-129.223	-135.980	99.062
400	19.589	95.669	90.672	1.999	-138.128	-136.449	74.552
500	19.734	100.071	92.172	3.972	-138.524	-135.984	59.430
600	19.790	103.676	93.761	5.949	-138.887	-135.440	49.334
700	19.812	106.728	95.401	7.929	-139.232	-134.838	42.098
800	19.826	109.375	96.986	9.911	-139.570	-134.189	36.659
900	19.835	111.710	98.495	11.894	-139.909	-133.494	32.417
1000	19.842	113.601	99.922	13.878	-140.267	-132.764	29.016
1100	19.847	115.692	101.271	15.863	-178.458	-129.947	25.818
1200	19.851	117.419	102.546	17.846	-178.370	-125.539	22.864
1300	19.854	119.008	103.752	19.833	-178.284	-121.141	20.366
1400	19.857	120.480	104.895	21.818	-178.199	-116.748	18.225
1500	19.859	121.850	105.980	23.804	-178.115	-112.362	16.371
1600	19.860	123.131	107.013	25.790	-178.032	-107.979	14.749
1700	19.861	124.335	107.996	27.776	-177.952	-103.606	13.319
1800	19.863	125.471	108.936	29.762	-177.873	-99.236	12.049
1900	19.863	126.545	109.835	31.749	-177.798	-94.869	10.912
2000	19.864	127.563	110.696	33.735	-177.726	-90.504	9.990
2100	19.865	128.533	111.522	35.721	-177.658	-86.156	8.965
2200	19.866	129.457	112.317	37.704	-177.597	-81.789	8.125
2300	19.866	130.340	113.081	39.695	-177.541	-77.436	7.358
2400	19.867	131.185	113.816	41.681	-177.493	-73.083	6.655
2500	19.867	131.996	114.529	43.668	-177.455	-68.735	6.009
2600	19.867	132.776	115.216	45.655	-177.424	-64.384	5.412
2700	19.868	133.525	115.880	47.641	-177.407	-60.040	4.860
2800	19.868	134.248	116.524	49.628	-177.405	-55.694	4.347
2900	19.868	134.945	117.147	51.615	-177.415	-51.343	3.869
3000	19.868	135.619	117.751	53.602	-177.440	-47.000	3.424
3100	19.869	136.270	118.338	55.589	-177.487	-42.647	3.007
3200	19.869	136.901	118.909	57.575	-177.553	-38.295	2.615
3300	19.869	137.512	119.463	59.562	-177.642	-33.946	2.248
3400	19.869	138.106	120.003	61.549	-177.757	-29.595	1.902
3500	19.869	138.681	120.528	63.536	-177.900	-25.232	1.575
3600	19.869	139.241	121.040	65.523	-178.076	-20.884	1.267
3700	19.869	139.786	121.540	67.510	-178.286	-16.500	0.975
3800	19.870	140.316	122.027	69.497	-178.538	-12.135	0.694
3900	19.870	140.832	122.502	71.484	-178.833	-7.760	0.434
4000	19.870	141.335	122.967	73.471	-179.177	-3.349	0.183
4100	19.870	141.825	123.421	75.458	-179.576	1.054	0.056
4200	19.870	142.304	123.865	77.445	-180.036	5.445	0.284
4300	19.870	142.772	124.299	79.432	-180.559	9.888	0.503
4400	19.870	143.229	124.724	81.419	-181.157	14.322	0.711
4500	19.870	143.675	125.140	83.406	-181.832	18.778	0.912
4600	19.870	144.112	125.548	85.393	-182.592	23.240	1.104
4700	19.870	144.539	125.948	87.380	-183.443	27.728	1.289
4800	19.870	144.957	126.339	89.367	-184.392	32.232	1.460
4900	19.870	145.367	126.723	91.354	-185.445	36.755	1.630
5000	19.870	145.769	127.100	93.341	-186.605	41.295	1.805
5100	19.871	146.162	127.470	95.328	-187.881	45.873	1.966
5200	19.871	146.548	127.833	97.315	-189.275	50.466	2.121
5300	19.871	146.926	128.190	99.302	-190.790	55.093	2.272
5400	19.871	147.298	128.541	101.289	-192.431	59.739	2.418
5500	19.871	147.662	128.885	103.276	-194.198	64.429	2.560
5600	19.871	148.020	129.223	105.263	-196.091	69.158	2.699
5700	19.871	148.372	129.556	107.251	-198.108	73.901	2.834
5800	19.871	148.716	129.884	109.238	-200.250	78.669	2.965
5900	19.871	149.057	130.206	111.225	-202.512	83.528	3.094
6000	19.871	149.391	130.523	113.212	-204.891	88.395	3.220

Dec. 31, 1961; Mar. 31, 1967

POTASSIUM BROMIDE, DIMERIC (K_2Br_2)
(IDEAL GAS)

$GF^\circ = 238.022$

Point Group [D_{2h}]
 $S^\circ_{298.15} = [89.3]$ gibbs/mol
Ground State Quantum Weight = [1]
 $\Delta H^\circ_0 = -125.0 \pm 4$ kcal/mol
 $\Delta H^\circ_{298.15} = -129.2 \pm 4$ kcal/mol

Vibrational Frequencies and Degeneracies		
ω , cm^{-1}	ω , cm^{-1}	w , cm^{-1}
[135] (1)	[135] (1)	[80] (1)
[130] (1)	[130] (1)	[80] (1)
[150] (1)		[150] (1)

Bond Distances: K-Br = [3.07] \AA K-K = [1.94] \AA Br-Br = [2.39] \AA
Bond Angles: Br-K-Br = [102] $^\circ$ K-Br-K = [76] $^\circ$ $\sigma = [4]$

Product of the Moments of Inertia: $I_A I_B I_C = [1.473 \times 10^{-11}]$ g³ cm⁶

Heat of Formation

Vapor densities and vapor pressures of KBr were measured, using a liquid gold isothermometer, by K. I. Hagenmark, M. Blander, and E. B. Luchalingen, J. Phys. Chem. **70**, 276 (1966), and K. I. Hagenmark, private communication, 3M Company, St. Paul, Minn., Feb. 6, 1967. Based on the equilibrium constants for the reaction $2KBr(g) = K_2Br_2(g)$ in the temperature range 1267-1434 $^\circ$ K, the enthalpy change (ΔH°_{298}) of this reaction is evaluated by the second and third law methods to be -42.80 \pm 4.26 and -43.12 kcal/mol, respectively. The heat of formation for $K_2Br_2(g)$ is calculated to be -129.2 \pm 4 kcal/mol, using the third law ΔH°_{298} value and $\Delta H^\circ_{298}(KBr,g) = -43.04$ kcal/mol. The drift in the third law ΔH°_{298} values is 0.01 \pm 3.2 eu.

Heat Capacity and Entropy

The molecular structure and bond distances were estimated by J. Berkowitz, J. Chem. Phys. **29**, 1386 (1958), and are tentatively adopted. J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960), has calculated vibrational frequencies on the basis of the potential function for an ionic model. These values are adjusted so that the third law ΔH°_{298} value for the reaction $2KBr(g) = K_2Br_2(g)$ agrees with the second law value. The three principal moments of inertia are: $I_A = 4.867 \times 10^{-38}$, $I_B = 1.513 \times 10^{-37}$, $I_C = 2.000 \times 10^{-37}$ g cm².





Lithium Bromide, Dimeric (Li_2Br_2)

(Ideal Gas) $\text{GFW} = 173.696$

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	-0.000	INFINITE	INFINITE	-3.900	-115.621	-115.621	INFINITE
100	11.439	58.709	89.497	3.009	-115.636	-115.636	261.971
200	16.141	68.315	76.743	1.686	-116.276	-116.276	135.348
298	17.937	75.148	75.148	0.000	-119.700	-123.111	93.175
300	17.958	75.259	75.148	0.033	-119.722	-127.157	92.634
400	18.613	84.772	77.627	1.864	-120.186	-130.881	59.891
500	19.125	90.477	79.257	3.708	-120.786	-134.073	55.991
600	19.346	94.281	79.794	5.482	-120.578	-137.813	46.556
700	19.482	96.274	80.168	7.634	-120.529	-141.492	39.805
800	19.571	97.481	81.068	9.587	-120.256	-144.728	34.728
900	19.628	98.221	82.366	11.066	-119.806	-147.566	30.456
1000	19.678	98.621	83.566	13.513	-119.200	-150.000	27.555
1100	19.711	100.139	86.083	15.483	-118.198	-152.086	24.901
1200	19.737	101.495	87.309	17.455	-117.455	-153.509	22.817
1300	19.757	102.635	88.469	19.430	-116.807	-154.749	20.972
1400	19.773	103.610	89.584	21.406	-116.241	-155.806	19.348
1500	19.785	104.459	90.679	23.384	-115.750	-156.622	18.012
1600	19.796	105.202	91.650	25.363	-115.326	-157.204	16.804
1700	19.804	105.852	92.558	27.343	-114.968	-157.678	15.755
1800	19.811	106.515	93.400	29.326	-114.665	-158.053	14.845
1900	19.816	107.188	94.180	31.306	-114.415	-158.333	14.031
2000	19.823	111.062	95.319	33.288	-114.215	-158.517	13.317
2100	19.827	112.930	96.134	35.270	-114.068	-158.607	12.696
2200	19.831	113.852	96.919	37.253	-113.978	-158.606	12.161
2300	19.836	114.734	97.675	39.236	-113.946	-158.516	11.711
2400	19.840	115.573	98.406	41.216	-113.872	-158.333	11.341
2500	19.844	116.388	99.106	43.204	-113.756	-158.060	11.031
2600	19.845	117.166	99.786	45.188	-113.598	-157.698	10.771
2700	19.845	117.915	100.444	47.172	-113.398	-157.241	10.561
2800	19.845	118.631	101.088	49.157	-113.155	-156.686	10.391
2900	19.845	119.313	101.716	51.141	-112.868	-156.033	10.261
3000	19.850	120.006	102.297	53.127	-112.536	-155.281	10.161
3100	19.851	120.657	102.879	55.112	-112.159	-154.431	10.091
3200	19.853	121.287	103.445	57.097	-111.736	-153.481	10.041
3300	19.855	121.895	103.999	59.082	-111.266	-152.431	10.001
3400	19.856	122.480	104.540	61.066	-110.750	-151.281	9.971
3500	19.856	123.047	105.051	63.053	-110.188	-150.031	9.941
3600	19.857	123.626	105.560	65.039	-109.588	-148.681	9.911
3700	19.857	124.170	106.055	67.024	-108.946	-147.231	9.881
3800	19.857	124.688	106.533	69.009	-108.163	-145.681	9.851
3900	19.859	125.175	107.011	70.994	-107.241	-144.031	9.821
4000	19.859	125.718	107.473	72.982	-106.178	-142.281	9.791
4100	19.860	126.209	107.924	74.968	-105.076	-140.431	9.761
4200	19.861	126.687	108.365	76.954	-103.936	-138.481	9.731
4300	19.861	127.153	108.796	78.940	-102.758	-136.431	9.701
4400	19.862	127.611	109.219	80.926	-101.536	-134.281	9.671
4500	19.862	128.057	109.632	82.912	-100.276	-132.031	9.641
4600	19.862	128.494	110.038	84.899	-98.976	-129.681	9.611
4700	19.863	128.921	110.435	86.885	-97.636	-127.231	9.581
4800	19.863	129.340	110.826	88.871	-96.256	-124.681	9.551
4900	19.864	129.749	111.217	90.857	-94.836	-122.031	9.521
5000	19.864	130.150	111.591	92.844	-93.376	-119.281	9.491
5100	19.864	130.544	111.949	94.830	-91.876	-116.431	9.461
5200	19.864	130.959	112.311	96.817	-90.336	-113.481	9.431
5300	19.864	131.317	112.666	98.804	-88.756	-110.431	9.401
5400	19.865	131.679	113.014	100.790	-87.136	-107.281	9.371
5500	19.865	132.043	113.357	102.776	-85.476	-104.031	9.341
5600	19.865	132.401	113.694	104.763	-83.776	-100.681	9.311
5700	19.866	132.751	114.025	106.749	-82.036	-97.231	9.281
5800	19.866	133.098	114.351	108.736	-80.256	-93.681	9.251
5900	19.866	133.438	114.672	110.722	-78.436	-90.031	9.221
6000	19.866	133.772	114.987	112.709	-76.576	-86.281	9.191

Sept. 30, 1981; June 30, 1966

LITHIUM BROMIDE, DIMERIC (Li_2Br_2)

(IDEAL GAS)

OPW = 173.696

Point Group D_{2h}
 $\Delta H_f^\circ = -115.6 \pm 5 \text{ kcal/mol}$
 $S_{298.15}^\circ = [75.15] \text{ gibbs/mol}$
 $\Delta H_f^\circ_{298.15} = -119.7 \pm 5 \text{ kcal/mol}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[202](1)	[327](1)	
[203](1)	413 (1)	
[353](1)	295 (1)	

Bond Distances: Li-Br = 2.35 Å

Bond Angle: Br-Li-Br = 110°

Product of the Moments of Inertia: $I_A I_B I_C = 4.220745 \times 10^{-113} \text{ g}^3 \text{ cm}^6$

Heat of Formation.

This was obtained from the heat of formation of the liquid and the selected heat of vaporization to the dimer, which derivation has been given in the LiBr(g) table.

Heat Capacity and Entropy.

J. Berkowitz, J. Chem. Phys. 29, 1386 (1958), 32, 1519 (1960), has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure for dimeric lithium bromide, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964). The selected bond distances and angle were obtained from the electron diffraction studies of monomer-dimer vapor by P. A. Kikichin and N. G. Rambidi, Z. Physik Chem. 213, 111 (1960). The bond distances ($r_{\text{Li-Br}} = 4.20 \text{ Å}$ and $r_{\text{Li-Li}} = 2.60 \text{ Å}$) calculated by Berkowitz are in reasonable agreement with those selected. The three principal moments of inertia are $I_A = 4.1866 \times 10^{-39}$, $I_B = 98.3352 \times 10^{-39}$ and $I_C = 102.5218 \times 10^{-39} \text{ g cm}^2$.

S. H. Bauer, T. Ino and R. P. Porter, J. Chem. Phys. 33, 685 (1960), have estimated six vibrational frequencies (576, 576, 202, 250, 329 and 385 cm⁻¹) for $\text{Li}_2\text{Br}_2(\text{g})$ in the electron diffraction studies of $\text{Li}_2\text{Cl}_2(\text{g})$. W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), have observed two fundamental vibrational frequencies (413 and 295 cm⁻¹) in the infrared spectrum and tentatively assigned them as ν_{2u} and ν_{3u} modes and these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from J. Berkowitz, loc. cit., because his model and derivation are self-consistent.



Magnesium Dibromide (MgBr₂)
(Crystal) GFW = 184.130

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0						
100						
200						
298	17.515	28.500	•000	- 124.000	- 119.320	87.464
300	17.520	28.608	•032	- 124.012	- 119.290	86.903
400	18.260	33.754	1.823	- 131.075	- 116.250	83.516
500	18.830	37.891	3.678	- 130.745	- 112.581	49.209
600	19.330	41.389	5.586	- 130.394	- 108.682	39.407
700	19.790	44.389	7.586	- 130.023	- 104.682	32.621
800	20.150	47.051	9.540	- 129.647	- 101.957	27.853
900	20.510	49.445	11.572	- 129.273	- 98.518	23.923
1000	20.880	51.625	13.643	- 128.902	- 94.958	20.749
1100	21.246	53.632	15.740	- 128.520	- 91.352	18.150
1200	21.600	55.496	17.860	- 128.129	- 87.799	15.990
1300	21.970	57.239	20.069	- 127.788	- 84.281	14.169
1400	22.330	58.880	22.284	- 127.423	- 80.818	12.538
1500	22.700	60.433	24.535	- 127.077	- 77.4676	10.880
1600	23.070	61.910	26.824	- 126.794	- 69.091	9.437
1700	23.440	63.319	29.145	- 126.481	- 58.090	7.953
1800	23.770	64.668	31.508	- 126.125	- 52.669	6.058
1900	24.124	65.963	33.903	- 125.738	- 47.303	5.169
2000	24.480	67.208	36.333	- 125.319	- 47.303	5.169

MAGNESIUM DIBROMIDE (MgBr₂) (CRYSTAL) OFW = 184.130

ΔH°_f = Unknown
 $\Delta H_{298.15}^\circ = -124.0 \pm 1 \text{ kcal/mol}$
 $\Delta H_m^\circ = 8.3 \pm 2 \text{ kcal/mol}$
 $S_{298.15}^\circ = [28.5 \pm 2] \text{ gibbs/mol}$
 $T_m = 984^\circ\text{K}$

Heat of Formation

The heat of formation was calculated from ΔH° values for Mg⁺⁺(H₂O) and Br⁻(H₂O) and ΔHsol°(H₂O) for MgBr₂(c). The value for Br⁻ was obtained from D. D. Wagman et al., NBS Tech. Note 270-1, Natl. Bur. of Std., Washington, D.C., 1965. Values for Mg⁺⁺ and ΔHsol° were taken from P. D. Rossini et al., NBS Circ. 500, Natl. Bur. of Std., Washington, D.C., 1952, since a survey of the literature revealed no new data which would significantly change these values. ΔHsol° is based on measurements of Beketoff, Bull. acad. sci. Russ. 34, 291 (1892), while Mg⁺⁺ is presumably based on data for MgCl₂.

The selected heat of formation is confirmed by ΔH°_f = -0.267 kcal/mol for MgBr₂(l) + HCl(g) = MgCl₂(l) + HBr(g) observed by J. Toguri, H. Flood and T. Forland, Acta Chem. Scand. 17, 1502 (1963). Based on JANAF functions, this leads to ΔH°_f = -124.9 kcal/mol for MgBr₂(c).

Heat Capacity and Entropy

The entropy and heat capacity were estimated by comparison with the corresponding values for MgCl₂, NaCl and NaBr. W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, 1952, has estimated $S_{298}^\circ = 29.4 \text{ eu}$ which is also a reasonable value. Use of 29.4 eu would give almost exact agreement between the selected ΔH° and the equilibrium data of Toguri et al., but this may be fortuitous because of uncertainties in the enthalpy and heat of melting for MgBr₂.

Melting Data

T_m and ΔH_m° are the values obtained by K. K. Kelley, USNM Bulletin 593, 1956, from phase diagrams for the systems MgBr₂ - NaBr and MgBr₂ - KBr studied by G. Kellner, Z. Anorg. Chem. 39, 137 (1912), and for MgBr₂ - LiBr studied by A. Ferrari and C. Colla, Atti accad. Lincei, ser. 6, 13, 78 (1931).



Magnesium Dibromide (MgBr₂)
(Liquid) GFW = 184.130

T, °K	Cp ^b	S ^c -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
0						
100						
200						
298	23.750	31.968	0.000	-118.337	-114.691	84.070
300	23.250	32.113	0.043	-118.338	-114.667	83.535
400	23.250	38.802	2.368	-124.867	-112.061	61.227
500	23.250	43.990	4.693	-124.867	-108.952	47.623
600	23.250	48.229	7.018	-123.299	-106.003	38.612
700	23.250	51.813	9.343	-123.250	-103.179	32.424
800	23.250	54.918	11.668	-121.856	-100.460	27.444
900	23.250	57.656	13.993	-121.190	-97.825	23.752
1000	23.250	60.106	16.318	-122.684	-95.081	20.780
1100	23.250	62.322	18.643	-122.063	-92.353	18.349
1200	23.250	64.345	20.968	-121.468	-89.678	16.333
1300	23.250	66.206	23.293	-120.901	-87.051	14.635
1400	23.250	67.959	25.618	-120.356	-84.471	13.111
1500	23.250	69.553	27.943	-119.830	-81.935	11.757
1600	23.250	71.033	30.268	-119.321	-79.441	10.567
1700	23.250	72.443	32.593	-118.826	-76.984	9.514
1800	23.250	73.772	34.918	-118.345	-74.564	8.604
1900	23.250	75.029	37.243	-117.878	-72.181	7.804
2000	23.250	76.221	39.568	-117.424	-69.834	7.106

June 30, 1966

MAGNESIUM DIBROMIDE (MgBr₂) (LIQUID)

OPW = 184.130

S^o_{298.15} = [31.968] gibbs/mol
T_m = 984°K
T_b = [1557]°K
ΔHf°_{298.15} = [-118.337] kcal/mol
ΔHm° = 8.3 kcal/mol
ΔHv° = [32.9] kcal/mol

Heat of Formation.

The ΔHf°_{298.15} was obtained from ΔHf°_{298.15}(c) by adding ΔHm° and the difference between H°_m - H°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was assumed constant and estimated as 23.25 gibbs/mol using 7.75 gibbs/g-atom as suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgBr₂(c) table.

Vaporization Data.

T_b was calculated as the temperature at which ΔGr° = 0 for MgBr₂(c) → MgBr₂(g). ΔHv° is the corresponding enthalpy change.

Br₂Mg

Br₂Mg

GFW = 184.130

(Ideal Gas)

MAGNESIUM DIBROMIDE (MgBr₂)

(IDEAL GAS)

OFW = 184.130

Point Group D_{∞h}

$S_{298.15}^{\circ} = [67.5 \pm 2] \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

$\Delta H_f^{\circ} = -70.8 \text{ kcal/mol}$

$\Delta H_{298.15}^{\circ} = -74.6 \pm 3 \text{ kcal/mol}$

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}

$\frac{1}{(179)(1)}$

$\frac{1}{(220)(2)}$

491 (1)

Bond Distances Mg-Br = 2.34 Å

Bond Angles Br-Mg-Br = 180°

Rotational Constant: B = 0.019264 cm⁻¹ $\sigma = 2$

Heat of Formation.

The $\Delta H_{298.15}^{\circ}$ was calculated from the $\Delta H_{298.15}^{\circ} = 49.4 \text{ kcal/mol}$ for the reaction $\text{MgBr}_2(\text{c}) = \text{MgBr}_2(\text{g})$.

based on third law analysis of pressures at 798 and 842°K determined from Knudsen effusion - mass spectrometric studies by J. Berkowitz and J. R. Marquert, J. Chem. Phys. **37**, 1853 (1962). Second law analysis of ion intensities (635 - 850°K) gave $\Delta H^{\circ} = 50.3 \text{ kcal/mol}$ at 727°K, corresponding to $\Delta H^{\circ} = 52.2 \text{ kcal/mol}$ at 298.15°K. The absolute pressure at 842°K was calibrated by integrating the ion current during complete volatilization of the sample. Data for $(\text{MgBr}_2)_2$ indicate that the dimer mole fraction (about 0.04 at 842°K) over the crystal increases with increasing temperature; this behavior is similar to that of the alkali halides.

Heat Capacity and Entropy.

Bond distance and bond angle were taken from the electron diffraction studies of P. A. Akishin, V. P. Spiridonov, G. A. Sobolev and V. A. Neumov, Zhur. Fiz. Khim. **31**, 461 (1957). Electric deflection experiments of A. Büchler, J. L. Steurfer and W. Klumperer, J. Am. Chem. Soc. **86**, 4544 (1964), also suggest a linear structure for MgBr_2 within the sensitivity of the measurements. The antisymmetric stretching vibration ν_3 is that observed in the infrared spectra of the vapor by S. P. Hendall, F. T. Greene and J. L. Margrave, J. Phys. Chem. **63**, 758 (1959). The other frequencies were estimated by L. Brewer, G. R. Somayajulu and E. Breckett, Chem. Rev. **63**, 111 (1963), from a valence force model using $k = 1.5$ and $k\delta/12 = 0.15 \text{ md/\AA}$.

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	10.047	54.314	78.938	2.462	70.802	70.802	INFINITE
200	12.474	68.760	68.760	1.353	70.829	74.746	163.358
298	13.714	67.532	67.532	∞	71.403	78.566	85.453
300	13.727	67.532	67.532	∞	71.403	81.537	94.783
400	14.190	71.637	68.077	1.424	74.619	81.600	94.445
500	14.430	74.832	69.120	2.856	82.074	82.402	45.023
600	14.568	77.476	70.398	4.307	82.273	82.473	36.049
700	14.654	79.729	71.489	5.768	82.398	82.526	30.050
800	14.711	81.690	72.644	7.230	82.550	82.572	25.776
900	14.751	83.425	73.747	8.717	82.736	82.563	22.558
1000	14.779	84.980	74.794	10.186	85.079	82.350	20.049
1100	14.800	86.390	75.785	11.6304	85.304	82.350	17.998
1200	14.817	87.679	76.723	13.116	85.553	82.069	16.306
1300	14.829	88.865	77.612	14.629	85.828	81.764	14.991
1400	14.840	89.964	78.456	16.112	86.121	81.436	13.691
1500	14.848	90.989	79.258	17.596	86.416	80.607	12.583
1600	14.855	91.947	80.021	19.082	86.703	78.049	11.372
1700	14.860	92.848	80.749	20.567	87.002	75.643	10.372
1800	14.865	93.697	81.445	22.054	87.306	73.042	9.377
1900	14.869	94.501	82.111	23.540	87.617	70.396	8.547
2000	14.872	95.264	82.750	25.027	87.935	67.854	7.805
2100	14.875	95.989	83.363	26.515	88.259	65.319	7.138
2200	14.878	96.682	83.953	28.002	88.586	62.785	6.534
2300	14.880	97.343	84.521	29.490	88.916	60.255	5.986
2400	14.882	97.976	85.069	30.978	89.247	57.727	5.485
2500	14.884	98.584	85.597	32.467	89.579	55.204	5.027
2600	14.885	99.168	86.108	33.955	89.908	52.685	4.606
2700	14.886	99.729	86.602	35.444	90.234	50.166	4.217
2800	14.888	100.271	87.081	36.932	90.556	47.652	3.857
2900	14.889	100.793	87.545	38.420	90.872	45.142	3.523
3000	14.890	101.298	87.995	39.910	91.183	42.629	3.213
3100	14.891	101.786	88.432	41.399	91.489	40.123	2.923
3200	14.891	102.259	88.856	42.888	91.790	37.615	2.656
3300	14.892	102.717	89.270	44.377	92.086	35.113	2.408
3400	14.893	103.162	89.672	45.867	92.377	32.612	2.160
3500	14.893	103.594	90.063	47.356	92.662	30.111	1.936
3600	14.894	104.013	90.445	48.845	92.942	27.614	1.724
3700	14.894	104.421	90.817	50.335	93.218	25.114	1.525
3800	14.895	104.818	91.180	51.824	93.490	22.617	1.336
3900	14.895	105.205	91.534	53.314	93.758	20.120	1.157
4000	14.896	105.587	91.882	54.803	94.022	17.626	0.988
4100	14.896	105.950	92.220	56.293	94.281	15.133	0.827
4200	14.897	106.304	92.551	57.782	94.536	12.640	0.674
4300	14.897	106.660	92.877	59.272	94.787	10.147	0.528
4400	14.897	107.002	93.193	60.762	95.034	7.655	0.389
4500	14.897	107.337	93.503	62.252	95.277	5.166	0.256
4600	14.898	107.664	93.808	63.741	95.516	2.663	0.129
4700	14.898	107.985	94.106	65.231	95.751	0.165	0.008
4800	14.898	108.298	94.396	66.721	95.981	-2.340	-0.108
4900	14.898	108.606	94.685	68.211	96.207	-4.828	-0.220
5000	14.899	108.907	94.967	69.701	96.429	-7.323	-0.327
5100	14.899	109.202	95.243	71.190	96.647	-9.824	-0.429
5200	14.899	109.491	95.514	72.680	96.861	-12.319	-0.528
5300	14.899	109.775	95.780	74.170	97.070	-14.826	-0.623
5400	14.899	110.053	96.042	75.660	97.277	-17.335	-0.715
5500	14.900	110.327	96.299	77.150	97.481	-19.839	-0.803
5600	14.900	110.595	96.552	78.640	97.681	-22.351	-0.898
5700	14.900	110.859	96.801	80.130	97.877	-24.863	-0.970
5800	14.900	111.118	97.046	81.620	98.069	-27.383	-1.050
5900	14.900	111.374	97.284	83.110	98.266	-29.900	-1.127
6000	14.900	111.623	97.523	84.600	98.460	-32.423	-1.201
						-34.944	-1.273

June 30, 1966

Sodium Bromide, Dimeric (Na_2Br_2)
(Ideal Gas) Mol. Wt. = 205.814

Br_2Na_2

(IDEAL GAS)

MOL. WT. = 205.814

Point Group $[D_{2h}]$
 $\Delta H_f^\circ = -111.93 \pm 0.90 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = -116.24 \pm 0.90 \text{ kcal. mole}^{-1}$
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm^{-1}	ω , cm^{-1}
[132] (1)	[134] (1)
[120] (1)	[188] (1)
[207] (1)	[228] (1)

Bond Distance: $\text{Na}-\text{Br} = [2.75] \text{ \AA}$

Bond Angle: $\text{Na}-\text{Br}-\text{Na} = [71]^\circ$

Product of the Moments of Inertia: $I_A I_B I_C = [3.9703 \times 10^{-112}] \text{ g. cm.}^2$

Heat of Formation.

The temperature dependence of the equilibrium constants ($1293-1434^\circ\text{K.}$) for the reaction $(\text{NaBr})_2(\text{g}) \rightleftharpoons 2\text{NaBr}(\text{g})$ has been studied by S. T. Smith, Jr. and E. H. Taylor, *J. Chem. Phys.*, **34**, 558 (1961). The dissociation energy ($\Delta E_{100^\circ\text{K.}}$) was evaluated to be $42.9 \pm 1.3 \text{ kcal. mole}^{-1}$. The vapor mixture contains 37 to 17% of dimers in the temperature range of 1293 to 1434°K. Hence the vapor pressure data on $\text{NaBr}(\text{g})$ reported by the previous investigators were reexamined. In other words, the reported vapor pressure of $\text{NaBr}(\text{g})$ is the sum of the partial pressures of both the monomer (NaBr) and the dimer (Na_2Br_2). The partial pressures of $\text{Na}_2\text{Br}_2(\text{g})$ thus obtained were used to evaluate the heats of vaporization by both the second and third law methods. The values of ΔH_f° 298.15 for $\text{Na}_2\text{Br}_2(\text{g})$ were then calculated. The results are presented as follows.

Investigator	Reaction	Third Law Value	Second Law Value	ΔH_f° 298.15° kcal. mole $^{-1}$
Niwa ¹	$2\text{NaBr}(\text{c}) \rightarrow \text{Na}_2\text{Br}_2(\text{g})$	56.51	54.84	-117.08
Cogin and Kimball ²	$2\text{NaBr}(\text{c}) \rightarrow \text{Na}_2\text{Br}_2(\text{g})$	56.80	56.69	-116.01
Mayer and Wintner ³	$2\text{NaBr}(\text{c}) \rightarrow \text{Na}_2\text{Br}_2(\text{g})$	57.13	68.78	-115.63**
Ruff and Mugdan ⁴	$2\text{NaBr}(\text{l}) \rightarrow \text{Na}_2\text{Br}_2(\text{g})$	45.70	46.71	-116.00
Wartenberg and Albrecht ⁵	$2\text{NaBr}(\text{l}) \rightarrow \text{Na}_2\text{Br}_2(\text{g})$	45.84	46.77	-116.00
Bloom et al. ⁶	$2\text{NaBr}(\text{l}) \rightarrow \text{Na}_2\text{Br}_2(\text{g})$	45.49	51.17	-116.72**

*Based on the average of the second and third law values.

**Only the third law value being used.

1 K. Niwa, *J. Fac. Sci., Hokkaido Univ., Ser. III*, **2**, 201 (1958).

2 G. E. Cogin and G. E. Kimball, *J. Chem. Phys.*, **16**, 1035 (1948).

3 J. E. Mayer and I. H. Wintner, *J. Chem. Phys.*, **5**, 301 (1938).

4 O. Ruff and S. Mugdan, *Z. anorg. allgem. Chem.*, **117**, 147 (1921).

5 H. von Wartenberg and P. Albrecht, *Z. Electrochem.*, **27**, 162 (1921).

6 H. Bloom, J. O'M. Bockris, N. E. Richards and R. G. Taylor, *J. Am. Chem. Soc.*, **80**, 2044 (1958).

The value of ΔH_f° 298.15 for $\text{Na}_2\text{Br}_2(\text{g})$ adopted is the average of the six ΔH_f° 298.15 values listed in the above table.

Heat Capacity and Entropy.

Bond distance and angles were calculated based on the related data reported by J. Berkowitz, *J. Chem. Phys.*, **29**, 1386 (1958). The vibrational frequencies were calculated by J. Berkowitz, *J. Chem. Phys.*, **32**, 1519 (1960), from an assumed model. The ground state quantum weight was estimated. The three principal moments of inertia are $I_A = 1.94452 \times 10^{-38}$, $I_B = 1.35619 \times 10^{-37}$ and $I_C = 1.53065 \times 10^{-37} \text{ g. cm.}^2$.

Sept. 30, 1964

Br_2Na_2

Lead Dibromide (PbBr₂)

(Crystal) Mol. Wt. = 367.04

INTERIM TABLE

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	16,000	19,000	19,000	19,000	4,488	63,199	63,199	19,000
100	16,290	19,003	19,003	19,003	4,488	63,199	63,199	19,003
200	16,495	19,016	19,016	19,016	4,488	63,199	63,199	19,016
298	16,626	19,036	19,036	19,036	4,488	63,199	63,199	19,036
300	19,250	36,777	36,777	36,777	4,488	63,199	63,199	36,777
400	19,470	44,345	44,345	44,345	4,488	63,199	63,199	44,345
500	19,690	48,713	48,713	48,713	4,488	63,199	63,199	48,713
600	19,910	52,323	52,323	52,323	4,488	63,199	63,199	52,323
700	20,130	55,116	55,116	55,116	4,488	63,199	63,199	55,116
800	20,350	57,111	57,111	57,111	4,488	63,199	63,199	57,111
900	20,570	58,520	58,520	58,520	4,488	63,199	63,199	58,520
1000	20,790	59,599	59,599	59,599	4,488	63,199	63,199	59,599
1100	21,010	60,491	60,491	60,491	4,488	63,199	63,199	60,491
1200	21,230	61,236	61,236	61,236	4,488	63,199	63,199	61,236
1300	21,450	61,853	61,853	61,853	4,488	63,199	63,199	61,853
1400	21,670	62,353	62,353	62,353	4,488	63,199	63,199	62,353
1500	21,890	62,737	62,737	62,737	4,488	63,199	63,199	62,737
1600	22,110	62,993	62,993	62,993	4,488	63,199	63,199	62,993
1700	22,330	63,131	63,131	63,131	4,488	63,199	63,199	63,131
1800	22,550	63,153	63,153	63,153	4,488	63,199	63,199	63,153
1900	22,770	63,161	63,161	63,161	4,488	63,199	63,199	63,161
2000	22,990	63,158	63,158	63,158	4,488	63,199	63,199	63,158
2100	23,210	63,145	63,145	63,145	4,488	63,199	63,199	63,145
2200	23,430	63,122	63,122	63,122	4,488	63,199	63,199	63,122
2300	23,650	63,089	63,089	63,089	4,488	63,199	63,199	63,089
2400	23,870	63,046	63,046	63,046	4,488	63,199	63,199	63,046
2500	24,090	63,033	63,033	63,033	4,488	63,199	63,199	63,033

Br₂Pb

Lead Dibromide (PbBr₂)

Mol. Wt. = 367.04

ΔH_f^o 298.15 = -66.07 ± 0.20 kcal. mole⁻¹

S_{298.15} = 38.66 ± 0.5 cal. deg⁻¹ mole⁻¹

ΔH_f^o 298.15 = 41.90 ± 0.17 kcal. mole⁻¹

T_m = 640°K.

ΔH_m = 4.96 kcal. mole⁻¹

Heat of Formation. Recalculated from the data reported by H. Braune and P. Koref, Z. anorg. Chem., 87, 175 (1914) and C. Krahmer, Z. Elektrochem., 26, 97 (1920).

Heat Capacity, Entropy, and Melting Data. C_p (18.4° to 297.0°K.) reported by N. M. Latimer and H. D. Hoernel, J. Am. Chem. Soc., 49, 19 (1926). Above 298.15°K., C_p given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. T_m and ΔH_m obtained from M. Blanc and G. Petit, Compt. rend., 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of H. Bloom, J. O'M. Bockris, R. E. Richards and R. G. Taylor, J. Am. Chem. Soc., 80, 2044 (1958), H. von Wartenberg and O. Basse, Z. Elektrochem., 28, 384 (1922), F. Volmer, Phys. Z., 30, 590 (1929), and B. Greiner and K. Jellinek, Z. physik. Chem., 165, 97 (1933) which are in good agreement.

Br₂Pb

INTERIM TABLE

T, K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	19.246	42.699	42.699	0.000	- 63.001	- 60.267	44.175
200	19.250	42.698	42.699	1.036	- 63.010	- 60.250	43.890
300	19.252	42.697	42.699	2.072	- 63.018	- 60.232	43.605
400	19.254	42.696	42.699	3.108	- 63.026	- 60.214	43.320
500	19.256	42.695	42.699	4.144	- 63.034	- 60.196	43.035
600	19.258	42.694	42.699	5.180	- 63.042	- 60.178	42.750
700	19.260	42.693	42.699	6.216	- 63.050	- 60.160	42.465
800	19.262	42.692	42.699	7.252	- 63.058	- 60.142	42.180
900	19.264	42.691	42.699	8.288	- 63.066	- 60.124	41.895
1000	19.266	42.690	42.699	9.324	- 63.074	- 60.106	41.610
1100	19.268	42.689	42.699	10.360	- 63.082	- 60.088	41.325
1200	19.270	42.688	42.699	11.396	- 63.090	- 60.070	41.040
1300	19.272	42.687	42.699	12.432	- 63.098	- 60.052	40.755
1400	19.274	42.686	42.699	13.468	- 63.106	- 60.034	40.470
1500	19.276	42.685	42.699	14.504	- 63.114	- 60.016	40.185
1600	19.278	42.684	42.699	15.540	- 63.122	- 60.000	39.900
1700	19.280	42.683	42.699	16.576	- 63.130	- 59.982	39.615
1800	19.282	42.682	42.699	17.612	- 63.138	- 59.964	39.330
1900	19.284	42.681	42.699	18.648	- 63.146	- 59.946	39.045
2000	19.286	42.680	42.699	19.684	- 63.154	- 59.928	38.760
2100	19.288	42.679	42.699	20.720	- 63.162	- 59.910	38.475
2200	19.290	42.678	42.699	21.756	- 63.170	- 59.892	38.190
2300	19.292	42.677	42.699	22.792	- 63.178	- 59.874	37.905
2400	19.294	42.676	42.699	23.828	- 63.186	- 59.856	37.620
2500	19.296	42.675	42.699	24.864	- 63.194	- 59.838	37.335
2600	19.298	42.674	42.699	25.900	- 63.202	- 59.820	37.050
2700	19.300	42.673	42.699	26.936	- 63.210	- 59.802	36.765
2800	19.302	42.672	42.699	27.972	- 63.218	- 59.784	36.480
2900	19.304	42.671	42.699	29.008	- 63.226	- 59.766	36.195
3000	19.306	42.670	42.699	30.044	- 63.234	- 59.748	35.910

March 31, 1962

Lead Dibromide (PbBr₂)

(Liquid)

Mol. Wt. = 367.04

ΔH_f^o 298.15 = [-63.00 ± 0.20] kcal. mole⁻¹S_{298.15} = [42.699] cal. deg.⁻¹ mole⁻¹T_m = 640°K.ΔH_m^o = 4.96 kcal. mole⁻¹T_b = 1187°K.ΔH_v^o = 27.44 ± 0.17 kcal. mole⁻¹

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1950). T_m and ΔH_m^o reported by M. Blanc and G. Petit, Compt. rend. 248, 1305-6 (1959). A glass transition temperature of 400°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v^o calculated from ΔH_f^o 298.15 and free energy functions for condensed and gaseous states.

Br₂PbBr₂Pb

Lead Dibromide (PbBr₂)

(Ideal Gas) Mol. Wt. = 367.04

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	2.4637	20.340	-20.340	-20.340	INFINITE
100	12.340	66.022	64.376	1.6335	20.399	-20.399	-20.399	51.706
200	13.424	77.009	83.672	1.3333	20.871	-20.871	-20.871	32.433
298	13.682	82.426	82.426	1.0000	24.176	-24.176	-33.287	24.399
300	13.685	82.511	82.427	0.985	24.186	-24.186	-33.333	24.389
400	13.781	88.663	82.665	0.798	31.714	-31.714	-34.658	19.085
500	13.827	89.344	83.084	0.669	31.669	-31.669	-35.626	15.571
600	13.853	92.067	85.127	0.564	32.083	-32.083	-36.354	13.241
700	13.868	94.204	86.275	0.480	33.460	-33.460	-36.860	11.501
800	13.876	95.966	87.384	0.413	34.536	-34.536	-37.330	10.192
900	13.879	97.481	88.451	0.357	35.411	-35.411	-37.771	9.145
1000	13.890	99.155	89.440	0.311	36.131	-36.131	-38.187	8.345
1100	13.893	100.479	90.384	0.274	36.742	-36.742	-38.583	7.695
1200	13.896	101.666	91.277	0.243	37.283	-37.283	-38.959	7.100
1300	13.900	102.830	92.121	0.217	37.766	-37.766	-39.318	6.560
1400	13.901	103.980	92.921	0.195	38.199	-38.199	-39.663	6.070
1500	13.901	104.789	93.680	0.176	38.589	-38.589	-39.992	5.627
1600	13.903	105.666	94.403	0.160	38.937	-38.937	-40.308	5.206
1700	13.904	106.529	95.092	0.146	39.243	-39.243	-40.610	4.820
1800	13.905	107.374	95.749	0.133	39.506	-39.506	-40.893	4.469
1900	13.905	108.204	96.374	0.122	39.734	-39.734	-41.160	4.150
2000	13.906	108.789	96.982	0.113	39.926	-39.926	-41.448	3.859
2100	13.906	109.467	97.560	0.105	40.088	-40.088	-41.751	3.591
2200	13.906	110.114	98.116	0.100	40.224	-40.224	-42.076	3.342
2300	13.906	110.722	98.657	0.096	40.338	-40.338	-42.426	3.110
2400	13.907	111.292	99.177	0.092	40.431	-40.431	-42.797	2.893
2500	13.907	111.822	99.675	0.089	40.506	-40.506	-43.186	2.690
2600	13.908	112.317	100.146	0.086	40.566	-40.566	-43.592	2.500
2700	13.908	112.782	100.611	0.084	40.614	-40.614	-44.014	2.321
2800	13.908	113.225	101.030	0.082	40.653	-40.653	-44.451	2.153
2900	13.909	113.646	101.407	0.081	40.684	-40.684	-44.902	1.996
3000	13.909	114.048	101.742	0.080	40.708	-40.708	-45.367	1.850
3100	13.909	114.434	102.031	0.079	40.726	-40.726	-45.846	1.714
3200	13.909	114.797	102.273	0.078	40.738	-40.738	-46.338	1.587
3300	13.909	115.139	102.477	0.077	40.744	-40.744	-46.842	1.468
3400	13.909	115.460	102.643	0.076	40.746	-40.746	-47.357	1.355
3500	13.909	115.772	102.784	0.075	40.743	-40.743	-47.882	1.247
3600	13.909	116.064	102.893	0.074	40.736	-40.736	-48.417	1.144
3700	13.909	116.345	102.972	0.073	40.724	-40.724	-48.962	1.046
3800	13.909	116.607	103.023	0.072	40.708	-40.708	-49.517	0.953
3900	13.909	116.852	103.048	0.071	40.688	-40.688	-50.082	0.865
4000	13.909	117.077	103.048	0.070	40.664	-40.664	-50.657	0.782
4100	13.910	117.273	103.023	0.069	40.636	-40.636	-51.242	0.704
4200	13.910	117.445	102.972	0.068	40.604	-40.604	-51.837	0.631
4300	13.910	117.595	102.903	0.067	40.568	-40.568	-52.442	0.563
4400	13.910	117.725	102.817	0.066	40.528	-40.528	-53.057	0.500
4500	13.910	117.834	102.717	0.065	40.484	-40.484	-53.682	0.442
4600	13.910	117.922	102.607	0.064	40.436	-40.436	-54.317	0.389
4700	13.910	117.990	102.487	0.063	40.384	-40.384	-54.962	0.340
4800	13.910	118.038	102.358	0.062	40.328	-40.328	-55.617	0.295
4900	13.910	118.067	102.221	0.061	40.268	-40.268	-56.282	0.254
5000	13.910	118.067	102.077	0.060	40.204	-40.204	-56.957	0.216
5100	13.910	118.038	101.927	0.059	40.136	-40.136	-57.642	0.181
5200	13.910	117.972	101.772	0.058	40.064	-40.064	-58.337	0.149
5300	13.910	117.872	101.607	0.057	39.988	-39.988	-59.042	0.120
5400	13.910	117.739	101.434	0.056	39.908	-39.908	-59.757	0.093
5500	13.910	117.572	101.254	0.055	39.824	-39.824	-60.482	0.068
5600	13.910	117.372	101.067	0.054	39.736	-39.736	-61.217	0.044
5700	13.910	117.139	100.872	0.053	39.644	-39.644	-61.962	0.021
5800	13.910	116.872	100.667	0.052	39.548	-39.548	-62.717	0.000
5900	13.910	116.572	100.452	0.051	39.448	-39.448	-63.482	-0.021
6000	13.910	116.239	100.227	0.050	39.344	-39.344	-64.257	-0.044

March 31, 1962

Br₂Pb

Lead Dibromide (PbBr₂) (Ideal Gas)

Mol. Wt. = 367.04

ΔH_f° 298.15 = -24.18 ± 0.26 kcal. mole⁻¹

S° 298.15 = 82.426 cal. deg⁻¹ mole⁻¹

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω, cm ⁻¹	
[140] (1)	
[45] (1)	
[200] (1)	

Pb-Br distance = 2.60 ± 0.03 Å BrPbBr angle = 95° σ = 2

I_A = 46.245 X 10⁻³⁹ g. cm.² I_B = 97.514 X 10⁻³⁹ g. cm.²

I_C = I_A + I_B = 143.759 X 10⁻³⁹ g. cm.²

Heat of Formation. Calculated from ΔH_f° 298.15 and ΔH_f° 298.15 for PbBr₂(c).

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the corresponding values for HgBr₂(g).

Br₂Pb

(Crystal)

GFW = 207.718

TITANIUM DIBROMIDE (TiBr₂)

(CRYSTAL)

GFW = 207.718

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0							
100	18.807	25.900	25.900	.000	- 96.900	- 91.590	67.137
200	18.812	26.016	25.900	.035	- 96.909	- 91.557	66.499
300	19.066	26.431	26.032	1.930	- 103.872	- 88.322	64.257
400	19.300	26.758	26.050	3.652	- 103.879	- 84.481	36.927
500	19.634	29.639	29.639	5.802	- 103.083	- 90.719	29.402
600	19.908	42.355	31.243	7.779	- 102.685	- 77.023	24.048
700	20.162	45.032	32.802	11.693	- 101.689	- 69.795	16.949
800	20.400	47.411	34.111	13.674	- 101.494	- 66.250	14.479
900	20.730	49.594	35.719	15.961	- 101.098	- 62.745	12.466
1000	21.004	51.583	37.072	18.329	- 101.639	- 58.736	10.786
1100	21.278	53.422	38.329	20.723	- 101.639	- 54.725	9.376
1200	21.552	55.116	40.783	23.166	- 100.582	- 52.254	8.157
1300	21.826	56.674	43.111	25.582	- 100.039	- 48.822	7.113
1400	22.100	58.258	45.422				
1500							

ΔH_{298.15}^o = [25.9 ± 2.0] gibbs/mol
S_{298.15}^o = [1208.8]°K
ΔH_{298.15}^o = -96.9 ± 5.0 kcal/mol
ΔH_{298.15}^o = [49.29] kcal/mol

Heat of Formation

The heat of formation of TiBr₂ crystal is derived from the data of Hall and Blocher (1) for the reaction 2TiBr₃(c) = TiBr₄(g) + TiBr₂(c). Second and third law analyses of these data are not useful because of the formation of solid solutions in the above process. Hall and Blocher obtained a value of ΔH_{298.15}^o of 31.3 kcal/mol for the reaction by integrating the incremental free energy changes over varying compositions of the solid solutions. The corresponding ΔH₂₉₈^o and ΔH₂₉₈^o are calculated as 34.6 kcal/mol and -96.9 kcal/mol, respectively, using auxiliary JANAF heats of formation and enthalpy data.

Heat Capacity and Entropy

The heat capacity of TiBr₂(c) was estimated by Kelley (2). The value of S_{298.15}^o is estimated from that of TiCl₂(c) and the difference between ionic entropy contributions of Cl⁻ and Br⁻.

Heat of Sublimation

The heat of sublimation of TiBr₂(c) is taken as the difference in the heats of formation of TiBr₂(c) and TiBr₂(g) at the sublimation temperature. The sublimation temperature is taken as the point at which ΔG^o = 0 for the reaction TiBr₂(c) = TiBr₂(g). The heat of formation of TiBr₂(g), upon which these quantities depend, is an estimated quantity.

References

1. E. H. Hall and J. H. Blocher, Jr., J. Phys. Chem. **63**, 1525 (1959).
2. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1960.

Dec. 31, 1961; June 30, 1964; June 30, 1968

Titanium Dibromide (TiBr₂)

(Ideal Gas)

GFW = 207.718

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	0.000	INFINITE	INFINITE	3.615	39.404	39.404	INFINITE
100	11.939	56.147	56.056	2.691	38.282	38.282	95.534
200	18.172	68.482	68.382	1.852	37.425	37.425	100.000
298	18.752	73.752	73.752	1.000	42.800	51.757	37.439
300	14.353	73.752	73.752	.027	42.817	51.812	37.745
400	14.581	76.005	74.319	1.475	50.227	53.293	29.118
500	14.694	81.273	75.394	2.939	50.292	54.053	23.627
600	14.756	83.958	76.604	4.412	50.373	54.798	19.960
700	14.795	86.235	77.822	5.890	50.474	55.529	17.337
800	14.822	88.213	79.000	7.370	50.600	56.243	15.365
900	14.844	89.960	80.122	8.854	50.750	56.939	13.827
1000	14.867	91.525	81.186	10.339	50.929	57.617	12.592
1100	14.894	92.943	82.191	11.827	51.132	58.275	11.578
1200	14.920	94.231	83.142	13.318	51.366	58.977	10.723
1300	14.945	95.437	84.062	14.810	51.619	59.620	9.969
1400	15.030	96.569	84.866	16.314	52.554	59.555	9.359
1500	15.096	97.588	85.708	17.820	52.701	60.479	8.812
1600	15.171	98.585	86.482	19.333	53.860	60.991	8.331
1700	15.254	99.487	87.220	20.855	53.031	61.494	7.906
1800	15.343	100.362	87.926	22.384	53.218	61.988	7.526
1900	15.437	101.194	88.602	23.923	53.418	62.469	7.186
2000	15.532	101.988	89.252	25.472	53.681	62.787	6.861
2100	15.628	102.748	89.877	27.030	53.987	63.016	6.588
2200	15.722	103.477	90.478	28.597	54.486	63.238	6.282
2300	15.815	104.178	91.059	30.174	54.676	63.449	6.009
2400	15.905	104.853	91.620	31.760	54.858	63.651	5.796
2500	15.990	105.504	92.162	33.355	55.032	63.847	5.582
2600	16.072	106.133	92.687	34.958	55.199	64.037	5.383
2700	16.149	106.741	93.197	36.569	55.359	64.221	5.198
2800	16.222	107.330	93.691	38.188	55.513	64.398	5.026
2900	16.290	107.900	94.171	39.813	55.661	64.567	4.866
3000	16.354	108.453	94.638	41.446	55.802	64.735	4.716
3100	16.414	108.991	95.092	43.084	55.940	64.895	4.575
3200	16.470	109.513	95.535	44.728	60.072	65.056	4.443
3300	16.523	110.020	95.964	46.378	60.200	65.210	4.319
3400	16.573	110.514	96.387	48.033	60.323	65.359	4.201
3500	16.620	110.995	96.797	49.692	60.444	65.505	4.080
3600	16.665	111.464	97.198	51.356	162.187	65.386	3.949
3700	16.707	111.921	97.590	53.025	162.271	62.497	3.793
3800	16.748	112.367	97.973	54.698	162.366	60.007	3.651
3900	16.787	112.803	98.348	56.375	162.471	57.307	3.421
4000	16.825	113.228	98.715	58.055	162.587	54.612	3.211
4100	16.861	113.644	99.074	59.739	162.713	51.911	2.987
4200	16.896	114.051	99.425	61.427	162.848	49.208	2.761
4300	16.930	114.449	99.770	63.119	162.992	46.501	2.533
4400	16.963	114.839	100.108	64.813	163.146	43.789	2.175
4500	16.995	115.220	100.440	66.511	163.308	41.075	1.995
4600	17.026	115.594	100.765	68.212	163.478	38.353	1.822
4700	17.056	115.960	101.085	69.916	163.656	35.630	1.657
4800	17.085	116.320	101.398	71.623	163.843	32.907	1.498
4900	17.113	116.672	101.706	73.333	164.036	30.179	1.346
5000	17.140	117.018	102.009	75.046	164.235	27.442	1.199
5100	17.166	117.358	102.307	76.761	164.442	24.707	1.059
5200	17.191	117.692	102.599	78.479	164.654	21.964	.923
5300	17.214	118.019	102.887	80.199	164.872	19.219	.792
5400	17.237	118.341	103.171	81.922	165.096	16.468	.666
5500	17.258	118.656	103.449	83.647	165.323	13.709	.545
5600	17.279	118.969	103.724	85.373	165.558	10.958	.428
5700	17.297	119.275	103.994	87.102	165.795	8.189	.314
5800	17.315	119.576	104.260	88.833	166.036	5.422	.204
5900	17.331	119.872	104.522	90.565	166.282	2.651	.098
6000	17.346	120.163	104.780	92.299	166.531	.117	.004

June 30, 1964; June 30, 1968

TITANIUM DIBROMIDE (TiBr₂)

(IDEAL GAS)

Point Group [D_{2h}, h³]ΔH_{f,0}^a = -39.4 ± 5.0 kcal/molS_{298.15}^a = [73.8 ± 3.0] gibbs/mol

Ground State Quantum Weight = [3]

ΔH_{f,298.15}^a = -42.8 ± 5.0 kcal/mol

Electronic Levels and Quantum Weights	g _i , cm ⁻¹	g _i
0	[3]	
[7000]	[6]	
[17000]	[6]	
[22000]	[15]	

Vibrational Frequencies and Degeneracies	ω, cm ⁻¹	g _i
[105] (2)		
[160] (1)		
[333] (1)		

Bond Distance: Ti-Br = [2.4] Å

Bond Angle: Br-Ti-Br = [180°]

Rotational Constant: B₀ = [0.0183] cm⁻¹

σ = 2

Heat of Formation

The heat of formation of TiBr₂(g) is calculated from the estimated Ti-Br bond energy. The bond energy is estimated as being the same as the average Ti-Cl bond energy of TiCl₂(g). This estimate is used because the measured average bond energies of TiBr₃(g) and TiCl₃(g) and those of TiBr₄(g) and TiCl₄(g) are very nearly equal.

Heat Capacity and Entropy

The interatomic distances are estimated from those of TiCl₂(g), TiCl₄(g) and TiBr₄(g). The vibrational frequencies are estimated from a valence force field model. The force constant k is estimated as 1.2 millidynes Å⁻¹, and the constant k_f/l² is assumed to be 0.06 millidynes Å⁻¹. These values are derived by a correlation with other dihalides.

The electronic levels are assumed to be the same as TiCl₂(g). The levels of TiCl₂(g) are estimated by assuming that they correspond to the inverted states of NiCl₂(g) (1). The linear configuration is adopted since experimental evidence indicates that other transition metal dihalides are linear (2, 3, 4, 5).

References

1. C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).
2. R. A. Berg and O. Sinanoglu, J. Chem. Phys. **32**, 1082 (1960).
3. J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1670 (1961).
4. G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. **36**, 2879 (1962).
5. A. Buehler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).



Zirconium Dibromide (ZrBr₂)

GFW = 251.038

(Crystal)

ZIRCONIUM DIBROMIDE (ZrBr₂)

(CRYSTAL)

GFW = 251.038

 ΔH_f° = Unknown $\Delta H_f^\circ_{298.15} = [-96.7 \pm 10] \text{ kcal/mol}$ $\Delta H_m^\circ = [15.0 \pm 10] \text{ kcal/mol}$ $\Delta H_{298.15}^\circ = [55.0 \pm 5] \text{ kcal/mol}$ $S_{298.15}^\circ = [27.7 \pm 3] \text{ gibbs/mol}$ $T_m = [900]^\circ\text{K}$

Heat of Formation

The value of $\Delta H_f^\circ(\text{ZrBr}_2, c) = -96.7 \text{ kcal/mol}$ is calculated from the estimated $\Delta H_{298}^\circ = 55 \pm 5 \text{ kcal/mol}$ for $\text{ZrBr}_2(c) \rightarrow \text{ZrBr}_2(g)$, using $\Delta H_{298}^\circ(\text{ZrBr}_2, g) = -41.7 \text{ kcal/mol}$ (1). The estimated ΔH_{298}° is obtained as an average of the heats of sublimation at 298°K for CrBr_2 , MnBr_2 , CoBr_2 , NiBr_2 , SrnBr_2 given by Brewer, Somayajulu and Brackett (2) and TiBr_2 and FeBr_2 listed in JANAF tables (3).

Heat Capacity and Entropy

The heat capacities of $\text{ZrBr}_2(c)$ are estimated from $\text{TiBr}_2(c)$ (3), based on the assumption $\text{Cp}(\text{ZrBr}_2) = \text{Cp}(\text{TiBr}_2) + 3/2 R \ln(\text{at. wt. of Zr}/\text{at. wt. of Ti})$. The entropy, $S_{298}^\circ = 27.7 \text{ eu}$, is estimated in a similar manner based on $\text{TiCl}_2(c)$ (4) and $\text{TiBr}_2(c)$ (3).

Melting Data

The heat of fusion is roughly estimated, so that the entropy of vaporization is about 20 eu. The melting point was estimated by Brewer (5).

References

1. JANAF $\text{ZrBr}_2(g)$ table dated June 30, 1970.
2. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
3. JANAF $\text{TiBr}_2(c)$ table dated June 30, 1968 and $\text{FeBr}_2(c)$ table dated Sept. 30, 1968.
4. JANAF $\text{TiCl}_2(c)$ table dated Dec. 31, 1968.
5. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill Ed., McGraw-Hill Book Company, New York, 1949.

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
100							
200	20.727	27.700	27.700	.000	-96.700	-91.334	66.950
298							
300	20.732	27.828	27.700	.038	-96.706	-91.300	66.512
400	20.706	28.577	27.700	2.125	-94.581	-88.276	46.122
500	21.240	30.587	30.068	6.260	-102.801	-84.299	36.044
600	21.554	32.451	31.815	6.361	-102.326	-80.675	20.368
700	21.828	34.074	33.579	6.550	-101.756	-77.054	24.057
800	22.102	35.577	35.293	10.747	-101.188	-73.563	20.097
900	22.376	37.060	36.956	14.934	-100.622	-70.184	17.033
1000	22.650	38.533	38.619	19.122	-100.062	-66.787	14.596
1100	22.924	39.999	40.289	23.310	-99.502	-63.487	12.614
1200	23.198	41.466	41.960	27.500	-98.935	-60.186	10.961
1300	23.472	42.933	43.632	31.690	-98.368	-56.914	9.568
1400	23.746	44.399	45.304	35.880	-97.801	-53.700	8.363
1500	24.020	45.866	46.976	40.070	-97.236	-50.540	7.364

Mar. 31, 1962; June 30, 1970

GFW = 251.038

(LIQUID)

ZIRCONIUM DIBROMIDE (ZrBr₂) $\Delta H_f^\circ = [-81.920] \text{ kcal/mol}$ $\Delta H_m^\circ = [15.0 \pm 10] \text{ kcal/mol}$ $\Delta H_v^\circ = [31.5] \text{ kcal/mol}$ $S_{298.15}^\circ = [43.983] \text{ gibbs/mol}$ $T_m = [900]^\circ\text{K}$ $T_b = [1555.1]^\circ\text{K}$ Heat of Formation

The ΔH_f° (ZrBr₂, l) is calculated from ΔH_f° (ZrBr₂, c) by adding ΔH_m° and the difference between $H_{900}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

See ZrBr₂(c) table for details.

Vaporization Data

T_b is the temperature at which the Gibbs energy change approaches zero for the process $\text{ZrBr}_2(l) + \text{ZrBr}_2(g)$. The difference between ΔH_f° for ZrBr₂(l) and ZrBr₂(g) at T_b is ΔH_v° .

Zirconium Dibromide (ZrBr₂)

GFW = 251.038

(Liquid)

T, °K	C _p	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log K _p
0							
100	21.750	43.983	43.983	.000	- 81.420	- 81.308	59.600
200	21.750	44.117	43.983	.040	- 81.423	- 81.304	59.230
300	21.750	50.375	44.636	2.215	- 84.511	- 79.723	43.559
400	21.750	55.228	46.447	4.390	- 87.470	- 77.402	33.920
500	21.750	59.193	48.251	6.565	- 87.261	- 75.406	27.539
600	21.750	62.546	50.060	8.740	- 86.685	- 73.710	23.013
700	21.750	65.451	51.806	10.915	- 86.139	- 71.693	19.640
800	21.750	66.012	53.468	13.090	- 85.624	- 70.184	17.033
900	21.750	66.304	55.039	15.265	- 85.138	- 68.450	14.960
1000	21.750	72.377	56.522	17.440	- 84.682	- 66.804	13.273
1100	21.750	76.269	57.923	19.615	- 85.106	- 65.166	11.665
1200	21.750	76.010	59.269	21.790	- 84.530	- 63.505	10.676
1300	21.750	77.622	60.504	23.965	- 83.866	- 61.809	9.664
1400	21.750	79.123	61.696	26.140	- 83.415	- 60.353	8.793
1500	21.750	80.526	62.829	28.315	- 82.877	- 58.833	8.036
1600	21.750	81.845	63.910	30.490	- 82.350	- 57.345	7.372
1700	21.750	83.084	64.941	32.665	- 81.836	- 55.891	6.786
1800	21.750	84.264	65.927	34.840	- 81.334	- 54.462	6.265
1900	21.750	85.380	66.872	37.015	- 80.845	- 53.062	5.798

GFW = 251.038

(IDEAL GAS)

ZIRCONIUM DIBROMIDE (ZrBr₂)

$\Delta H_f^\circ = [-38.2 \pm 10] \text{ kcal/mol}$

Point Group $[D_{2h}]$

$\Delta H_f^\circ_{298.15} = [-41.7 \pm 10] \text{ kcal/mol}$

$S^\circ_{298.15} = [75.7 \pm 3] \text{ gibbs/mol}$

Ground State Quantum Weight = [3]

Zirconium Dibromide (ZrBr₂)

GFW = 251.038

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	Log Kp
0	.000	INFINITE	INFINITE	3.720	34.280	INFINITE
100	12.573	49.270	77.000	3.720	34.280	51.281
200	14.973	49.270	77.000	3.720	34.280	37.120
298	14.504	75.684	75.684	.000	41.710	36.931
300	14.509	75.774	75.685	.087	41.717	36.505
400	14.676	79.974	76.256	1.486	40.120	33.135
500	14.750	83.238	77.340	2.459	37.673	
600	14.801	85.953	78.558	4.437	34.270	19.549
700	14.828	88.237	79.781	5.910	30.387	16.983
800	14.847	90.218	80.965	7.403	25.532	14.053
900	14.864	91.966	82.092	8.868	20.767	11.547
1000	14.883	93.535	83.159	10.376	16.106	9.237
1100	14.908	94.955	84.168	11.865	11.548	7.095
1200	14.941	96.253	85.122	13.357	7.095	5.124
1300	14.984	97.451	86.025	14.854	2.644	3.493
1400	15.039	98.563	86.881	16.352	-1.814	2.166
1500	15.100	99.592	87.695	17.850	-6.262	1.061
1600	15.176	100.540	88.470	19.376	-10.739	0.160
1700	15.260	101.502	89.210	20.898	-15.236	-0.744
1800	15.349	102.377	89.917	22.408	-19.744	-1.744
1900	15.441	103.210	90.595	23.897	-24.261	-2.744
2000	15.536	104.004	91.246	25.356	-28.788	-3.744
2100	15.631	104.764	91.872	27.005	-33.326	-4.744
2200	15.726	105.498	92.476	28.642	-37.874	-5.744
2300	15.818	106.195	93.056	30.270	-42.432	-6.744
2400	15.907	106.870	93.617	31.880	-46.999	-7.744
2500	15.993	107.521	94.160	33.481	-51.576	-8.744
2600	16.074	108.150	94.687	35.064	-56.164	-9.744
2700	16.151	108.759	95.196	36.631	-60.762	-10.744
2800	16.224	109.347	95.691	38.183	-65.370	-11.744
2900	16.292	109.914	96.170	39.720	-69.988	-12.744
3000	16.355	110.471	96.640	41.243	-74.616	-13.744
3100	16.415	111.008	97.094	43.131	-79.264	-14.744
3200	16.471	111.530	97.537	44.776	-83.932	-15.744
3300	16.524	112.036	97.969	46.285	-88.610	-16.744
3400	16.574	112.526	98.390	47.776	-93.300	-17.744
3500	16.621	113.013	98.801	49.240	-97.999	-18.744
3600	16.666	113.482	99.202	51.405	-102.708	-19.744
3700	16.708	113.939	99.595	53.073	-107.427	-20.744
3800	16.749	114.385	99.978	54.766	-112.156	-21.744
3900	16.788	114.821	100.351	56.444	-116.894	-22.744
4000	16.826	115.246	100.720	58.104	-121.642	-23.744
4100	16.862	115.662	101.079	59.768	-126.400	-24.744
4200	16.897	116.069	101.431	61.427	-131.168	-25.744
4300	16.931	116.467	101.777	63.081	-135.946	-26.744
4400	16.964	116.856	102.117	64.730	-140.734	-27.744
4500	16.996	117.238	102.447	66.540	-145.532	-28.744
4600	17.027	117.612	102.772	68.261	-150.350	-29.744
4700	17.057	117.978	103.092	69.966	-155.188	-30.744
4800	17.086	118.336	103.406	71.657	-160.046	-31.744
4900	17.114	118.687	103.715	73.333	-164.924	-32.744
5000	17.140	119.036	104.017	75.005	-169.822	-33.744
5100	17.166	119.376	104.315	76.671	-174.740	-34.744
5200	17.191	119.710	104.604	78.329	-179.678	-35.744
5300	17.215	120.039	104.888	80.000	-184.636	-36.744
5400	17.239	120.363	105.166	81.672	-189.614	-37.744
5500	17.259	120.676	105.458	83.496	-194.612	-38.744
5600	17.279	120.987	105.743	85.423	-199.630	-39.744
5700	17.298	121.293	106.003	87.452	-204.678	-40.744
5800	17.316	121.594	106.259	89.483	-209.746	-41.744
5900	17.333	121.890	106.531	91.515	-214.834	-42.744
6000	17.347	122.191	106.790	93.549	-219.942	-43.744

Mar. 31, 1962; June 30, 1970

Phosphoryl Bromide (POBr₃)

(Ideal Gas) Mol. Wt. = 286.723

Br₃OP

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	INFINITE
100	16.159	66.247	103.348	-3.710	-87.056	-89.940	190.555
200	18.200	77.635	87.881	-2.009	-88.185	-92.139	100.676
298	21.778	85.978	85.978	0.000	-88.185	-92.139	68.485
300	21.508	86.111	85.979	0.040	-88.185	-92.139	68.063
400	22.770	92.487	86.839	2.259	-104.055	-110.305	49.884
500	23.567	97.660	88.502	4.579	-103.996	-108.125	38.517
600	24.105	102.007	90.401	6.964	-103.921	-106.944	30.944
700	24.480	105.753	92.332	9.394	-103.852	-106.803	25.539
800	24.751	109.040	94.220	11.856	-103.786	-106.699	22.938
900	24.951	111.968	96.032	14.342	-103.720	-106.615	18.172
1000	25.102	114.605	97.760	16.845	-103.650	-106.540	13.166
1100	25.218	117.003	99.402	19.361	-103.575	-106.465	8.113
1200	25.309	119.201	100.961	21.888	-103.500	-106.390	3.174
1300	25.382	121.230	102.443	24.422	-103.425	-106.315	0.000
1400	25.441	123.113	103.853	26.964	-103.350	-106.240	9.953
1500	25.489	124.870	105.196	29.510	-103.275	-106.165	8.481
1600	25.529	126.516	106.478	32.061	-103.200	-106.090	7.209
1700	25.563	128.065	107.703	34.616	-103.125	-106.015	6.098
1800	25.591	129.527	108.875	37.174	-103.050	-105.940	5.121
1900	25.615	130.911	109.999	39.734	-102.975	-105.865	4.254
2000	25.636	132.226	111.077	42.296	-102.900	-105.790	3.481
2100	25.654	133.477	112.116	44.861	-102.825	-105.715	2.787
2200	25.670	134.671	113.113	47.427	-102.750	-105.640	2.160
2300	25.683	135.812	114.075	49.995	-102.675	-105.565	1.591
2400	25.693	136.905	115.004	52.564	-102.600	-105.490	1.073
2500	25.700	137.955	115.901	55.134	-102.525	-105.415	0.600
2600	25.716	138.963	116.769	57.705	-102.450	-105.340	0.165
2700	25.724	139.934	117.609	60.277	-102.375	-105.265	0.000
2800	25.732	140.869	118.423	62.850	-102.300	-105.190	0.000
2900	25.739	141.772	119.213	65.423	-102.225	-105.115	0.000
3000	25.745	142.645	119.979	67.997	-102.150	-105.040	0.000
3100	25.750	143.489	120.724	70.572	-102.075	-104.965	0.000
3200	25.756	144.307	121.448	73.148	-102.000	-104.890	0.000
3300	25.760	145.100	122.153	75.723	-101.925	-104.815	0.000
3400	25.764	145.869	122.839	78.300	-101.850	-104.740	0.000
3500	25.768	146.615	123.508	80.876	-101.775	-104.665	0.000
3600	25.772	147.341	124.160	83.453	-101.700	-104.590	0.000
3700	25.775	148.048	124.796	86.031	-101.625	-104.515	0.000
3800	25.778	148.735	125.417	88.608	-101.550	-104.440	0.000
3900	25.781	149.405	126.024	91.186	-101.475	-104.365	0.000
4000	25.784	150.057	126.616	93.764	-101.400	-104.290	0.000
4100	25.786	150.694	127.196	96.343	-101.325	-104.215	0.000
4200	25.788	151.316	127.763	98.922	-101.250	-104.140	0.000
4300	25.790	151.922	128.318	101.501	-101.175	-104.065	0.000
4400	25.792	152.515	128.861	104.080	-101.100	-103.990	0.000
4500	25.794	153.093	129.393	106.659	-101.025	-103.915	0.000
4600	25.796	153.662	129.914	109.239	-100.950	-103.840	0.000
4700	25.798	154.217	130.426	111.818	-100.875	-103.765	0.000
4800	25.799	154.760	130.927	114.398	-100.800	-103.690	0.000
4900	25.801	155.292	131.419	116.978	-100.725	-103.615	0.000
5000	25.802	155.813	131.901	119.558	-100.650	-103.540	0.000
5100	25.803	156.324	132.375	122.138	-100.575	-103.465	0.000
5200	25.804	156.825	132.841	124.719	-100.500	-103.390	0.000
5300	25.805	157.317	133.298	127.299	-100.425	-103.315	0.000
5400	25.806	157.799	133.747	129.880	-100.350	-103.240	0.000
5500	25.807	158.273	134.189	132.461	-100.275	-103.165	0.000
5600	25.808	158.738	134.623	135.041	-100.200	-103.090	0.000
5700	25.809	159.194	135.050	137.622	-100.125	-103.015	0.000
5800	25.810	159.643	135.470	140.203	-100.050	-102.940	0.000
5900	25.811	160.084	135.884	142.784	-99.975	-102.865	0.000
6000	25.812	160.518	136.291	145.365	-99.900	-102.790	0.000

Mar. 31, 1963; Dec. 31, 1965

PHOSPHORYL BROMIDE (POBr₃)

Point Group C_{3v}

S_{298.15} = 85.978 cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

MOL. WT. = 286.723

ΔH_f⁰ = [-87] kcal. mole⁻¹

ΔH_f⁰ 298.15 = [-92] kcal. mole⁻¹

Bond Distances P-O = 1.41 ± 0.07 Å P-Br = 2.06 ± 0.03 Å

Bond Angles Br-P-Br = 108° ± 3°

Product of the Moments of Inertia I_AI_BI_C = 2.2602 × 10⁻¹¹² g.³ cm.⁶

Heat of Formation.

The ΔH_f⁰ 298.15 of POBr₃(g) was calculated from the heat of formation of the crystal and the heat of sublimation. The heat of sublimation was obtained by combining the ΔH_f⁰ and an estimated ΔH_{sub}⁰. The heat of formation of the crystal was derived from the heats observed for the reaction: POBr₃(c) + (n+3)H₂O(l) → [H₃PO₄·3HBr] in nH₂O(l). The data used in these calculations may be summarized as follows:

Data
ΔH_f⁰ 298.15 (water solutions) H₃PO₄

ΔH_f⁰ 298.15 (water solutions) HBr

ΔH_f⁰ 298.15 (liquid) H₂O = -68.3174 kcal. mole⁻¹

ΔH_f⁰ 298.15 (crystal) POBr₃ = -109.1 kcal. mole⁻¹

ΔH_m 298.15 = [3.7] kcal. mole⁻¹

ΔH_v 298.15 = [12.1] kcal. mole⁻¹

Heat Capacity and Entropy.

The molecular constants used were calculated from electron diffraction measurements by J. H. Searlet and L. O. Brockway, J. Am. Chem. Soc. 56, 1941 (1944). The calculated moments are I_A = 8.69174 × 10⁻⁵⁹ g.² cm.² and I_C = 1.474471 × 10⁻⁵⁷ g.² cm.²

From the Raman spectra of POBr₃ the vibrational frequencies were measured and assigned by H. Gerding and M. van Driel, Rec. Trav. Chim. 62, 419 (1942). The Raman spectra was studied and the vibrational frequencies were listed by M. L. Delaunay and P. Francois, Compt. Rend. 220, 817 (1945). The frequencies may also be found in Compt. Rend. 222, 550 (1946) and J. Chim. Phys. 46, 67 (1949) by Delaunay and Francois.

Source
Obtained graphically from M. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).

Obtained graphically from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds. Circular 500.

"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.

Recalculated from heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).

Estimated from comparison with POCl₃.

Estimated from the ΔH_f⁰ (10.6 kcal. mole⁻¹ at 464.9°K). ΔH_v was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Obtained graphically from M. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).

Obtained graphically from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds. Circular 500.

"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.

Recalculated from heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).

Estimated from comparison with POCl₃.

Estimated from the ΔH_f⁰ (10.6 kcal. mole⁻¹ at 464.9°K). ΔH_v was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Obtained graphically from M. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).

Obtained graphically from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds. Circular 500.

"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.

Recalculated from heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).

Estimated from comparison with POCl₃.

Estimated from the ΔH_f⁰ (10.6 kcal. mole⁻¹ at 464.9°K). ΔH_v was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Obtained graphically from M. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).

Obtained graphically from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds. Circular 500.

"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.

Recalculated from heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).

Estimated from comparison with POCl₃.

Estimated from the ΔH_f⁰ (10.6 kcal. mole⁻¹ at 464.9°K). ΔH_v was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Obtained graphically from M. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962).

Obtained graphically from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Stds. Circular 500.

"Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500.

Recalculated from heats observed by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953).

Estimated from comparison with POCl₃.

Estimated from the ΔH_f⁰ (10.6 kcal. mole⁻¹ at 464.9°K). ΔH_v was calculated from a least squares treatment of the v.p. data of M. Van Driel, Rec. Trav. Chim. 61, 748 (1942).

Br₃OP

Phosphorus Tribromide (PBr₃)
(Ideal Gas) Mol. Wt. = 270.723

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	∞	∞	∞	25.293	25.293	INFINITE
100	13.090	65.896	98.214	25.474	25.484	65.308
200	16.674	76.227	84.829	25.638	25.648	37.359
298	18.173	83.206	70.000	30.700	30.711	27.568
300	18.191	83.206	0.034	30.725	30.735	27.429
400	18.863	88.655	8.929	41.763	41.797	16.034
500	19.206	92.905	3.796	41.751	41.751	10.034
600	19.402	96.426	86.881	41.753	41.753	12.992
700	19.503	99.457	6.674	41.779	41.779	10.820
800	19.573	101.922	11.593	62.669	62.669	8.722
900	19.629	104.332	91.470	61.890	61.890	7.247
1000	19.699	106.425	92.863	61.861	61.861	6.019
1100	19.759	108.304	94.183	61.713	61.713	4.999
1200	19.778	110.022	95.432	61.536	61.536	4.156
1300	19.793	111.596	96.618	61.338	61.338	3.442
1400	19.798	113.059	97.740	61.188	61.188	2.826
1500	19.795	114.434	98.808	61.017	61.017	2.266
1600	19.804	115.712	99.825	60.847	60.847	1.750
1700	19.818	116.945	100.795	60.680	60.680	1.273
1800	19.824	118.117	101.722	60.524	60.524	0.842
1900	19.824	119.234	102.610	60.377	60.377	0.456
2000	19.829	120.314	103.461	60.186	60.186	0.104
2100	19.833	121.352	104.278	60.330	60.330	0.245
2200	19.839	122.356	105.071	59.708	59.708	0.207
2300	19.842	123.321	105.842	59.208	59.208	0.175
2400	19.842	124.251	106.550	58.725	58.725	0.146
2500	19.844	125.151	107.224	58.265	58.265	0.118
2600	19.847	126.018	107.865	57.826	57.826	0.094
2700	19.848	126.858	108.476	57.406	57.406	0.071
2800	19.850	127.671	109.061	56.999	56.999	0.049
2900	19.852	128.456	109.650	56.601	56.601	0.027
3000	19.853	129.218	110.240	56.214	56.214	0.005
3100	19.854	129.951	110.829	55.834	55.834	0.000
3200	19.855	130.656	111.414	55.459	55.459	0.000
3300	19.856	131.332	112.000	55.084	55.084	0.000
3400	19.857	131.979	112.586	54.709	54.709	0.000
3500	19.858	132.607	113.172	54.334	54.334	0.000
3600	19.859	133.215	113.755	53.959	53.959	0.000
3700	19.860	133.800	114.338	53.584	53.584	0.000
3800	19.860	134.373	114.921	53.209	53.209	0.000
3900	19.861	134.934	115.504	52.834	52.834	0.000
4000	19.862	135.495	116.087	52.459	52.459	0.000
4100	19.862	136.056	116.670	52.084	52.084	0.000
4200	19.863	136.617	117.253	51.709	51.709	0.000
4300	19.863	137.178	117.836	51.334	51.334	0.000
4400	19.863	137.739	118.419	50.959	50.959	0.000
4500	19.864	138.299	118.999	50.584	50.584	0.000
4600	19.864	138.860	119.582	50.209	50.209	0.000
4700	19.865	139.421	120.165	49.834	49.834	0.000
4800	19.865	139.982	120.748	49.459	49.459	0.000
4900	19.865	140.543	121.331	49.084	49.084	0.000
5000	19.866	141.104	121.914	48.709	48.709	0.000
5100	19.866	141.665	122.497	48.334	48.334	0.000
5200	19.866	142.226	123.080	47.959	47.959	0.000
5300	19.866	142.787	123.663	47.584	47.584	0.000
5400	19.867	143.348	124.246	47.209	47.209	0.000
5500	19.867	143.909	124.829	46.834	46.834	0.000
5600	19.867	144.470	125.412	46.459	46.459	0.000
5700	19.867	145.031	125.995	46.084	46.084	0.000
5800	19.867	145.592	126.578	45.709	45.709	0.000
5900	19.868	146.153	127.161	45.334	45.334	0.000
6000	19.868	146.714	127.744	44.959	44.959	0.000

Dec. 31, 1963

PHOSPHORUS TRIBROMIDE (PBr₃) (IDEAL GAS)

MOL. WT. = 270.723

Point Group C_{3v}
ΔH_f⁰ = -25.3 ± 1.5 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -30.7 ± 1.5 kcal. mole⁻¹
S_{298.15}⁰ = 83.206 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
392 (1)	392.2 (2)
161.3 (1)	115.7 (2)

Bond Distance: P-Br = 2.20 ± 0.03 Å

Bond Angle: Br-P-Br = 106° ± 3°

Product of the Moments of Inertia: I_AI_BI_C = 1.1897 X 10⁻¹¹ g.³ cm.⁶

Heat of Formation.

The heat of formation of PBr₃ gas from white (α) phosphorus, -34.9 kcal. mole⁻¹, was obtained by T. Charnley and H. A. Skinner, J. Chem. Soc. 450 (1953). This was changed from white (α) to the red (V) phosphorus reference state to give the value used in this table (-30.7 kcal. mole⁻¹). To obtain their value (-34.9 kcal. mole⁻¹), Charnley and Skinner measured the heat of formation of the liquid, and combined it and their estimate of the liquid enthalpy with the heat of vaporization (9.5 kcal. mole⁻¹), calculated by M. Van Driel and H. Gerdings, Rec. Trav. Chim. 50, 943 (1941). For the liquid heat of formation Charnley and Skinner observed the ΔH_f⁰ = -67.2 ± 0.6 kcal. mole⁻¹ for PBr₃(l) + (n+3)H₂O(l) → [H₃PO₃ + 3HBr] in nH₂O(l). Van Driel and Gerdings measured the vapor pressure over PBr₃(l) and calculated the heat of vaporization with the aid of a modified Clapeyron equation. The uncertainties on the heats of formation are estimates.

Heat Capacity and Entropy.

Q. Williams and W. Gordy, Phys. Rev. 79, 225 (1950) have reported moments of inertia from the microwave spectrum of PBr₃. From this data D. H. Whiffen in "Tables of Interatomic Distances and Configuration in Molecules and Ions", Scientific Editor, L. E. Sutton, Special Publication No. 11, The Chemical Society (London) 1958, has calculated the selected molecular constants. From these constants the principal moments of inertia were calculated as I_A = I_B = 8.5214 X 10⁻³⁸ g. cm.² and I_C = 1.6383 X 10⁻³⁷ g. cm.²

M. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 393 (1941) have reported P-Br = 2.23 ± 0.04 Å and the angle P-Br-P = 100° ± 2°. S. M. Swingle has measured P-Br = 2.18 ± 0.03 Å and the angle P-Br-P = 101.5° ± 1.5°. The work of Swingle was reported in a private communication from L. Pauling and V. Schomaker, California Institute of Technology to P. W. Allen and L. E. Sutton, Acta. Cryst. 3, 46 (1950). Swingle's data as well as that of Lister and Sutton was obtained by electron diffraction. The 106° angle was selected since 101.5° and 100° give imaginary force constants with the ranges allowed for the type A, 392 cm.⁻¹ frequency and the form of the potential function assumed by P. W. Davis and R. A. Oetjen, J. Molecular Spec. 2, 253 (1958).

The vibrational frequencies were measured and assigned in the infrared by Davis and Oetjen. Raman measurements and assignments by J. Cabannes and A. Rausset, Ann. Phys. (Paris) 19, 229 (1933) were also listed by M. L. Delaunay, Compt. Rend. 222, 1391 (1946) and Compt. Rend. 224, 389 (1947). The Raman assignments were as follows: type A, 380 cm.⁻¹ and 162 cm.⁻¹ and type E, 400 cm.⁻¹ and 116 cm.⁻¹.

Br₃P

Thiophosphoryl Bromide (PSBr₃)

(Ideal Gas) Mol. Wt. = 302.789

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	5.064	-57.361	-57.361	INFINITE
100	15.556	67.925	107.578	3.965	-57.519	-61.935	-61.935	135.352
200	20.462	80.447	91.099	2.131	-58.152	-61.935	-61.935	72.253
298	22.690	89.084	89.084	∞	-63.000	-63.000	-63.000	50.861
300	22.719	89.225	89.085	∞	-63.026	-63.026	-63.026	50.575
400	23.861	95.934	89.992	2.377	-74.683	-69.261	-69.261	37.841
500	24.491	101.333	91.738	4.797	-75.097	-67.858	-67.858	29.659
600	24.868	105.634	93.723	7.267	-75.417	-66.380	-66.380	24.178
700	25.120	109.040	95.777	9.777	-75.640	-64.858	-64.858	19.078
800	25.270	111.951	97.493	12.286	-75.781	-63.288	-63.288	15.078
900	25.384	114.634	99.569	14.819	-75.841	-61.671	-61.671	11.761
1000	25.467	117.113	101.951	17.362	-75.822	-60.012	-60.012	13.115
1100	25.529	121.144	103.042	19.912	-75.722	-58.311	-58.311	10.957
1200	25.571	125.116	104.164	22.477	-75.541	-56.566	-56.566	9.150
1300	25.614	127.416	106.164	25.027	-75.281	-54.781	-54.781	7.650
1400	25.644	127.315	107.608	27.560	-74.946	-52.956	-52.956	6.356
1500	25.668	129.085	108.982	30.155	-74.536	-51.086	-51.086	5.239
1600	25.688	130.763	110.290	32.723	-74.051	-49.161	-49.161	4.264
1700	25.705	132.300	111.530	35.268	-73.496	-47.186	-47.186	3.424
1800	25.718	133.770	112.734	37.786	-72.876	-45.161	-45.161	2.696
1900	25.730	135.161	113.878	40.237	-72.196	-43.086	-43.086	2.067
2000	25.740	136.481	114.976	42.622	-71.461	-40.961	-40.961	1.539
2100	25.749	137.737	116.030	44.955	-70.681	-38.786	-38.786	1.099
2200	25.757	138.937	117.043	47.236	-69.856	-36.561	-36.561	0.743
2300	25.763	140.080	118.021	50.736	-68.986	-34.286	-34.286	0.442
2400	25.769	141.177	118.963	54.461	-68.071	-31.961	-31.961	0.196
2500	25.774	142.229	119.873	58.400	-67.111	-29.586	-29.586	0.000
2600	25.779	143.240	120.752	58.467	-66.111	-27.161	-27.161	1.287
2700	25.783	144.213	121.608	63.045	-65.046	-24.686	-24.686	1.609
2800	25.786	145.151	122.437	68.203	-63.886	-22.161	-22.161	1.967
2900	25.789	146.055	123.227	66.203	-62.636	-19.586	-19.586	2.445
3000	25.792	146.930	124.002	64.782	-61.386	-16.961	-16.961	2.967
3100	25.795	147.775	124.756	71.361	-60.036	-14.286	-14.286	2.686
3200	25.798	148.588	125.488	76.921	-58.686	-11.561	-11.561	2.432
3300	25.800	149.368	126.196	82.461	-57.246	-8.786	-8.786	2.192
3400	25.802	150.119	126.884	79.101	-55.716	-5.961	-5.961	1.967
3500	25.803	150.906	127.569	81.681	-54.096	-3.086	-3.086	1.758
3600	25.805	151.633	128.228	84.261	-52.386	-0.161	-0.161	1.567
3700	25.808	152.309	128.869	86.841	-50.586	2.716	2.716	1.396
3800	25.808	152.929	129.496	89.421	-48.696	5.596	5.596	1.246
3900	25.809	153.659	130.108	92.004	-46.716	8.476	8.476	1.116
4000	25.811	154.353	130.706	94.585	-44.646	11.356	11.356	1.006
4100	25.812	154.990	131.291	97.166	-42.486	14.236	14.236	0.906
4200	25.814	155.619	131.862	100.747	-40.236	17.116	17.116	0.816
4300	25.815	156.213	132.422	104.328	-37.886	20.006	20.006	0.736
4400	25.816	156.773	132.970	107.909	-35.436	22.886	22.886	0.666
4500	25.816	157.393	133.506	107.491	-32.986	25.766	25.766	0.606
4600	25.816	157.960	134.031	110.073	-30.536	28.646	28.646	0.556
4700	25.818	158.059	134.052	112.655	-28.086	31.526	31.526	0.516
4800	25.818	158.059	134.052	115.236	-25.536	34.406	34.406	0.486
4900	25.819	160.113	136.033	117.818	-22.986	37.286	37.286	0.456
5000	25.819	160.113	136.033	120.400	-20.436	40.166	40.166	0.426
5100	25.820	160.624	136.510	122.982	-17.886	43.046	43.046	0.396
5200	25.820	161.151	137.029	125.564	-15.336	45.926	45.926	0.366
5300	25.821	161.618	137.439	128.146	-12.786	48.806	48.806	0.336
5400	25.821	162.100	137.891	130.728	-10.236	51.686	51.686	0.306
5500	25.822	162.574	138.336	133.310	-7.686	54.566	54.566	0.276
5600	25.822	163.039	138.773	135.892	-5.136	57.446	57.446	0.246
5700	25.823	163.495	139.205	138.475	-2.586	60.326	60.326	0.216
5800	25.823	163.945	139.625	141.057	0.000	63.206	63.206	0.186
5900	25.823	164.387	140.041	143.639	2.586	66.086	66.086	0.156
6000	25.824	164.821	140.451	146.222	5.171	68.966	68.966	0.126

March 31, 1963

Br₃PS

THIOPHOSPHORYL BROMIDE (PSBr₃)

MOL. WT. = 302.789

(IDEAL GAS)

Point Group C_{3v}
 $\Delta H_f^0 = [-57] \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 89.084 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 298.15 = [-63] \text{ kcal. mole}^{-1}$
 Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	
299 (1)	
438 (2)	
718 (1)	
115 (2)	
165 (1)	
179 (2)	

Bond Distance: P-Br = $2.13 \pm 0.05 \text{ \AA}$ P-S = $1.89 \pm 0.06 \text{ \AA}$
 Bond Angle: Br-P-Br = $106^\circ \pm 3^\circ$ $\sigma = 3$
 Product of the Moments of Inertia: $I_{AB}^0 = 1.8780 \times 10^{-111} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The $\Delta H_f^0 298.15$ of PSBr₃(g) was calculated from the $\Delta H_f^0 298.15$ of POBr₃(g) and estimated strengths for P-S and P-O bonds.

The difference in the P-S and P-O bond strengths was assumed to be the same for POBr₃ - PSBr₃ and POBr₃ - PSBr₃. For the P-S bond strength in PSBr₃, C. B. Henderson and R. S. Scheffer, "Survey of Thermochemical Data," January 1960, Atlantic Research Corp., Alexandria, Virginia, estimated 91 kcal., from a consideration of unpublished data. The P-O bond was estimated to be 115 kcal. by E. Neale and L. T. D. Williams, J. Chem. Soc. 2465 (1955) and E. Neale, L. T. D. Williams, and V. T. Moores, J. Chem. Soc., 422 (1956).

The $\Delta H_f^0 298.15$ of POBr₃(g), [-93] kcal. mole⁻¹, was taken from the March 31, 1963, JANAP Table. The $\Delta H_f^0 298.15$ of O(g) and S(g) were taken from June 30, 1962, and March 31, 1961, JANAP Tables.

Heat Capacity and Entropy.

The molecular constants were determined from electron diffraction data by J. H. Sechrist and L. O. Brockway, J. Am. Chem. Soc. 66, 1941 (1944). The principal moments of inertia calculated from these constants were $I_A = 1.105941 \times 10^{-37} \text{ g. cm.}^2$, and $I_C = 1.535429 \times 10^{-37} \text{ g. cm.}^2$.

The vibrational frequencies obtained from the Raman spectra of PSBr₃ were reported by M. L. Delvaux and P. Francois, Compt. Rend. 224, 1422 (1947).

Br₃PS

(Crystal) GFW = 287.627

T, °K	C _p ^o	S ^o -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	16.600	INFINITE	5.460	-127.050	-127.050	INFINITE
100	18.467	63.709	2.507	-127.517	-127.517	13.6226
200	20.334	42.171	1.000	-131.500	-125.618	92.080
298	21.308	42.171	0.045	-131.516	-125.560	91.485
300	21.325	42.171	2.516	-142.022	-121.415	66.336
400	25.591	45.424	5.148	-141.361	-116.337	56.651
500	27.416	55.287	8.017	-140.490	-111.410	40.561
600	29.597	60.511	11.159	-139.373	-106.649	33.597
700	32.794	65.350	14.570	-136.017	-102.064	27.693
800	35.920	69.800	18.145	-136.525	-97.469	23.115
900	36.300	74.110	21.633	-133.284	-89.350	17.752
1000	37.446	77.995	25.631	-132.502	-85.382	15.552
1100	38.500	81.614	29.530	-130.583	-81.583	13.709
1200	39.463	85.006	33.520	-128.586	-77.686	12.152
1300	40.333	88.169	37.594	-126.555	-74.255	10.824
1400	41.113	91.217	41.740			
1500	41.600	94.078				

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TRIBROMIDE (TiBr₃)

(CRYSTAL)

GFW = 287.627

$\Delta H_f^\circ = -127.0 \pm 2.0$ kcal/mol
 $\Delta H_{298.15}^\circ = -131.5 \pm 2.0$ kcal/mol
 $\Delta H_t^\circ = 0$ kcal/mol
 $\Delta H_s^\circ = 33.165$ kcal/mol

 $S_{298.15}^\circ = 42.2 \pm 0.8$ gibbs/mol $T_t = 179.9^\circ\text{K}$ $T_s = 1067.2^\circ\text{K}$

Heat of Formation

The heat of formation of TiBr₃(c) is based on the vapor pressure data reported by Hall and Blocher (1) for the process $1/2\text{Hg}_2\text{Br}_2(\text{c}) + \text{TiBr}_3(\text{c}) = \text{TiBr}_4(\text{g}) + \text{Hg}(\text{l})$ over the temperature range 430 to 545°K. Second and third law analyses of these data give values for the heat of reaction of 24.2 ± 0.3 and 24.4 kcal/mol, respectively, for seventy three points, with ten points rejected due to failure of a statistical test. The third law drift in the data is calculated as 0.6 ± 0.6 eu. The third law value of 24.4 kcal/mol is combined with the JANAF heats of formation of TiBr₄(g) and Hg₂Br₂(c) to obtain the adopted heat of formation.

Heat Capacity and Entropy

The heat capacity and entropy of TiBr₃(c) have been measured over the temperature range 51° to 800°K by King et al. (2). Heat capacities above 800°K are estimated from graphical extrapolation. The value of S_{298}° is derived from these data, based on $S_{51}^\circ = 8.60$ eu. The value of S_{51}° is estimated from a Debye-Einstein extrapolation of the measured heat capacities, the equation being $C_p = D(70.0/T) + E(120/T) + 2E(306/T)$. It is assumed that all electronic entropy is contained within the measured and extrapolated heat capacities.

Transition Data

A second order transition at 179.9°K was observed by King et al. (2). The heat capacity at this temperature is in excess of 56.1 gibbs/mol. King et al. measured the value of $H_{188}^\circ - H_{160}^\circ$ as 0.773 kcal/mol.

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of TiBr₃(c) and TiBr₃(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta G_r = 0$ for the process $\text{TiBr}_3(\text{c}) = \text{TiBr}_3(\text{g})$.

References

1. E. H. Hall and J. M. Blocher, Jr., J. Electrochem. Soc. 105, 40 (1958).
2. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI5799, 1961.

Titanium Tribromide (TiBr₃)

(Ideal Gas) GFW = 287.627

T, °K	C _p	S° ⁰ - (C _p - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	4.000	INFINITE	4.331	-	83.991	INFINITE
100	13.193	48.168	3.183	-	84.788	10.645
200	21.526	61.160	1.778	-	84.788	10.645
298	18.561	85.177	1.000	-	89.600	70.897
300	18.985	85.495	1.035	-	89.625	70.897
400	19.462	91.493	1.983	-	100.655	52.930
500	20.271	95.974	3.992	-	100.617	41.934
600	20.462	99.689	6.030	-	100.577	34.004
700	20.547	102.851	8.101	-	100.551	29.372
800	20.579	105.597	10.138	-	100.549	25.448
900	20.567	108.021	12.196	-	100.573	22.396
1000	20.565	110.191	14.255	-	100.629	19.553
1100	20.579	112.152	16.313	-	100.712	17.953
1200	20.571	113.942	18.371	-	101.761	16.278
1300	20.562	115.589	20.427	-	101.776	14.852
1400	20.553	117.112	22.483	-	101.809	13.630
1500	20.544	118.530	24.538	-	101.861	12.570
1600	20.535	119.855	26.592	-	101.933	11.642
1700	20.526	121.100	28.645	-	102.028	10.822
1800	20.518	122.273	30.697	-	102.147	10.094
1900	20.509	123.382	32.748	-	102.291	9.440
2000	20.501	124.434	34.799	-	102.451	8.835
2100	20.494	125.434	36.849	-	102.627	8.278
2200	20.487	126.387	38.898	-	102.816	7.771
2300	20.480	127.298	40.946	-	103.012	7.307
2400	20.474	128.169	42.994	-	103.213	6.882
2500	20.468	129.005	45.041	-	103.421	6.489
2600	20.463	129.800	47.088	-	103.637	6.127
2700	20.458	130.560	49.134	-	103.862	5.790
2800	20.453	131.284	51.179	-	104.094	5.477
2900	20.449	132.041	53.224	-	104.331	5.185
3000	20.445	132.735	55.269	-	104.573	4.912
3100	20.441	133.405	57.313	-	104.822	4.656
3200	20.437	134.054	59.357	-	105.077	4.416
3300	20.433	134.683	61.401	-	105.320	4.190
3400	20.429	135.293	63.444	-	105.569	3.977
3500	20.425	135.885	65.486	-	105.822	3.776
3600	20.421	136.460	67.529	-	106.079	3.570
3700	20.417	137.020	69.571	-	106.338	3.372
3800	20.413	137.564	71.612	-	106.598	3.172
3900	20.409	138.094	73.653	-	106.859	2.972
4000	20.405	138.611	75.694	-	107.122	2.783
4100	20.401	139.115	77.734	-	107.388	2.600
4200	20.397	139.606	79.774	-	107.656	2.424
4300	20.392	140.086	81.814	-	107.926	2.254
4400	20.388	140.555	83.853	-	108.197	2.089
4500	20.383	141.013	85.891	-	108.469	1.926
4600	20.379	141.461	87.929	-	108.742	1.764
4700	20.374	141.899	89.967	-	109.016	1.604
4800	20.370	142.328	92.004	-	109.291	1.444
4900	20.365	142.748	94.041	-	109.566	1.284
5000	20.360	143.159	96.077	-	109.842	1.124
5100	20.355	143.562	98.113	-	110.118	0.964
5200	20.350	143.958	100.148	-	110.394	0.804
5300	20.346	144.345	102.183	-	110.670	0.644
5400	20.341	144.726	104.217	-	110.946	0.484
5500	20.336	145.099	106.251	-	111.222	0.324
5600	20.331	145.465	108.284	-	111.498	0.164
5700	20.326	145.825	110.317	-	111.774	0.004
5800	20.321	146.178	112.349	-	112.049	-0.156
5900	20.316	146.526	114.381	-	112.325	-0.316
6000	20.311	146.867	116.413	-	112.599	-0.476

June 30, 1964; June 30, 1968

TITANIUM TRIBROMIDE (TiBr₃)

(IDEAL GAS)

GFW = 287.627

Point Group C_{3v}ΔH°₀ = -84.0 ± 2.5 kcal/molS°_{298.15} = (85.8 ± 1.2) gibbs/molΔH°_{298.15} = -89.6 ± 2.5 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	$\epsilon_2, \text{cm}^{-1}$	$\epsilon_3, \text{cm}^{-1}$	$\epsilon_4, \text{cm}^{-1}$
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
[380] (1)	[427] (2)	
[162] (1)	[103] (2)	

Bond Distance: Ti-Br = [2.4] Å

Bond Angle: Br-Ti-Br = [100°]

Product of the Moments of Inertia: $I_A I_B I_C = 11.70 \times 10^{-11} \text{ g cm}^5$

σ = 3

Heat of Formation

The heat of formation of TiBr₃(g) is calculated from the heat of sublimation of TiBr₃(c). A tentative equation for the vapor pressure of TiBr₃(c) was reported by Hall and Blocher (1). Second and third law analyses of the equation over the temperature range 700° to 900°K give values of ΔH°₂₉₈ of 45.2 and 41.9 kcal/mol, respectively, with a third law drift of -4.2 eu. The chosen value of ΔH°₂₉₈ is based on the third law ΔH°₂₉₈.

Heat Capacity and Entropy

The interatomic distance is estimated from those of TiCl₄, TiCl₃ and TiBr₄. The pyramidal bond angle is estimated by assuming that TiBr₃(g) is similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 9.76 \times 10^{-38} \text{ g cm}^2$ and $I_C = 1.78 \text{ g cm}^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti³⁺ (2).

References

1. E. H. Hall and J. M. Blocher, J. Phys. Chem. **53**, 1525 (1959).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.



T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	5.347	-147.242	-147.242	INFINITE	INFINITE
100	17.787	17.852	61.092	-4.324	-147.433	321.144	321.144
200	22.283	31.907	43.257	-2.270	-147.658	159.940	159.940
298	23.777	41.122	0.000	-152.000	-145.213	106.439	106.439
300	23.796	41.269	41.122	-152.016	-145.170	106.751	106.751
400	24.500	43.222	2.044	-135.514	-128.514	56.125	56.125
500	24.800	53.733	43.068	-102.119	-102.119	23.683	23.683
600	25.000	58.274	45.302	-74.423	-74.423	10.809	10.809
700	25.100	62.136	47.952	-50.929	-50.929	8.409	8.409
800	25.200	65.439	50.439	-30.439	-30.439	6.409	6.409
900	25.300	68.469	52.722	-12.752	-12.752	4.409	4.409
1000	25.350	71.137	53.635	17.502	17.502	23.683	23.683
1100	25.370	73.554	55.138	20.038	20.038	20.710	20.710
1200	25.390	75.763	56.949	22.576	22.576	18.064	18.064
1300	25.420	77.679	58.926	25.146	25.146	15.824	15.824
1400	25.430	81.634	61.300	30.200	30.200	12.254	12.254
1500	25.440	83.075	62.610	32.744	32.744	10.809	10.809
1600	25.450	84.618	63.860	35.288	35.288	9.537	9.537
1700	25.460	86.161	65.054	37.832	37.832	8.409	8.409
1800	25.470	87.704	66.197	40.376	40.376	7.409	7.409
1900	25.480	89.247	67.292	42.920	42.920	6.409	6.409
2000	25.480	88.756	67.292	42.928	42.928	5.9473	5.9473

Mar. 31, 1962; June 30, 1964

ZIRCONIUM TRIBROMIDE (ZrBr₃)

(CRYSTAL)

MOL. WT. = 330.968

$$\Delta H_f^o = [-147] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o \text{ 298.15} = [-152] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o \text{ 298.15} = [49] \text{ kcal. mole}^{-1}$$

$$S^o \text{ 298.15} = [41.12] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$T_g = [1100]^{\circ}\text{K.}$$

Heat of Formation.

E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956), studied the reaction $\text{Zr}(c) + 3\text{ZrBr}_4(g) = 4\text{ZrBr}_3(c)$ in the temperature range 473 to 973°K. and pressure range 5 to 15 atm. They present a plot of the fractional reaction, for a series of temperatures, as a function of the reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The free energy function change for this reaction was calculated at 100° intervals from 500 to 1100°K. At each temperature, the equilibrium constant was assumed to be 1, and ΔH_f^o 298 accordingly calculated. These values and the heat of formation of $\text{ZrBr}_4(g)$ [see ZrBr₄ table] were used to compute a series of values for the standard heat of formation of $\text{ZrBr}_3(c)$. The following table gives representative values at four temperatures.

T(°K.)	K _p	ΔH _f ^o 298	ΔH _f ^o 298.15 [ZrBr ₃ (c)]
500	1	-70.26 kcal. mole ⁻¹	-132.8 kcal. mole ⁻¹
700	1	-96.48 kcal. mole ⁻¹	-139.3 kcal. mole ⁻¹
900	1	-121.75 kcal. mole ⁻¹	-145.6 kcal. mole ⁻¹
1100	1	-146.28 kcal. mole ⁻¹	-151.8 kcal. mole ⁻¹

If one assumes an initial pressure of from 5 to 10 atm. for ZrBr_4 and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of ZrBr_4 to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larsen and Leddy indicate about 82% reaction at 973°K. It was assumed that around 1100°K. the equilibrium constant attains a value of 1 giving -152 kcal. mole⁻¹ for the heat of formation of $\text{ZrBr}_3(c)$ at 298.15°K. The limits of error were taken to be ±16 kcal. mole⁻¹ which corresponds to a ±500° temperature spread in the above table.

A second law calculation of their data was carried out but the results are of doubtful value in view of the uncertainty in the attainment of equilibrium at the lower temperatures.

Heat Capacity and Entropy.

The heat capacity was estimated in the same manner as for $\text{ZrBr}_4(c)$ [see ZrBr₄(c) table]. The values for C_p and S_g were taken to be the same as those estimated for $\text{ZrBr}_4(c)$. The internal contribution was obtained from the estimated ZrBr_3 vibrational frequencies and the anharmonicity factor "a" was taken to be 2.5×10^{-3} . The specific heat above 300°K. was obtained by graphical extrapolation.

It was assumed, in the above estimation, that the crystalline lattice is made up of ZrBr_3 molecules. However, E. Holze [see R. P. Rolsten, "Iodide Metals and Metal Iodides", John Wiley & Sons, Inc., New York, 1961, page 46] concluded that crystalline ZrI_3 was composed of a chain lattice of $(\text{ZrI}_2)_n$ units. A chain lattice of $(\text{ZrBr}_2)_n$ units is probably a better representation of the solid state structure of ZrBr_3 . Until more quantitative data becomes available, however, it is felt that the above analysis gives a fair approximation to the heat capacity of ZrBr_3 .

Temperature of Disproportionation.

As detailed in the "Heat of Formation" section, this was assumed to be $1100 \pm 500^{\circ}\text{K.}$

Liquid Phase.

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data.

The heat of sublimation at 298.15°K. was obtained from the difference in the heats of formation of the gas and solid at 298.15°K. The sublimation point was obtained from the free energy crossover between gas and solid.



Zirconium Tribromide (ZrBr_3)
(Ideal Gas) Mol. Wt. = 330.968

T. °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	INFINITE	4.613	- 97.508	- 97.508	INFINITE
100	18.892	60.838	104.918	- 97.616	- 97.616	223.637
200	18.063	81.371	90.401	- 98.214	- 98.214	116.732
298	18.968	88.787	88.787	- 98.000	- 110.424	80.939
300	18.998	88.905	88.787	- 98.000	- 110.424	80.473
400	19.365	94.427	89.538	- 98.000	- 110.424	60.470
500	19.543	98.770	90.666	- 98.000	- 110.424	48.001
600	19.642	102.342	92.473	- 98.000	- 110.424	39.683
700	19.702	105.375	93.795	- 98.000	- 110.424	33.257
800	19.742	108.009	95.757	- 98.000	- 110.424	28.274
900	19.769	110.336	97.250	- 98.000	- 110.424	23.799
1000	19.789	112.420	98.665	- 98.000	- 110.424	20.015
1100	19.803	114.266	100.002	- 98.000	- 110.424	16.736
1200	19.811	115.893	101.266	- 98.000	- 110.424	13.700
1300	19.813	117.316	102.464	- 98.000	- 110.424	10.805
1400	19.830	118.586	103.600	- 98.000	- 110.424	8.138
1500	19.835	119.745	104.678	- 98.000	- 110.424	5.769
1600	19.840	120.834	105.705	- 98.000	- 99.086	3.534
1700	19.843	121.871	106.687	- 98.000	- 96.879	1.762
1800	19.847	122.864	107.618	- 98.000	- 95.756	1.014
1900	19.849	123.814	108.515	- 98.000	- 94.628	0.340
2000	19.852	124.727	109.370	- 98.000	- 93.486	0.000
2100	19.853	125.603	110.193	- 98.000	- 92.331	0.000
2200	19.855	126.444	110.980	- 98.000	- 91.164	0.000
2300	19.857	127.251	111.745	- 98.000	- 89.984	0.000
2400	19.858	128.028	112.480	- 98.000	- 88.794	0.000
2500	19.859	128.773	113.188	- 98.000	- 87.594	0.000
2600	19.860	129.492	113.872	- 98.000	- 86.384	0.000
2700	19.861	130.184	114.536	- 98.000	- 85.164	0.000
2800	19.862	130.854	115.176	- 98.000	- 83.934	0.000
2900	19.863	131.501	115.797	- 98.000	- 82.694	0.000
3000	19.863	132.121	116.400	- 98.000	- 81.444	0.000
3100	19.864	132.714	116.985	- 98.000	- 80.184	0.000
3200	19.865	133.284	117.554	- 98.000	- 78.914	0.000
3300	19.865	133.831	118.107	- 98.000	- 77.634	0.000
3400	19.865	134.356	118.645	- 98.000	- 76.344	0.000
3500	19.866	134.857	119.169	- 98.000	- 75.044	0.000
3600	19.866	135.336	119.680	- 98.000	- 73.734	0.000
3700	19.867	135.794	120.176	- 98.000	- 72.414	0.000
3800	19.867	136.231	120.654	- 98.000	- 71.084	0.000
3900	19.867	136.648	121.119	- 98.000	- 69.744	0.000
4000	19.867	137.045	121.570	- 98.000	- 68.394	0.000
4100	19.868	137.421	122.005	- 98.000	- 67.034	0.000
4200	19.868	137.777	122.424	- 98.000	- 65.664	0.000
4300	19.868	138.114	122.824	- 98.000	- 64.284	0.000
4400	19.868	138.431	123.204	- 98.000	- 62.894	0.000
4500	19.868	138.729	123.566	- 98.000	- 61.494	0.000
4600	19.869	139.006	123.911	- 98.000	- 60.084	0.000
4700	19.869	139.264	124.236	- 98.000	- 58.664	0.000
4800	19.869	139.501	124.544	- 98.000	- 57.234	0.000
4900	19.869	139.719	124.836	- 98.000	- 55.794	0.000
5000	19.869	139.917	125.114	- 98.000	- 54.344	0.000
5100	19.869	140.194	125.377	- 98.000	- 52.884	0.000
5200	19.869	140.451	125.624	- 98.000	- 51.414	0.000
5300	19.870	140.688	125.856	- 98.000	- 49.934	0.000
5400	19.870	140.906	126.074	- 98.000	- 48.444	0.000
5500	19.870	141.104	126.276	- 98.000	- 46.944	0.000
5600	19.870	141.281	126.464	- 98.000	- 45.434	0.000
5700	19.870	141.439	126.636	- 98.000	- 43.914	0.000
5800	19.870	141.577	126.794	- 98.000	- 42.384	0.000
5900	19.870	141.694	126.936	- 98.000	- 40.844	0.000
6000	19.870	141.791	127.064	- 98.000	- 39.294	0.000

ZIRCONIUM TRIBROMIDE (ZrBr_3) (IDEAL GAS) MOL. WT. = 330.968

Point Group = $[C_{3v}]$

$S_{298.15}^\circ = [88.73] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$

Ground State Quantum Weight = [2]

$\Delta H_f^\circ 0 = [-98] \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ 298.15 = [-103] \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ω , cm.^{-1}	Deg.
[255] (1)	3
[120] (1)	3
[273] (2)	2
[95] (2)	2

Bond Distances: Zr-Br = $[2.33] \text{ \AA}$

Bond Angle: Br-Zr-Br = $[98^\circ]$

Product of the Moments of Inertia: $I_A I_B I_C = [1.7757 \times 10^{-111}] \text{ gm.}^3 \text{ cm.}^6$

Heat of Formation

The heats of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium-halide bond energy, taken as 1/4 of this heat of formation, was found to be linear with internuclear separation. From gaseous titanium tri- and tetrachloride, it was found that the bond energy of the trichloride was around 7 kcal. mole⁻¹ greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium tribromide, the heat of formation from the gaseous atoms was -329 kcal. mole⁻¹ and from the elements in their standard state, -103 kcal. mole⁻¹.

Heat Capacity and Entropy

The measured internuclear distances for the tribromides of P, As, and Sb were plotted as a function of the atomic weight of these atoms and a smooth curve was drawn through the points. The internuclear distance for ZrBr_3 was taken from this plot. The bond angle was taken to be 98° . The individual moments of inertia are $I_A = I_B = 101.408 \times 10^{-39} \text{ gm. cm.}^2$, $I_C = 172.669 \text{ gm. cm.}^2$.

The measured vibrational frequencies for the tribromides of phosphorus, arsenic, and antimony were plotted as a function of internuclear distance. Smooth curves through these points were obtained for ω_1 , ω_2 , and ω_4 for ZrBr_3 . Force constants, assuming a valence force field and a Br-Zr-Br angle of 98° , were derived from the above values for ω_1 and ω_2 . These force constants were then used to derive values for ω_3 and ω_4 . By a process of successive approximation, a set of force constants was obtained which gave frequencies in good agreement with the three correlation values. The three correlation frequencies and the derived frequency were used in this table.



Iron Dibromide, Dimeric (Fe₂Br₄)
(Ideal Gas) GFW = 431.330

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔC _p ^o	Log K _p
0	0.000	INFINITE	-7.937	-54.569	-	INFINITE
100	27.659	90.000	150.521	-54.167	-60.599	13.915
200	31.234	110.500	280.000	-54.000	-71.674	12.509
298	31.234	123.304	300.000	-60.500	-71.674	12.509
300	31.240	123.497	304.058	-60.530	-71.742	12.509
400	31.479	132.522	324.533	-75.125	-72.481	11.962
500	31.593	139.560	346.860	-75.286	-71.826	11.395
600	31.659	145.326	369.472	-75.160	-71.170	10.828
700	31.704	150.210	392.094	-75.355	-70.492	10.268
800	31.759	154.447	414.630	-75.710	-69.776	9.710
900	31.817	158.151	437.063	-76.279	-69.001	9.156
1000	31.886	161.547	459.329	-77.208	-68.147	8.604
1100	31.970	164.590	481.489	-78.569	-67.167	8.053
1200	32.063	167.376	503.532	-79.500	-66.100	7.503
1300	32.164	169.946	525.466	-80.013	-64.971	6.953
1400	32.270	172.331	547.301	-80.013	-63.824	6.403
1500	32.377	174.565	569.045	-80.013	-62.664	5.853
1600	32.482	176.656	590.706	-80.615	-61.473	5.303
1700	32.584	178.609	612.281	-81.532	-60.256	4.753
1800	32.681	180.494	633.767	-82.073	-59.009	4.203
1900	32.770	182.263	655.160	-82.073	-57.746	3.653
2000	32.859	183.946	676.551	-82.073	-56.473	3.103
2100	32.942	185.551	697.946	-82.073	-55.196	2.553
2200	32.995	187.084	719.341	-82.073	-53.919	2.003
2300	33.039	188.551	740.736	-82.073	-52.642	1.453
2400	33.076	189.964	762.131	-82.073	-51.365	0.903
2500	33.121	191.310	783.526	-82.073	-50.088	0.353
2600	33.169	192.609	804.921	-82.073	-48.811	-0.197
2700	33.217	193.861	826.316	-82.073	-47.534	-0.747
2800	33.265	195.068	847.711	-82.073	-46.257	-1.297
2900	33.315	196.231	869.106	-82.073	-44.980	-1.847
3000	33.367	197.358	890.501	-82.073	-43.703	-2.397
3100	33.419	198.446	911.896	-82.073	-42.426	-2.947
3200	33.470	199.500	933.291	-82.073	-41.149	-3.497
3300	33.518	200.521	954.686	-82.073	-39.872	-4.047
3400	33.566	201.511	976.081	-82.073	-38.595	-4.597
3500	33.612	202.473	997.476	-82.073	-37.318	-5.147
3600	33.656	203.406	1018.871	-82.073	-36.041	-5.697
3700	33.700	204.314	1040.266	-82.073	-34.764	-6.247
3800	33.744	205.197	1061.661	-82.073	-33.487	-6.797
3900	33.788	206.056	1083.056	-82.073	-32.210	-7.347
4000	33.832	206.893	1104.451	-82.073	-30.933	-7.897
4100	33.876	207.709	1125.846	-82.073	-29.656	-8.447
4200	33.920	208.504	1147.241	-82.073	-28.379	-8.997
4300	33.964	209.281	1168.636	-82.073	-27.102	-9.547
4400	34.008	210.036	1189.931	-82.073	-25.825	-10.097
4500	34.052	210.779	1211.326	-82.073	-24.548	-10.647
4600	34.096	211.502	1232.721	-82.073	-23.271	-11.197
4700	34.140	212.209	1254.116	-82.073	-22.000	-11.747
4800	34.184	212.901	1275.511	-82.073	-20.723	-12.297
4900	34.228	213.576	1296.906	-82.073	-19.446	-12.847
5000	34.272	214.241	1318.301	-82.073	-18.169	-13.397
5100	34.316	214.890	1339.696	-82.073	-16.892	-13.947
5200	34.360	215.527	1361.091	-82.073	-15.615	-14.497
5300	34.404	216.150	1382.486	-82.073	-14.338	-15.047
5400	34.448	216.764	1403.881	-82.073	-13.061	-15.597
5500	34.492	217.369	1425.276	-82.073	-11.784	-16.147
5600	34.536	217.964	1446.671	-82.073	-10.507	-16.697
5700	34.580	218.559	1468.066	-82.073	-9.230	-17.247
5800	34.624	219.150	1489.461	-82.073	-7.953	-17.797
5900	34.668	219.736	1510.856	-82.073	-6.676	-18.347
6000	34.712	220.321	1532.251	-82.073	-5.399	-18.897

Sept. 30, 1966

IRON DIBROMIDE, DIMERIC (Fe₂Br₄)

(IDEAL GAS)

GFW = 431.330

Point Group [D_{2h}]

S_{298.15} = [123.3] gibb/mol

ΔH₀^o = [-54.6 ± 2] kcal/mol

ΔH_{298.15}^o = [-60.5 ± 2] kcal/mol

Electronic Levels and Quantum Weights

ε ₁ , cm ⁻¹	g ₁
0	[5]
[4450]	[5]
[8900]	[5]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
[110] (1)	[75] (1)	[95] (2)
[70] (1)	[100] (1)	[24] (2)
[110] (1)	[115] (1)	[190] (2)

Bond Distances: Fe-Br = [2.24] Å

Bond Angles: Fe-Br-Br-Fe = [90]^o

Er-Fe-Br-Br-Fe = [135]^o

Product of the Moments of Inertia: I_AI_BI_C = [1.4498 × 10⁻¹¹⁰] g³ cm⁶

Br-Br-Br-Br-Br-Br = [90]^o

σ = [4]

Heat of Formation.

The chemical equilibria, 622-665°K, for the reaction Fe₂Br₄(g) = 2 FeBr₂(g) were studied by R. P. Porter and R. C. Schoonmaker, J. Phys. Chem. 63, 626 (1959), using a mass spectrometer. Based on the reported partial pressures for the two species, the enthalpy change (ΔH_{298.15}^o) for the reaction was evaluated by both the second and third law methods to be 40.36 ± 2.0 and 40.75 ± 0.2 kcal/mol, respectively. Using the third law ΔH^o value and ΔH_{298.15}^o (FeBr₂, g) = -9.9 ± 0.5 kcal/mol, the heat of formation (ΔH_{298.15}^o) for Fe₂Br₄(g) was calculated as -60.5 ± 2.0 kcal/mol and was adopted.

Heat Capacity and Entropy.

The molecular structure is assumed to be planar. The two Fe atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two Br atoms. The two remaining Br atoms are situated outside the square on a straight line joining the two Fe atoms. The Fe-Br bond distance was estimated to be the same as that in the FeBr₂(g) molecule. The first six vibrational frequencies were estimated by comparison with those for K₂Br₂(g) calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The last three degenerate frequencies were assigned arbitrarily in order to give good second and third law agreement for the heats of dissociation of dimer to monomer. The order of the frequencies listed above is arbitrary and not related to their species types.

The electronic levels and quantum weights were estimated by comparison with those for FeBr₂(g). The three principal moments of inertia are: I_A = 6.6576 × 10⁻³⁸, I_B = 4.3456 × 10⁻³⁷ and I_C = 5.0113 × 10⁻³⁷ g cm².

Br₄Fe₂

Br₄Fe₂

Lead Tetrabromide (PbBr₄)

(Ideal Gas) Mol. Wt. = 526.87

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	6.169	- 36.827	- 36.827	INFINITE
100	20.684	76.248	123.241	- 4.699	- 37.096	- 41.267	90.184
200	25.109	91.924	104.016	- 2.418	- 37.760	- 45.192	49.381
298	25.008	101.750	101.750	0.000	- 44.000	- 48.024	35.201
300	25.018	101.905	101.751	0.046	- 44.032	- 48.048	35.002
400	25.365	109.156	102.737	2.568	- 46.362	- 46.363	25.341
500	25.530	114.836	104.609	5.113	- 58.536	- 43.333	18.940
600	25.622	119.500	106.714	7.671	- 58.444	- 40.300	14.679
700	25.674	122.865	110.877	12.806	- 59.478	- 37.891	10.258
800	25.714	126.865	115.879	15.379	- 59.415	- 30.695	7.453
900	25.739	129.915	118.827	17.694	- 59.346	- 27.506	6.011
1000	25.757	132.628	119.674	19.850	- 59.273	- 24.328	4.833
1100	25.771	135.084	119.620	21.850	- 59.109	- 17.485	3.025
1200	25.781	137.327	119.632	23.698	- 59.027	- 14.826	2.314
1300	25.789	139.391	119.632	25.387	- 58.948	- 11.672	1.700
1400	25.795	141.302	121.112	28.266	- 58.872	- 8.522	1.164
1500	25.800	143.082	122.518	30.845	- 58.801	- 5.376	0.691
1600	25.804	144.747	123.956	33.426	- 58.736	- 2.239	0.272
1700	25.808	146.312	125.431	36.006	- 58.677	- 4.033	0.441
1800	25.811	147.787	126.949	38.587	- 58.626	- 8.718	0.907
1900	25.813	149.182	127.515	41.168	- 58.581	- 19.159	1.820
2000	25.815	150.506	128.031	43.750	- 58.541	- 24.374	2.219
2100	25.817	151.766	128.503	46.331	- 58.505	- 29.583	2.566
2200	25.818	152.975	129.000	48.912	- 58.472	- 34.792	2.824
2300	25.820	154.115	130.725	51.495	- 58.440	- 39.999	3.028
2400	25.821	155.214	132.681	54.077	- 58.410	- 45.206	3.184
2500	25.822	156.268	134.604	56.659	- 58.381	- 50.416	3.299
2600	25.823	157.280	136.495	59.242	- 58.354	- 55.625	3.382
2700	25.824	158.255	138.352	61.826	- 58.328	- 60.837	3.429
2800	25.825	159.194	140.182	64.406	- 58.303	- 66.051	3.451
2900	25.825	160.100	137.001	66.989	- 58.279	- 71.264	3.461
3000	25.826	160.976	137.785	69.571	- 58.256	- 76.476	3.461
3100	25.826	161.823	138.547	72.154	- 58.234	- 81.688	3.452
3200	25.827	162.637	140.007	74.737	- 58.212	- 86.901	3.438
3300	25.827	163.417	141.408	77.319	- 58.191	- 92.114	3.416
3400	25.828	164.169	142.708	79.902	- 58.170	- 97.327	3.387
3500	25.828	164.957	144.390	82.485	- 58.149	- 102.540	3.352
3600	25.829	165.685	146.055	85.068	- 58.128	- 107.753	3.312
3700	25.829	166.372	147.705	87.651	- 58.107	- 112.966	3.267
3800	25.829	167.081	149.335	90.234	- 58.086	- 118.179	3.217
3900	25.829	167.752	150.953	92.816	- 58.065	- 123.392	3.162
4000	25.830	168.406	152.556	95.400	- 58.044	- 128.605	3.102
4100	25.830	169.044	154.146	97.982	- 58.023	- 133.818	3.037
4200	25.830	169.657	155.726	100.565	- 58.002	- 139.031	2.967
4300	25.830	170.276	157.296	103.148	- 57.981	- 144.244	2.892
4400	25.831	170.868	158.838	105.732	- 57.960	- 149.457	2.812
4500	25.831	171.449	160.431	108.315	- 57.939	- 154.670	2.727
4600	25.831	172.016	162.008	110.898	- 57.918	- 159.883	2.637
4700	25.831	172.571	163.561	113.481	- 57.897	- 165.096	2.542
4800	25.831	173.116	165.094	116.064	- 57.876	- 170.309	2.442
4900	25.831	173.648	166.647	118.647	- 57.855	- 175.522	2.337
5000	25.831	174.170	168.224	121.230	- 57.834	- 180.735	2.227
5100	25.832	174.682	169.796	123.813	- 57.813	- 185.948	2.112
5200	25.832	175.185	171.369	126.396	- 57.792	- 191.161	1.992
5300	25.832	175.675	172.939	128.979	- 57.771	- 196.374	1.867
5400	25.832	176.158	174.512	131.562	- 57.750	- 201.587	1.737
5500	25.832	176.632	176.085	134.145	- 57.729	- 206.800	1.602
5600	25.832	177.098	177.658	136.728	- 57.708	- 212.013	1.462
5700	25.832	177.555	179.231	139.311	- 57.687	- 217.226	1.317
5800	25.832	178.005	180.794	141.894	- 57.666	- 222.439	1.167
5900	25.832	178.446	182.367	144.477	- 57.645	- 227.652	1.012
6000	25.832	178.880	184.000	147.060	- 57.624	- 232.865	0.852

Lead tetrabromide (PbBr₄)

(Ideal Gas)

Mol. Wt. = 526.87

ΔH_f⁰ 298.15 = [-44] kcal. mole⁻¹S_{298.15} = 101.8 cal. deg.⁻¹ mole⁻¹Point group T_d

Vibrational Levels and Multiplicities

ω, cm.⁻¹

207 (1)

59 (2)

231 (3)

73 (3)

Pb-Br distance = 2.54 Å

Br-Pb-Br angle = 109° 28'

σ⁻ = 12I_A¹ = 1.920 X 10⁻¹¹⁰ g.² cm.²Heat of formation. ΔH_f⁰ 298.15 was estimated by comparison with the value of ΔH_f⁰ 298.15 for PbBr₂(s).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Titanium Tetrabromide (TiBr₄)
(Crystal)

GFW = 367.536

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	-0.00	0.00	INFINITE	-	-	-	INFINITE
100	22.460	28.901	83.641	- 6.425	- 141.655	- 141.655	310.107
200	26.059	46.402	60.992	- 5.474	- 141.774	- 141.693	155.069
298	31.430	56.227	56.227	- 2.918	- 142.018	- 141.925	103.468
300	31.505	56.422	56.228	- 0.58	- 142.719	- 141.139	102.820
400	31.974	67.612	57.479	- 1.253	- 161.622	- 136.049	74.333
500	31.974	74.746	61.845	6.450	- 160.837	- 129.749	56.713
600	31.974	80.576	64.496	9.448	- 160.981	- 123.603	45.072
700	31.974	85.705	66.721	12.446	- 158.260	- 111.262	30.505
800	31.974	89.774	69.721	16.443	- 155.995	- 105.827	25.698
900	31.974	93.540	72.142	19.240	- 157.362	- 100.064	21.869
1000	31.974	96.909	74.472	22.437	- 156.757	- 94.363	18.748
1100	31.974	99.956	76.452	25.435	- 156.730	- 88.002	13.954
1200	31.974	102.728	78.144	32.030	- 156.144	- 81.379	12.079
1300	31.974	105.268	80.640	35.427	- 155.788	- 77.401	10.461
1400	31.974	107.667	82.505	38.424	- 155.152	- 71.801	
1500	31.974	109.873	84.257				

Dec. 31, 1961; June 30, 1964; June 30, 1968

TITANIUM TETRABROMIDE (TiBr₄)

(CRYSTAL)

GFW = 367.536

ΔHf° = -141.7 ± 1.1 kcal/mol
ΔHf°_{298.15} = -147.7 ± 1.0 kcal/mol
ΔHm° = 3.08 kcal/mol

S°_{298.15} = 58.2 ± 1.6 kcal/mol
Tm = 311.4°K

Heat of Formation

The heat of formation, ΔHf°₂₉₈, of TiBr₄(c) has been determined calorimetrically by several investigators as follows.

Investigators	Reaction	ΔHf° _{298.15} kcal/mol
Nelson, Johnson and Prosen (1)	Ti(c) + 2Br ₂ (g) = TiBr ₄ (c)	-147.3 ± 1.1
Johnson, Gilliland and Prosen (2)	TiCl ₄ (l) + 2Br ₂ (l) = TiBr ₄ (c) + 2Cl ₂ (g)	-147.6 ± 1.3
Schlafer and Schmidtke (3)	Ti(c) + 2Br ₂ (l) = TiBr ₄ (c)	-147.7 ± 0.3
Gross, Hayman and Levi (4)	Ti(c) + 2Br ₂ (l) = TiBr ₄ (c)	-148.1 ± 0.3

The chosen value of ΔHf°₂₉₈ is the average of these determinations. The value from the work of Nelson et al. (1) is obtained from their heat of reaction and the JANAF value for the heat of vaporization of bromine. The value obtained from Johnson et al. (2) is a combination of their heat of reaction and the JANAF value for the heat of formation of TiCl₄(l).

Heat Capacity and Entropy

The heat capacity of TiBr₄(c) has been measured over the temperature range 51° to 298°K by King et al. (5). They reported a value of 42.74 eu for S°₂₉₈ - S°₅₁ based on their measurements. The value of S°₅₁ is estimated as 15.46 eu. King et al. (5) reported an estimate of 14.75 ± 1.60 for the same quantity. The former estimate is used so that the values of ΔHf°₂₉₈ obtained by both second and third law methods are in agreement. See TiBr₄(g) table for details. The value of H°₅₁ - H°₀ is estimated as 0.372 kcal/mol. This estimate is based on a Debye-Einstein extrapolation of the measured heat capacity with vibrational contributions removed.

Melting Data

The melting temperature and heat of melting were reported by King et al. (5).

References

1. R. A. Nelson, W. H. Johnson and E. J. Prosen, J. Res. Natl. Bur. Std. **62**, 67 (1959).
2. W. H. Johnson, A. Gilliland and E. J. Prosen, J. Res. Natl. Bur. Std. **63**, 161 (1959).
3. H. L. Schlafer and H. H. Schmidtke, Z. Physik. Chem. **11**, 297 (1959).
4. P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. **53**, 1601 (1957).
5. E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Br₄Ti

Titanium Tetrabromide (TiBr₄)

(Liquid)

GFW = 367.536

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o - TS ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	36.300	67.918	.000	-144.681	-141.051	103.393
300	36.300	68.142	.007	-144.651	-141.027	102.736
400	36.300	76.565	3.697	-138.159	-136.840	94.640
500	36.300	86.685	7.327	-130.941	-131.022	85.100
600	36.300	93.304	10.957	-125.753	-126.911	76.227
700	36.300	98.599	14.567	-122.197	-122.197	68.152
800	36.300	103.746	18.217	-117.646	-117.646	60.139
900	36.300	108.022	21.847	-113.234	-113.234	52.497
1000	36.300	111.647	25.477	-108.942	-108.942	45.209
1100	36.300	115.306	29.107	-104.757	-104.757	38.113
1200	36.300	118.465	32.737	-100.626	-100.626	31.377
1300	36.300	121.370	36.367	-96.540	-96.540	25.230
1400	36.300	124.060	39.997	-92.500	-92.500	19.446
1500	36.300	126.565	43.627	-88.617	-88.617	14.111

TITANIUM TETRABROMIDE (TiBr₄)

(LIQUID)

GFW = 367.536

S_{298.15}^o = 67.918 ± 1.8 gibbs/molΔH_f^o_{298.15} = -144.681 ± 1.0 kcal/molT_m = 311.4°KΔH_m^o = 3.08 kcal/molT_b = 504.1°KΔH_v^o = 10.80 kcal/mol

Heat of Formation

The heat of formation of TiBr₄(l) is calculated from the heat of melting, ΔH_m^o_{311.4}, the heat of formation of TiBr₄(c), and the values of H_{311.4} - H_{298.15} for both crystal and liquid.

Heat Capacity and Entropy

King et al. (1) reported the heat capacity of TiBr₄(l) between the melting point and normal boiling point. The entropy, S₂₉₈^o, of TiBr₄(l) is calculated from ΔS_{311.4} - S_{298.15} of both crystal and liquid and the value of S_{298.15} of TiBr₄(c).

Melting Data

The melting temperature and heat of melting were reported by King et al. (1).

Vaporization Data

The boiling temperature, T_b, is taken as the point at which K_p = 1 for the reaction TiBr₄(l) = TiBr₄(g). The heat of vaporization is calculated as the difference between ΔH_f^o of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for TiBr₄(g).

Reference

1. E. G. King, W. W. Meller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ₂₉₈ ^o)/T	kcal/mol ΔH ^o - H ₂₉₈ ^o	ΔG ^o	Log K _p
0	∞.000	INFINITE	∞.713	-124.343	INFINITE
100	18.359	71.735	-4.367	-128.870	781.644
200	22.669	85.929	-2.295	-135.105	148.245
298	24.070	93.246	∞.000	-136.018	99.704
300	24.089	93.395	∞.005	-131.532	99.108
400	24.793	102.434	96.201	-134.538	73.508
500	25.148	108.008	98.025	-136.095	57.539
600	25.350	112.611	100.083	-136.011	46.499
700	25.475	116.531	102.160	-135.942	39.303
800	25.557	119.638	104.174	-135.892	33.609
900	25.614	122.952	106.096	-135.865	29.181
1000	25.655	126.553	107.919	-135.866	25.638
1100	25.686	129.999	109.446	-135.891	22.740
1200	25.709	133.335	111.277	-135.930	20.317
1300	25.727	136.594	113.282	-136.000	18.260
1400	25.742	139.781	115.460	-136.100	16.497
1500	25.753	142.908	117.804	-136.230	14.969
1600	25.761	145.974	120.312	-136.380	13.632
1700	25.767	148.989	122.981	-136.550	12.453
1800	25.771	151.954	125.814	-136.740	11.405
1900	25.773	154.870	128.801	-136.950	10.465
2000	25.776	157.737	131.942	-137.180	9.604
2100	25.782	160.554	135.158	-137.430	8.815
2200	25.786	163.321	138.431	-137.700	8.098
2300	25.789	166.038	141.764	-137.990	7.442
2400	25.792	168.705	145.158	-138.300	6.841
2500	25.795	171.322	148.612	-138.630	6.287
2600	25.797	173.890	152.126	-138.980	5.776
2700	25.800	176.418	155.699	-139.350	5.303
2800	25.801	178.900	159.332	-139.740	4.862
2900	25.802	181.347	163.026	-140.150	4.452
3000	25.813	183.759	166.780	-140.580	4.069
3100	25.816	186.132	170.594	-141.030	3.710
3200	25.816	188.466	174.463	-141.500	3.374
3300	25.817	190.761	178.396	-141.990	3.057
3400	25.818	193.018	182.391	-142.500	2.759
3500	25.818	195.233	186.451	-143.030	2.478
3600	25.819	197.406	190.574	-143.580	2.216
3700	25.820	199.536	194.759	-144.150	1.978
3800	25.821	201.621	198.999	-144.740	1.764
3900	25.821	203.661	203.299	-145.350	1.572
4000	25.822	205.656	207.659	-146.000	1.400
4100	25.822	207.606	212.079	-146.680	1.247
4200	25.823	209.511	216.559	-147.390	1.112
4300	25.823	211.371	221.099	-148.130	1.000
4400	25.824	213.186	225.699	-148.900	0.900
4500	25.824	214.956	230.359	-149.700	0.810
4600	25.825	216.681	235.079	-150.530	0.730
4700	25.825	218.361	239.859	-151.390	0.660
4800	25.825	220.001	244.699	-152.280	0.600
4900	25.826	221.601	249.599	-153.200	0.550
5000	25.826	223.161	254.559	-154.150	0.510
5100	25.826	224.681	259.579	-155.130	0.480
5200	25.827	226.161	264.659	-156.140	0.450
5300	25.827	227.601	269.799	-157.180	0.430
5400	25.827	229.001	274.999	-158.250	0.410
5500	25.827	230.361	280.259	-159.350	0.390
5600	25.828	231.681	285.579	-160.480	0.380
5700	25.828	232.961	290.959	-161.640	0.370
5800	25.828	234.201	296.399	-162.830	0.360
5900	25.828	235.401	301.899	-164.050	0.350
6000	25.828	236.561	307.459	-165.300	0.340

Dec. 31, 1961; June 30, 1964; June 30, 1968

Point Group T_d

S_{298.15} = 95.25 ± 1.0 gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
229.5 (1)	74 (2)
382 (3)	90.5 (3)

Bond Distance: Ti-Br = 2.31 Å

Bond Angle: Br-Ti-Br = 109° 28'

Product of the Moments of Inertia: I_AI_BI_C = 6.76 × 10⁻¹¹¹ g³ cm⁶

Heat of Formation

The heat of formation of TiBr₄(g) is calculated from those of TiBr₄(c) and TiBr₄(l) and the heats of reaction for the processes (A) TiBr₄(c) = TiBr₄(g) and (B) TiBr₄(l) = TiBr₄(g). Second and third law analyses of the vapor pressure data for these processes yield the following results. The first four investigations employed the spoon gauge method, the last investigation being a manometric determination.

Source	Reaction	No. Pts.	Range T, °K	ΔH ₂₉₈ ^o , kcal/mol	Drift, au	ΔH _{298.15} ^o , kcal/mol
Boni, 1966 (1)	A	13	275 - 311	16.4 ± 0.2	-0.6 ± 0.5	-131.5
Funaki et al., 1961 (2)	B	14	385 - 493	12.2 ± 0.3	1.6 ± 0.3	-131.8
Seki, 1941 (3)	A	12	286 - 306	15.4 ± 0.5	1.6 ± 1.6	-131.5
Hall et al., 1958 (4)	B	89*	341 - 499	13.2 ± 0.1	-0.1 ± 0.1	-131.5
Keavney & Smith, 1960 (5)	A	14	287 - 310	16.1 ± 0.3	0.2 ± 0.8	-131.6

* Four points rejected due to failure of a statistical test.

** Calculation based on third law ΔH₂₉₈^o.

The adopted value of 131.5 kcal/mol is that obtained from the data of Hall et al. (4), whose third law drift was adjusted to zero by changing the entropy of the crystal within its uncertainty.

Heat Capacity and Entropy

The interatomic distance was reported by Lister and Sutton (6). The tetrahedral configuration is confirmed by spectroscopic studies (7, 8). The individual moments of inertia are I_A = I_B = I_C = 1.89 × 10⁻³⁷ g cm².

The vibrational frequencies have been reported by Delvaux and Francois (7) and by Miller and Carlson (8). These values are based primarily on the Raman and infrared spectra of TiBr₄(l), the value of ν₃ being the only frequency measured for TiBr₄(g).

The electronic spectra of TiBr₄ in solution have been measured by Dijkgraaf (9). Di Sipio et al. (10) have reported the near ultraviolet spectra of TiBr₄(g). Both of these studies indicate that TiBr₄ has no low lying electronic levels which would contribute significantly to the entropy.

References

1. A. A. Boni, J. Electrochem. Soc. **113**, 1089 (1966).
2. K. Funaki, K. Uchimura and Y. Kuniya, Kogyo Kagaku Zasshi **64**, 1914 (1961).
3. S. Seki, J. Chem. Soc. Japan **62**, 789 (1961).
4. E. H. Hall, J. M. Biocher and I. E. Campbell, J. Electrochem. Soc. **105**, 271 (1958).
5. J. J. Keavney and N. O. Smith, J. Phys. Chem. **64**, 737 (1960).
6. M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941).
7. H. L. Delvaux and F. Francois, Compt. Rend. **220**, 173 (1945).
8. F. A. Miller and G. L. Carlson, Spectrochim. Acta **16**, 6 (1960).
9. C. Dijkgraaf, Spectrochim. Acta **21**, 769 (1965).
10. L. Di Sipio, G. DeMichelis, E. Tondello and L. Olardi, Gazz. Chim. Ital. **96**, 1785 (1966).

Zirconium Tetrabromide (ZrBr₄)
(Crystal) Mol. Wt. = 410.884

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	6.731	175.296	175.296	INFINITE
100	22.377	24.695	5.391	175.504	175.504	32.540
200	28.856	26.605	5.391	175.615	175.615	190.680
298	29.856	28.155	5.391	175.615	175.615	126.909
300	29.856	28.155	5.391	175.615	175.615	126.909
400	30.900	29.615	5.391	175.615	175.615	126.909
500	31.600	29.615	5.391	175.615	175.615	126.909
600	31.900	29.615	5.391	175.615	175.615	126.909
700	32.150	29.615	5.391	175.615	175.615	126.909
800	32.400	29.615	5.391	175.615	175.615	126.909
900	32.550	29.615	5.391	175.615	175.615	126.909
1000	32.600	29.615	5.391	175.615	175.615	126.909
1100	32.620	29.615	5.391	175.615	175.615	126.909
1200	32.640	29.615	5.391	175.615	175.615	126.909
1300	32.650	29.615	5.391	175.615	175.615	126.909
1400	32.660	29.615	5.391	175.615	175.615	126.909
1500	32.670	29.615	5.391	175.615	175.615	126.909

Mar. 31, 1962; Mar. 31, 1964

Br₄Zr

MOL. WT. = 410.884

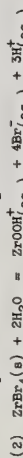
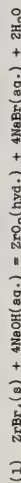
(CRYSTAL)

ZIRCONIUM TETRABROMIDE (ZrBr₄)

S_{298.15} = [53.70 cal. deg.⁻¹ mole⁻¹
T_m = 723°K.
T_b = 630°K.
ΔH_f⁰ = -175.3 ± 0.8 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -181.6 ± 0.6 kcal. mole⁻¹
ΔH_g⁰ 298.15 = 28.0 ± 1.0 kcal. mole⁻¹

Heat of Formation.

A. G. Turnbull, J. Phys. Chem. 65, 1852 (1961), measured the heat effect accompanying the following reactions:



Turnbull also measured the chlorine analogue of the above reactions. He used the measured heat of formation of zirconium tetrachloride, reported by Gross, Hyman and Levi [see ZrCl₄ table], to calculate the heats of formation of ZrO₂(hyd.) and ZrO₂(aq.). The heat of formation of solid zirconium tetrabromide from reaction (1) was -182.2 ± 0.7 kcal. mole⁻¹ and from reaction (2) was -181.0 ± 0.6 kcal. mole⁻¹. An average of the two was taken to represent the heat of formation of the tetrabromide.

Heat Capacity and Entropy.

The heat capacity from 0 to 300°K. was calculated by means of the relationship $C_p = C_{vm}(s_D = 85^\circ\text{K.}) + C_{VR}(Q_2 = 155^\circ\text{K.}) + C_{Vl} + a^2 C_{VT}$, where C_{VR} represents the hindered translational, C_{Vl} the librational, and C_{VT} the internal vibrational contributions to the heat capacity of the solid. $C_v = C_{VT} + C_{VR} + C_{Vl}$ represents the constant volume heat capacity to which $a^2 C_{VT}$, the anharmonic contribution, is added to convert to a heat capacity at constant pressure. The internal contribution, C_{Vl} , was obtained from the estimated vibrational frequencies [see gas table]. The values for Q_2 and Q_3 were obtained from an elaborate correlation with the corresponding values for ZrCl₄ [see ZrCl₄ crystal table]. C_p was computed using a number of values for the constant term "a". The value, $a = 2.5 \times 10^{-3}$, was chosen from a consideration of the sublimation calculations [see below]. The heat capacity above 300°K. was obtained by a graphical extrapolation.

Melting Point.

This was reported by O. Rahlfs and M. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).

Sublimation Data.

Vapor pressure measurements have been reported by Rahlfs and Fischer (loc. cit.) and by H. L. Schlafer and H. Skoludek, Z. Elektrochem. 56, 367 (1952). The heat of sublimation results, for two values of "a", are given in the following table.

Reference	"a"	ΔH _g (298) [3rd Law]	ΔH _g (298) [2nd Law]
Schlafer	3.0 X 10 ⁻³	27.43	A
	2.5 X 10 ⁻³	27.73	B
Rahlfs	3.0 X 10 ⁻³	27.52	28.82
	2.5 X 10 ⁻³	27.85	28.68
Rahlfs	3.0 X 10 ⁻³	27.85	28.35
	2.5 X 10 ⁻³	27.99	28.15
Rahlfs	3.0 X 10 ⁻³	27.85	27.99
	2.5 X 10 ⁻³	27.85	27.99

All heat values are in kcal. mole⁻¹. Two sets of second law heat values are given; set "A" was obtained from the slope reported by the authors and set "B" from a least squares fit performed at The Dow Thermal Laboratory. Various high temperature extrapolations were carried out for a particular value of "a" but only insignificant changes in the heat of sublimation resulted. The data of Schlafer and Skoludek showed a considerable temperature dependent third law heat of sublimation at 298°K. when "a" was taken as 3.0 X 10⁻³, and a moderate temperature dependence when "a" was taken as 2.5 X 10⁻³. The data of Rahlfs and Fischer showed a very slight temperature dependence for a = 3.0 X 10⁻³ and no temperature dependence for a = 2.5 X 10⁻³.

In both sets of data there are large differences between 2nd and 3rd law values for a = 3.0 X 10⁻³, good 2nd and 3rd law agreement for the data of Rahlfs and Fischer and a = 2.5 X 10⁻³, and only fair agreement for the data of Schlafer and Skoludek and a = 2.5 X 10⁻³. Extrapolation of the data of Schlafer and Skoludek for a = 2.0 X 10⁻³ indicated a continuing temperature dependent third law heat of sublimation and disagreement between 2nd and 3rd law values. The heat of sublimation was taken as the average of the third law and two second law values calculated from the data of Rahlfs and Fischer using "a" = 2.5 X 10⁻³. The results of this analysis should not be considered conclusive since all of the data is estimated.

The sublimation point reported by Rahlfs and Fischer (loc. cit.) was 630°K., that calculated from the data of Schlafer and Skoludek was 624°K. and that obtained from the free energy crossover between solid and gas was 630°K. The sublimation point was taken as 630°K.

Since the sublimation point is lower than the melting point, the liquid phase is thermodynamically unstable under ordinary conditions.

Br₄Zr

Zirconium Tetrabromide (ZrBr₄)
(Ideal Gas) Mol. Wt. = 410.884

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	-(H°-H° ₂₉₈)	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	19.371	74.781	110.035	4.515	-166.527	-166.527	INFINITE
200	23.211	80.622	101.482	4.352	-166.628	-151.195	330.422
298	24.211	84.173	99.173	4.000	-167.330	-154.505	164.920
300	24.525	99.325	99.174	4.045	-153.632	-158.727	115.627
400	25.066	106.464	100.143	2.528	-168.264	-157.419	86.006
500	25.332	112.089	101.990	5.050	-168.179	-154.718	67.624
600	25.482	116.722	104.071	7.591	-168.118	-152.032	55.375
700	25.573	120.636	106.166	10.144	-168.076	-149.356	46.629
800	25.634	124.077	108.196	12.705	-168.045	-146.684	40.070
900	25.675	127.099	110.132	15.270	-168.021	-144.015	34.970
1000	25.705	129.805	111.966	17.839	-168.006	-141.346	30.860
1100	25.728	132.256	113.701	20.411	-168.008	-138.682	27.552
1200	25.744	134.456	115.342	22.983	-168.078	-135.967	24.762
1300	25.758	136.457	116.896	25.560	-168.087	-133.215	22.394
1400	25.768	138.466	118.360	28.136	-168.005	-130.465	20.365
1500	25.777	140.244	119.764	30.713	-169.032	-127.712	18.607
1600	25.784	141.908	121.101	33.291	-169.067	-124.953	17.067
1700	25.789	143.472	122.371	35.869	-169.111	-122.193	15.708
1800	25.794	144.946	123.585	38.449	-169.163	-119.435	14.501
1900	25.798	146.340	124.746	41.029	-169.223	-116.668	13.410
2000	25.802	147.664	125.859	43.609	-169.295	-113.905	12.446
2100	25.805	148.923	126.928	46.189	-169.373	-111.143	11.565
2200	25.808	150.123	127.955	48.770	-170.464	-108.381	10.747
2300	25.810	151.271	128.944	51.351	-171.564	-105.619	9.994
2400	25.812	152.369	129.897	53.932	-172.672	-102.857	9.303
2500	25.814	153.423	130.818	56.513	-173.787	-100.095	8.667
2600	25.815	154.435	131.707	59.095	-174.908	-97.333	8.070
2700	25.817	155.410	132.556	61.676	-176.036	-94.571	7.535
2800	25.818	156.348	133.369	64.258	-177.172	-91.809	7.029
2900	25.819	157.254	134.126	66.840	-178.316	-89.047	6.558
3000	25.820	158.130	134.849	69.422	-179.466	-86.285	6.118
3100	25.821	158.976	135.549	72.004	-180.622	-83.523	5.706
3200	25.822	159.796	136.228	74.586	-181.784	-80.761	5.320
3300	25.823	160.591	136.888	77.168	-182.952	-78.000	4.957
3400	25.824	161.362	137.500	79.750	-184.126	-75.238	4.614
3500	25.824	162.110	138.057	82.333	-185.306	-72.476	4.291
3600	25.824	162.838	138.550	84.915	-186.492	-69.714	3.987
3700	25.825	163.545	139.000	87.498	-187.684	-66.952	3.698
3800	25.825	164.234	140.459	90.080	-188.882	-64.190	3.424
3900	25.826	164.905	141.146	92.663	-190.086	-61.428	3.164
4000	25.826	165.559	141.747	95.245	-191.296	-58.666	2.917
4100	25.827	166.196	142.266	97.828	-192.512	-55.904	2.681
4200	25.827	166.819	142.811	100.411	-193.734	-53.142	2.457
4300	25.827	167.426	143.347	102.993	-194.962	-50.380	2.243
4400	25.828	168.020	143.875	105.576	-196.196	-47.618	2.038
4500	25.828	168.601	144.405	108.159	-197.436	-44.856	1.843
4600	25.828	169.168	144.934	110.742	-198.682	-42.094	1.656
4700	25.828	169.724	145.462	113.324	-199.934	-39.332	1.476
4800	25.829	170.268	146.010	115.907	-201.192	-36.570	1.301
4900	25.829	170.800	146.618	118.490	-202.456	-33.808	1.130
5000	25.829	171.332	147.107	121.073	-203.726	-31.046	0.962
5100	25.829	171.833	147.597	123.656	-205.000	-28.284	0.799
5200	25.830	172.335	148.058	126.239	-206.278	-25.522	0.641
5300	25.830	172.837	148.521	128.822	-207.560	-22.760	0.487
5400	25.830	173.310	148.976	131.405	-208.846	-20.000	0.337
5500	25.830	173.784	149.472	133.988	-210.136	-17.240	0.190
5600	25.830	174.249	149.962	136.571	-211.432	-14.480	0.046
5700	25.830	174.706	150.454	139.154	-212.734	-11.720	0.000
5800	25.831	175.156	150.918	141.737	-214.042	-8.960	0.000
5900	25.831	175.597	151.376	144.320	-215.356	-6.200	0.000
6000	25.831	176.031	151.957	146.903	-216.676	-3.440	0.000

Mar. 31, 1962; Mar. 31, 1964

ZIRCONIUM TETRABROMIDE (ZrBr₄)

(IDEAL GAS)

MOL. WT. = 410.884

Point Group = [m₃]

S°_{298.15} = [99.17] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f⁰ = [-146.5 ± 1.6] kcal. mole⁻¹
ΔH_f⁰ 298.15 = -153.6 ± 1.6 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	[1217] (1)	[60] (2)	[322] (3)	[70] (3)

Bond Distances: Zr-Br = [2.45] Å

Bond Angle: Br-Zr-Br = [109° 29']

Product of the Moments of Inertia: I_AI_BI_C = [9.5782 x 10⁻¹¹¹] gm.³ cm.⁶

Calculated from the heats of formation and sublimation for the crystal at 298.15°K. (see crystal table for details).

Heat Capacity and Entropy.

The interatomic distance was obtained from an involved correlation of the interatomic distances and covalent radii of the tetrahalides of Pb, Si, Ti, Ge, and Sn. I. N. Godnev, A. M. Aleksandrovskaya, and I. V. Regina, Optics and Spectroscopy 7, 172 (1953), estimated the interatomic distance and report 2.47 Å as the Zr-Br distance. The bond angle was taken to be the tetrahedral angle. The three principal moments of inertia are: I_A = I_B = I_C = 2.1237 x 10⁻³⁷ gm. cm.².

The fundamental vibrational frequencies are all estimated. The product of ω₁ and ω₂ versus internuclear distance for these molecules gave nearly linear smooth curves. Values of ω₁ and ω₂ obtained from these plots were 216 cm.⁻¹ and 58 cm.⁻¹ respectively. These values for ω₁ and ω₂ were used in a valence force field calculation to derive values for ω₃ and ω₄. Central and valence force field calculations, using estimated force constants were carried out but the results proved to be inconsistent. Therefore, ω₁ was taken as the average of the two empirically derived values, ω₂ as its empirically derived value, and ω₃ and ω₄ as those derived from the empirical values and the valence force field calculation. Godnev, Aleksandrovskaya, and Regina (loc. cit.) estimated the vibrational frequencies; they obtained ω₁ = 224 cm.⁻¹, ω₂ = 65 cm.⁻¹, ω₃ = 309 cm.⁻¹, and ω₄ = 78 cm.⁻¹.

Br₄Zr

Br₄Zr

Tungsten Pentabromide (WBr₅)
(Crystal) GFW = 583.395

T, °K	C _p ^a	gibbs/mol S ^b	-(G ^c -H ²⁹⁸)/T	H ^c -H ²⁹⁸	kcal/mol ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	37.156	45.000	65.000	•000	- 74.500	- 64.433	47.230
300	37.200	45.230	65.001	•069	- 74.525	- 64.369	46.893
500	39.600	76.260	66.488	3.909	- 91.874	- 57.361	31.340
600	42.000	85.351	67.987	7.987	- 90.604	- 48.877	21.384
600	44.400	93.231	72.710	12.313	- 89.109	- 40.668	14.613
700	46.800	100.255	76.152	16.873	- 87.403	- 32.726	10.218
800	49.200	106.661	79.570	21.673	- 85.876	- 25.046	6.842
900	51.600	112.595	82.914	26.713	- 83.323	- 17.618	4.278
1000	54.000	118.155	86.183	31.993	- 80.947	- 10.440	2.282

TUNGSTEN PENTABROMIDE (WBr₅)

(CRYSTAL)

Br₅W

GFW = 583.395

ΔH_f⁰ = Unknown

ΔH_f^{298.15} = -74.5 ± 3 kcal/mol

ΔH_m⁰ = 4.10 kcal/mol

S^{298.15} = [65 ± 5] gibbs/mol

T_m = 559° ± 10°K

Heat of Formation

S. A. Shchukarev and G. A. Kokovin (1) have measured calorimetrically the heat of reaction ΔH_r²⁹⁸ = -187.475 ± 0.9 kcal/mol for WBr₅(c) + 1/2Br₂(l) + 8NaOH(77.4H₂O) → Na₂WO₄(c) + 6NaBr(c) + 4H₂O(l). This leads to ΔH_f²⁹⁸(WBr₅, c) = -74.5 ± 3 kcal/mol, using ΔH_f²⁹⁸(NaOH(77.4H₂O)) = -112.348 kcal/mol (2), ΔH_f²⁹⁸(NaWO₄, c) = -369.2 kcal/mol (3), ΔH_f²⁹⁸(NaBr, c) = -86.38 kcal/mol (4) and ΔH_f²⁹⁸(H₂O, l) = -68.315 kcal/mol (5).

Heat Capacity and Entropy

C_p200 = 6.2 gibbs/g-atom and C_p559 = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans (6). Between 300°K and 559°K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, S₂₉₈ = 65 eu, is estimated from that of WCl₅(c) (7) and the entropy difference between bromides and chlorides. The latter is estimated to be 13 eu based on an extrapolation to pentavalent compounds of the entropy values of bromides and chlorides given by V. M. Latimer (8). Both WBr₅ and WCl₅ are paramagnetic with an effective moment of about 1.1 Bohr magnetons as indicated by B. N. Figgis and J. L. Lewis, "Progress in Inorg. Chem.," Vol. 6, page 121, Interscience Publishers, New York, 1964.

Melting Data

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin (8) have found the melting point, 559°K, by the thermographic method and 568°K by the tensimetric method. The value of 559°K is adopted in the tabulation.

The heat of melting is calculated from the difference between the heats of sublimation and vaporization at the melting point. The heats are both calculated from a second law analysis of the vapor pressure data reported by Shchukarev et al. (8), who gave the uncorrected heat of fusion, 5 kcal/mol. This value, when corrected for ΔC_p of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

References

1. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
2. The value ΔH_f²⁹⁸(NaOH(77.4H₂O)) = -112.348 kcal/mol is calculated from ΔH_f⁰(NaOH(=H₂O)) = -112.448 kcal/mol and φ_L = 100 cal/mol for NaOH(=H₂O) → NaOH(77.4H₂O). The former is obtained from JANAF NaOH(c) Table (Mar. 31, 1966) and the latter is obtained from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
3. JANAF Na₂WO₄(c) table (June 30, 1967).
4. JANAF NaBr(c) table (Sept. 30, 1964).
5. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
6. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
7. JANAF WCl₅(c) table (Dec. 31, 1966).
8. S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).
9. W. M. Latimer, J. Am. Chem. Soc. **73**, 1480 (1951).

Br₅W

T, °K	C _p	$\frac{\mu\text{bbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	Kcal/mol ΔH°	ΔG°	Log K _p
0							
100							
200							
298	43.500	70.113	70.113	.000	- 71.236	- 62.693	45.955
300	43.500	70.382	70.114	.080	- 71.249	- 62.639	45.632
400	43.500	82.866	71.850	8.530	- 86.589	- 78.252	41.232
500	43.500	92.693	75.562	16.530	- 96.089	- 84.744	37.176
600	43.500	100.534	78.650	13.130	- 85.028	- 80.568	34.923
700	43.500	107.240	82.257	17.480	- 83.531	- 78.744	33.535
800	43.500	113.048	85.760	21.830	- 82.034	- 76.734	32.303
900	43.500	118.172	89.092	26.180	- 80.541	- 74.595	31.211
1000	43.500	122.755	92.224	30.330	- 79.143	- 73.238	30.263

TUNGSTEN PENTABROMIDE (WBr₅)

(LIQUID)

GFW = 583.395

$$S_{298.15}^\circ = [70.113] \text{ gibbs/mol}$$

$$T_m = 559^\circ \pm 10^\circ \text{K}$$

$$T_b = 633.5^\circ \text{K}$$

$$\Delta H_{298.15}^\circ = [-71.236] \text{ kcal/mol}$$

$$\Delta H_m^\circ = 4.10 \text{ kcal/mol}$$

$$\Delta H_v^\circ = 19.48 \text{ kcal/mol}$$

Heat of Formation

The heat of formation, ΔH_{298}° (WBr₅, l) = -71.236 kcal/mol, is calculated from that of WBr₅(c) by adding the heat of melting and the difference between $H_{559}^\circ - H_{298}^\circ$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be a constant, 7.25 gibbs/g-atom.

The entropy, $S_{298}^\circ = 70.113$ eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data

See WBr₅(c) table (June 30, 1967) for details.

Vaporization Data

T_b is calculated as the temperature at which the Gibbs energy of reaction $\text{WBr}_5(l) \rightarrow \text{WBr}_5(g)$ approaches zero. The difference between the heats of formation for liquid and gas at the boiling point is ΔH_v° .

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. 3, 2185 (1959), derived the boiling point 665°K and the heat of vaporization 14.5 ± 0.5 kcal/mol from vapor pressure data. Our second law values, corrected for ΔC_p , are $T_b = 666^\circ \text{K}$ and $\Delta H_v^\circ = 13.8$ kcal/mol. The adopted values are significantly different because the second law value of ΔS_v is not adopted in the table.

Tungsten Pentabromide (WBr₅)
(Ideal Gas) GFW = 583.395

TUNGSTEN PENTABROMIDE (WBr₅)

(IDEAL GAS)

Br₅W

GFW = 583.395

$\Delta H_f^\circ = -39.9 \pm 5 \text{ kcal/mol}$

$\Delta H_f^\circ(298.15) = -47.6 \pm 5 \text{ kcal/mol}$

Point Group {D_{3h}}

S^{298.15} = [110.3] gibbs/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[300] (1)	[240] (2)
[250] (1)	[200] (2)
[235] (1)	[70] (2)
[90] (1)	[110] (2)

Bond Distance: W-Br = [2.40] Å

Bond Angles: Br-W-Br* = [120°], Br*-W-Br** = [90°]

Br*-W-Br** = [180°]

*Equatorial **Axial

Product of the Moments of Inertia: $I_A I_B I_C = [1.640] \times 10^{-110} \text{ g cm}^2$

Heat of Formation

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **5**, 2185 (1958), measured the vapor pressure of WBr₅(c, l) using a null manometer. Their results are given as below. The adopted heat of formation is -47.6 kcal/mol.

Reactions	No. of Exptl.	Temp. Range (°K)	$\Delta H_f^\circ(298)$ (kcal/mol)	Drift (kcal/mol)
WBr ₅ (l) + WBr ₅ (g)	13	18.37	24.11	573.3-657.5
WBr ₅ (c) + WBr ₅ (g)	6	21.61	26.46	443.5-496.5
				9.440.4

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of MoCl₅ determined by electron diffraction (1). The bond distance is estimated to be the same as that in WBr₅(g). The three principal moments of inertia are $I_A = I_B = 267.5 \times 10^{-39}$ and $I_C = 229.3 \times 10^{-39} \text{ g cm}^2$.

All vibrational frequencies are estimated from those of WCl₅(g) (2), using the average value of $\nu(\text{WBr}_2)/\nu(\text{WCl}_2) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX₅, SnX₅ and PtX₅ summarized by H. Siebert (3) and K. Nakamoto (4).

The electronic levels and quantum weights are estimated to be the same as those in WCl₅(g) (2).

References

1. R. V. G. Evans and H. W. Lister, Trans. Faraday Soc. **34**, 1358 (1938).
2. JANAF WCl₅(g) table (Dec. 31, 1966).
3. H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin, 1966.
4. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

Dec. 31, 1962; June 30, 1967

Br₅W

T, °K	C _p	S ⁰ - (C _p - T ⁰)/T	kcal/mol ΔH_f°	Log K _p
0	0.000	INFINITE	-39.939	INFINITE
100	21.608	79.255	-39.202	95.615
200	28.928	98.376	-39.921	52.490
298	30.404	110.252	-47.600	37.402
300	30.420	110.461	-47.637	37.186
400	30.700	115.281	-45.751	26.371
500	31.279	126.233	-45.444	19.302
600	31.434	131.951	-45.132	14.544
700	31.529	136.804	-44.844	11.162
800	31.591	141.019	-44.561	8.637
900	31.629	144.677	-44.281	6.637
1000	31.672	148.077	-44.025	5.123
1100	31.704	151.097	-43.775	3.894
1200	31.735	153.857	-43.536	2.799
1300	31.765	156.389	-43.302	1.911
1400	31.794	158.745	-43.072	1.265
1500	31.825	160.950	-42.845	0.807
1600	31.859	163.007	-42.623	0.475
1700	31.937	164.941	-42.408	0.241
1800	31.999	166.691	-42.200	0.102
1900	32.053	168.285	-42.000	0.046
2000	32.093	170.144	-41.814	0.018
2100	32.149	171.711	-41.656	0.006
2200	32.204	173.208	-41.527	0.001
2300	32.259	174.641	-41.420	0.000
2400	32.312	176.012	-41.332	0.000
2500	32.367	177.335	-41.259	0.000
2600	32.419	178.605	-41.200	0.000
2700	32.469	179.830	-41.150	0.000
2800	32.516	181.012	-41.110	0.000
2900	32.560	182.152	-41.075	0.000
3000	32.600	183.258	-41.051	0.000
3100	32.651	184.328	-41.034	0.000
3200	32.691	185.365	-41.020	0.000
3300	32.728	186.372	-41.008	0.000
3400	32.763	187.352	-40.998	0.000
3500	32.797	188.300	-40.990	0.000
3600	32.828	189.224	-40.984	0.000
3700	32.856	190.124	-40.980	0.000
3800	32.882	191.000	-40.977	0.000
3900	32.906	191.851	-40.975	0.000
4000	32.929	192.688	-40.973	0.000
4100	32.949	193.502	-40.970	0.000
4200	32.967	194.296	-40.967	0.000
4300	32.983	195.072	-40.964	0.000
4400	32.997	195.832	-40.961	0.000
4500	33.010	196.572	-40.958	0.000
4600	33.020	197.298	-40.955	0.000
4700	33.030	198.008	-40.952	0.000
4800	33.044	198.700	-40.949	0.000
4900	33.054	199.375	-40.946	0.000
5000	33.069	200.052	-40.942	0.000
5100	33.082	200.707	-40.939	0.000
5200	33.095	201.349	-40.936	0.000
5300	33.108	201.976	-40.933	0.000
5400	33.120	202.596	-40.930	0.000
5500	33.135	203.203	-40.927	0.000
5600	33.154	203.798	-40.924	0.000
5700	33.173	204.383	-40.921	0.000
5800	33.192	204.956	-40.918	0.000
5900	33.211	205.516	-40.915	0.000
6000	33.239	206.076	-40.912	0.000

T, °K	C _p ^o	gibbs/mol S ^o - (C ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
100						
200						
298	43,352	75,000	0.00	82.000	69.499	50.938
300	43,400	75,268	0.00	82.030	69.411	50.566
400	46,000	86,110	4,550	102.669	60.855	33,250
500	48,600	98,654	9,280	101.389	50.520	22,082
600	51,200	112,742	13,641	97.724	40.593	18,753
700	54,800	127,432	19,250	95.535	31,360	15,641
800	58,400	143,186	25,030	93.101	22,252	12,975
900	59,000	179,979	30,800	90.425	3,408	
1000	61,600	136,330	36,499			

TUNGSTEN HEXABROMIDE (WBr₆)

(CRYSTAL)

GFW = 663.304

ΔH_f^o = Unknown

ΔH_f^o_{298.15} = -82.0 ± 3 kcal/mol

S_{298.15}^o = [75 ± 5] gibbs/mol

ΔH_m^o = Unknown

T_m = 582°K

Heat of Formation

S. A. Shchukarev and G. A. Kokovin (1) have measured calorimetrically the heat of reaction ΔH_r^o₂₉₈ = -180.0 ± 0.8 kcal/mol for WBr₆(c) + 6NaOH(77.4H₂O) + Na₂WO₄(c) + 6NaBr(c) + 4H₂O(l). This leads to ΔH_f^o₂₉₈(WBr₆, c) = -82.0 ± 3 kcal/mol, using ΔH_f^o₂₉₈(NaOH·77.4H₂O) = -112.348 kcal/mol (2), ΔH_f^o₂₉₈(Na₂WO₄, c) = -369.2 kcal/mol (3), ΔH_f^o₂₉₈(NaBr, c) = -86.38 kcal/mol (4) and ΔH_f^o₂₉₈(H₂O, l) = -68.315 kcal/mol (5).

Heat Capacity and Entropy

C_p300 = 6.2 gibbs/g-atom and C_p582 = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans (6). Between 300° and 582°K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, S₂₉₈^o(WBr₆, c) = 75 eu, is estimated by assuming S₂₉₈^o(WBr₆) = S₂₉₈^o(WCl₆) + 6[S₂₉₈^o(Br⁻) - S₂₉₈^o(Cl⁻)]. The value, S₂₉₈^o(WCl₆, c) = 57 eu, is obtained from the JANAF WCl₆(c) table (Dec. 31, 1966); and the value, S₂₉₈^o(Br⁻) - S₂₉₈^o(Cl⁻) = 3 gibbs/mol, is obtained from the average entropy values for Br⁻ and Cl⁻ ions given by W. M. Latimer (7) and K. K. Kelley (8).

Melting Data

S. A. Shchukarev, G. I. Novikov and G. A. Kokovin (3) have found the melting point, 582°K, under 50 atm pressure of Br₂(g) by the thermographic method. The heat of fusion is unknown.

References

1. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
2. This value, ΔH_f^o₂₉₈(NaOH·77.4H₂O) = -112.348 kcal/mol is calculated from ΔH_f^o₂₉₈(NaOH·H₂O) = 112.448 kcal/mol and Δ_h^o = 100 cal/mol for NaOH(H₂O) + NaOH(77.4H₂O). The former is obtained from JANAF NaOH(c) table (Mar. 31, 1966) and the latter is obtained from V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
3. JANAF Na₂WO₄(c) table (June 30, 1967).
4. JANAF NaBr(c) table (June 30, 1964).
5. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
6. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
7. W. M. Latimer, J. Am. Chem. Soc. **73**, 1480 (1951).
8. K. K. Kelley, private communication, June, 1960.
9. S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).

Tungsten Hexabromide (WBr₆)
(Ideal Gas) GFW = 663.304

Br₆W

GFW = 663.304

TUNGSTEN HEXABROMIDE (WBr₆)

(IDEAL GAS)

Point Group [O_h]

$\Delta H_f^\circ = [-47.7 \pm 10] \text{ kcal/mol}$

$\Delta H_{298.15}^\circ = [-58.1 \pm 10] \text{ kcal/mol}$

$S_{298.15}^\circ = [115.3 \pm 10] \text{ gibbs/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	$\frac{\omega}{\text{cm}^{-1}}$	[110] (3)	[130] (3)	[70] (3)
[250] (1)				
[200] (2)				
[250] (3)				

Bond Distance: W-Br = [2.40] Å

Bond Angle: Br-W-Br = [90°]

Product of the Moments of Inertia: $I_A I_B I_C = [2.857] \times 10^{-110} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The heat of formation, $\Delta H_{298}^\circ(\text{WBr}_6, g) = -58.1 \text{ kcal/mol}$, is calculated from that of the crystal plus the estimated heat of sublimation $\Delta H_{298}^\circ = 23.9 \text{ kcal/mol}$ for $\text{WBr}_6(c) \rightarrow \text{WBr}_6(g)$. The value of ΔH_{298}° is assumed to be the same as that for $\text{WCl}_6(c) + \text{WCl}_6(g)$. See WCl_6 table (Dec. 31, 1966) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be an octahedron similar to those of $\text{WF}_6(g)$, and $\text{WCl}_6(g)$ determined by electron diffraction. The bond distance is estimated to be 2.40 Å by assuming $r_{\text{W-Br}} = r_{\text{W-Cl}} + (r_{\text{Na-Br}} - r_{\text{Na-Cl}})$. The bond distances W-Cl, Na-Br and Na-Cl are given in JANAF $\text{WCl}_6(g)$ and $\text{NaBr}(g)$ and $\text{NaCl}(g)$ tables, as 2.26 Å, 2.50 Å and 2.36 Å, respectively. The three principal moments of inertia are: $I_A = I_B = I_C = 305.7 \times 10^{-38} \text{ g cm}^2$. All vibrational frequencies are estimated from those of $\text{WCl}_6(g)$ (1), using the average value of $\nu(\text{WBr}_6)/\nu(\text{WCl}_6) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX_6 , SnX_6 and PtX_6 summarized by H. Siebert (2), and K. Nakamoto (3).

References

1. J. C. Evans and G. Y-S Lo, The Dow Chemical Company, private communication, June 8, 1967, have obtained the six fundamental vibrational frequencies of 408, 312, 367, 165, 206 and 97 cm^{-1} for $\text{WCl}_6(g)$ by infrared spectrometry.
2. H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer-Verlag, Berlin.
3. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

T, °K	C _p	$\frac{\text{gibbs/mol}}{S^\circ - (C_p^\circ - H^\circ)/T}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
0	27.938	INFINITE	- 87.748	- 87.748	INFINITE
100	27.938	79.306	- 48.172	- 52.012	113.671
200	28.178	101.161	- 38.567	- 40.460	148.527
298	30.178	115.340	- 30.100	- 37.618	162.239
300	36.196	115.364	- 29.67	- 36.143	162.239
400	36.958	126.081	- 24.770	- 32.970	162.239
500	37.175	134.343	- 21.488	- 30.341	162.239
600	37.351	141.138	- 19.155	- 28.755	162.239
700	37.487	146.904	- 17.625	- 27.449	162.239
800	37.527	151.911	- 16.645	- 26.345	162.239
900	37.575	156.334	- 15.845	- 25.472	162.239
1000	37.609	160.295	- 15.156	- 24.716	162.239
1100	37.636	163.880	- 14.570	- 24.063	162.239
1200	37.654	167.156	- 14.084	- 23.502	162.239
1300	37.669	170.170	- 13.681	- 23.022	162.239
1400	37.681	172.962	- 13.320	- 22.615	162.239
1500	37.691	175.562	- 13.000	- 22.271	162.239
1600	37.698	177.995	- 12.718	- 21.983	162.239
1700	37.705	180.281	- 12.470	- 21.735	162.239
1800	37.711	182.436	- 12.252	- 21.524	162.239
1900	37.715	184.475	- 12.060	- 21.346	162.239
2000	37.719	186.410	- 11.892	- 21.197	162.239
2100	37.723	188.250	- 11.746	- 21.073	162.239
2200	37.726	190.005	- 11.618	- 20.962	162.239
2300	37.728	191.682	- 11.504	- 20.862	162.239
2400	37.730	193.288	- 11.400	- 20.773	162.239
2500	37.732	194.828	- 11.304	- 20.693	162.239
2600	37.734	196.308	- 11.216	- 20.621	162.239
2700	37.736	197.732	- 11.134	- 20.557	162.239
2800	37.737	199.105	- 11.058	- 20.500	162.239
2900	37.739	200.429	- 10.986	- 20.449	162.239
3000	37.740	201.708	- 10.919	- 20.402	162.239
3100	37.741	202.946	- 10.856	- 20.359	162.239
3200	37.742	204.144	- 10.795	- 20.319	162.239
3300	37.743	205.305	- 10.738	- 20.282	162.239
3400	37.743	206.432	- 10.684	- 20.248	162.239
3500	37.744	207.526	- 10.634	- 20.216	162.239
3600	37.745	208.590	- 10.586	- 20.186	162.239
3700	37.745	209.624	- 10.540	- 20.158	162.239
3800	37.746	210.630	- 10.495	- 20.131	162.239
3900	37.746	211.611	- 10.451	- 20.105	162.239
4000	37.747	212.567	- 10.408	- 20.080	162.239
4100	37.747	213.499	- 10.366	- 20.056	162.239
4200	37.748	214.408	- 10.324	- 20.032	162.239
4300	37.748	215.296	- 10.282	- 20.008	162.239
4400	37.749	216.164	- 10.241	- 19.984	162.239
4500	37.749	217.013	- 10.199	- 19.960	162.239
4600	37.749	217.842	- 10.156	- 19.936	162.239
4700	37.749	218.654	- 10.113	- 19.912	162.239
4800	37.750	219.449	- 10.070	- 19.888	162.239
4900	37.750	220.227	- 10.027	- 19.864	162.239
5000	37.750	220.990	- 9.984	- 19.840	162.239
5100	37.750	221.737	- 9.941	- 19.816	162.239
5200	37.751	222.467	- 9.898	- 19.792	162.239
5300	37.751	223.190	- 9.855	- 19.768	162.239
5400	37.751	223.895	- 9.812	- 19.744	162.239
5500	37.751	224.588	- 9.769	- 19.719	162.239
5600	37.751	225.268	- 9.726	- 19.695	162.239
5700	37.752	225.936	- 9.683	- 19.671	162.239
5800	37.752	226.593	- 9.640	- 19.647	162.239
5900	37.752	227.238	- 9.597	- 19.623	162.239
6000	37.752	227.873	- 9.554	- 19.599	162.239

Dec. 31, 1962; June 30, 1967

Br₆W

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	0.000	0.000	0.000	0.000
100	1.000	0.591	0.000	0.000	0.000	0.000
200	1.202	0.720	0.160	0.000	0.000	0.000
298	2.038	1.359	0.000	0.000	0.000	0.000
300	2.034	1.372	0.004	0.000	0.000	0.000
400	2.481	1.875	0.000	0.000	0.000	0.000
500	3.496	2.764	0.000	0.000	0.000	0.000
600	4.038	3.471	0.000	0.000	0.000	0.000
700	4.340	4.126	1.372	0.000	0.000	0.000
800	4.740	4.739	2.449	0.000	0.000	0.000
900	5.140	5.311	3.511	0.000	0.000	0.000
1000	5.149	5.844	5.020	0.000	0.000	0.000
1100	5.304	6.300	3.347	0.000	0.000	0.000
1200	5.430	6.609	3.573	0.000	0.000	0.000
1300	5.527	7.246	4.432	0.000	0.000	0.000
1400	5.651	7.851	4.098	0.000	0.000	0.000
1500	5.689	8.436	5.352	0.000	0.000	0.000
1600	5.721	8.417	6.412	0.000	0.000	0.000
1700	5.765	8.627	6.696	0.000	0.000	0.000
1800	5.803	9.095	7.875	0.000	0.000	0.000
1900	5.836	9.411	8.411	0.000	0.000	0.000
2000	5.885	9.711	6.442	0.000	0.000	0.000
2100	5.891	9.998	5.688	0.000	0.000	0.000
2200	5.914	10.272	5.900	0.000	0.000	0.000
2300	5.936	10.749	6.096	0.000	0.000	0.000
2400	5.966	11.212	10.212	0.000	0.000	0.000
2500	5.974	11.032	6.471	0.000	0.000	0.000
2600	5.992	11.287	6.631	0.000	0.000	0.000
2700	6.009	11.493	6.826	0.000	0.000	0.000
2800	6.026	11.652	7.977	0.000	0.000	0.000
2900	6.042	11.824	8.124	0.000	0.000	0.000
3000	6.057	12.159	7.325	0.000	0.000	0.000
3100	6.073	12.328	7.483	0.000	0.000	0.000
3200	6.086	12.521	7.638	0.000	0.000	0.000
3300	6.103	12.697	18.239	0.000	0.000	0.000
3400	6.119	12.892	7.598	0.000	0.000	0.000
3500	6.134	13.068	8.080	0.000	0.000	0.000
3600	6.150	13.241	8.221	0.000	0.000	0.000
3700	6.165	13.410	8.359	0.000	0.000	0.000
3800	6.181	13.574	18.307	0.000	0.000	0.000
3900	6.197	13.746	8.484	0.000	0.000	0.000
4000	6.213	13.893	8.756	0.000	0.000	0.000
4100	6.230	14.046	8.883	0.000	0.000	0.000
4200	6.247	14.197	21.792	0.000	0.000	0.000
4300	6.264	14.346	8.980	0.000	0.000	0.000
4400	6.281	14.488	9.250	0.000	0.000	0.000
4500	6.299	14.639	9.368	0.000	0.000	0.000
4600	6.317	14.788	9.484	0.000	0.000	0.000
4700	6.335	14.904	28.937	0.000	0.000	0.000
4800	6.353	15.024	9.598	0.000	0.000	0.000
4900	6.373	15.149	9.620	0.000	0.000	0.000
5000	6.392	15.288	9.928	0.000	0.000	0.000
5100	6.412	15.424	10.035	0.000	0.000	0.000
5200	6.432	15.589	10.140	0.000	0.000	0.000
5300	6.452	15.742	10.248	0.000	0.000	0.000
5400	6.473	15.793	10.343	0.000	0.000	0.000
5500	6.494	15.912	10.445	0.000	0.000	0.000
5600	6.516	16.029	10.543	0.000	0.000	0.000
5700	6.536	16.148	10.641	0.000	0.000	0.000
5800	6.556	16.268	10.740	0.000	0.000	0.000
5900	6.583	16.371	10.831	0.000	0.000	0.000
6000	6.606	16.461	10.924	0.000	0.000	0.000

March 31, 1961

ΔH°_f 298.15 = 0ΔS°_f 298.15 = 1.359 cal. deg.⁻¹ mole⁻¹ΔH°_f 298.15 = 170.89 ± 0.5 kcal. mole⁻¹

Heat of Formation

Zero by definition.

Heat Capacity and Extrapolation

The low temperature C_p measurements of F. H. Keesom and N. Pearlman (1° to 4°K. and 10° to 20°K.), Phys. Rev. 99, 1119 (1955), and of W. Desorbo and G. E. Nichols (1° to 20°K.), The Phys. and Chem. of Solids 6, 352 (1956), were joined smoothly with the C_p measurements of W. Desorbo and W. W. Tyler (13° to 300°K.), J. Chem. Phys. 21, 1860 (1953). C_p values above 300°K were taken from National Bureau of Standards Report 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960. Heat capacity values above 1000°K were adjusted to give smooth results. Above 4000°K. the C_p values are estimated.

S°_f and H°_f were calculated to be 0.00265 cal. deg.⁻¹ mole⁻¹ and 0.03982 cal. mole⁻¹ respectively from smooth C_p values using Meddle's rule.

Carbon, Monatomic (C)

(Ideal Gas) At. Wt. = 12.011

C

AT. WT. = 12.011

(IDEAL GAS)

CARBON, MONATOMIC (C)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	5.000	INFINITE	1.562	169.376	169.376	INFINITE
100	5.085	32.283	1.562	169.376	169.376	INFINITE
200	5.197	36.217	1.562	169.376	169.376	INFINITE
298	5.291	37.761	1.562	169.376	169.376	INFINITE
300	5.291	37.761	1.562	169.376	169.376	INFINITE
400	5.491	39.224	1.562	169.376	169.376	INFINITE
500	5.693	40.334	1.562	169.376	169.376	INFINITE
600	5.871	41.240	1.562	169.376	169.376	INFINITE
700	6.027	42.000	1.562	169.376	169.376	INFINITE
800	6.160	42.620	1.562	169.376	169.376	INFINITE
900	6.273	43.120	1.562	169.376	169.376	INFINITE
1000	6.369	43.599	1.562	169.376	169.376	INFINITE
1100	6.449	44.058	1.562	169.376	169.376	INFINITE
1200	6.514	44.498	1.562	169.376	169.376	INFINITE
1300	6.566	44.920	1.562	169.376	169.376	INFINITE
1400	6.607	45.325	1.562	169.376	169.376	INFINITE
1500	6.638	45.704	1.562	169.376	169.376	INFINITE
1600	6.660	46.058	1.562	169.376	169.376	INFINITE
1700	6.674	46.388	1.562	169.376	169.376	INFINITE
1800	6.681	46.693	1.562	169.376	169.376	INFINITE
1900	6.681	46.973	1.562	169.376	169.376	INFINITE
2000	6.674	47.229	1.562	169.376	169.376	INFINITE
2100	6.660	47.464	1.562	169.376	169.376	INFINITE
2200	6.638	47.678	1.562	169.376	169.376	INFINITE
2300	6.607	47.870	1.562	169.376	169.376	INFINITE
2400	6.566	48.040	1.562	169.376	169.376	INFINITE
2500	6.514	48.187	1.562	169.376	169.376	INFINITE
2600	6.449	48.313	1.562	169.376	169.376	INFINITE
2700	6.369	48.418	1.562	169.376	169.376	INFINITE
2800	6.273	48.504	1.562	169.376	169.376	INFINITE
2900	6.160	48.573	1.562	169.376	169.376	INFINITE
3000	6.027	48.626	1.562	169.376	169.376	INFINITE
3100	5.871	48.664	1.562	169.376	169.376	INFINITE
3200	5.693	48.688	1.562	169.376	169.376	INFINITE
3300	5.491	48.698	1.562	169.376	169.376	INFINITE
3400	5.291	48.694	1.562	169.376	169.376	INFINITE
3500	5.085	48.676	1.562	169.376	169.376	INFINITE
3600	4.871	48.644	1.562	169.376	169.376	INFINITE
3700	4.649	48.588	1.562	169.376	169.376	INFINITE
3800	4.418	48.509	1.562	169.376	169.376	INFINITE
3900	4.179	48.408	1.562	169.376	169.376	INFINITE
4000	3.933	48.285	1.562	169.376	169.376	INFINITE
4100	3.680	48.140	1.562	169.376	169.376	INFINITE
4200	3.420	47.973	1.562	169.376	169.376	INFINITE
4300	3.154	47.785	1.562	169.376	169.376	INFINITE
4400	2.883	47.576	1.562	169.376	169.376	INFINITE
4500	2.607	47.346	1.562	169.376	169.376	INFINITE
4600	2.326	47.094	1.562	169.376	169.376	INFINITE
4700	2.040	46.820	1.562	169.376	169.376	INFINITE
4800	1.750	46.524	1.562	169.376	169.376	INFINITE
4900	1.456	46.206	1.562	169.376	169.376	INFINITE
5000	1.158	45.866	1.562	169.376	169.376	INFINITE
5100	0.857	45.504	1.562	169.376	169.376	INFINITE
5200	0.552	45.120	1.562	169.376	169.376	INFINITE
5300	0.244	44.714	1.562	169.376	169.376	INFINITE
5400	0.033	44.286	1.562	169.376	169.376	INFINITE
5500	-0.181	43.836	1.562	169.376	169.376	INFINITE
5600	-0.388	43.364	1.562	169.376	169.376	INFINITE
5700	-0.586	42.870	1.562	169.376	169.376	INFINITE
5800	-0.774	42.354	1.562	169.376	169.376	INFINITE
5900	-0.951	41.816	1.562	169.376	169.376	INFINITE
6000	-1.117	41.256	1.562	169.376	169.376	INFINITE

March 31, 1961

$\Delta H_{f,0}^0 = 169.58 \pm 0.45$ kcal. mole⁻¹
 $\Delta H_{f,0}^0 = 170.89 \pm 0.45$ kcal. mole⁻¹
 $\Delta H_{f,0}^0 = 37.76 \pm 0.01$ cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities

ϵ_i cm. ⁻¹	ϵ_i	ϵ_i
0	1	9
16.4	3	3
43.5	5	15
10,194	5	34
21,648	1	99
33,735	5	401

Heat of Formation

The $\Delta H_{f,0}^0$ is given by the following cycle at 0°K.

(I) C(c) + 1/2 O ₂ (g) = CO(g)	-27.1955 kcal. mole ⁻¹
(II) CO(g) = C(g) + O(g)	255.764
(III) O(g) = 1/2 O ₂ (g)	-58.989

For details concerning (I), (II), and (III) see the CO(g) and O₂(g) sheets. A definitive review of the heat of sublimation of carbon is given by L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem. 7, 259 (1956).

Heat Capacities and Entropies

The electronic energy levels are those listed by C. E. Moore, Nat. Bur. Standards (U. S.) Circ. 467, (1949). Levels above 50,000 cm.⁻¹ have been averaged.

Carbon Uninegative Ion (C⁻)

(Ideal Gas) At. Wt. = 12.0117

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T kcal. mole ⁻¹	ΔH _f kcal. mole ⁻¹	ΔF _f kcal. mole ⁻¹	Log K _F
0					
100	4.968	36.156	0.00	140.500	131.612 - 96.470
200	4.968	36.187	0.09	140.496	131.557 - 95.835
298	4.968	36.351	0.506	140.250	128.613 - 70.267
300	4.968	36.724	1.053	139.851	129.759 - 54.950
400	4.968	39.630	1.500	139.553	122.935 - 44.777
500	4.968	40.396	1.996	139.128	120.200 - 37.526
600	4.968	41.059	2.493	138.669	117.527 - 32.105
700	4.968	41.645	2.990	138.182	114.911 - 27.603
800	4.968	42.168	3.487	137.676	112.353 - 24.554
900	4.968	42.642	3.984	137.153	109.844 - 21.623
1000	4.968	43.074	4.481	136.617	107.386 - 19.557
1200	4.968	43.472	4.977	136.068	104.972 - 17.647
1300	4.968	43.840	5.474	135.512	102.602 - 16.016
1400	4.968	44.182	5.971	134.948	100.272 - 14.609
1500	4.968	44.503	6.468	134.378	97.978 - 13.383
1600	4.968	44.804	6.965	133.804	95.720 - 12.305
1700	4.968	45.088	7.461	133.225	93.498 - 11.352
1800	4.968	45.357	7.956	132.643	91.305 - 10.502
1900	4.969	45.612	8.453	132.058	89.144 - 9.741
2000	4.970	45.854	8.952	131.471	87.016 - 9.055
2100	4.971	46.085	9.449	130.880	84.911 - 8.435
2200	4.972	46.306	9.946	130.289	82.838 - 7.871
2300	4.973	46.516	10.443	129.696	80.796 - 7.366
2400	4.974	46.721	10.941	129.099	78.759 - 6.885
2500	4.982	46.917	11.439	128.501	76.756 - 6.452
2600	4.987	47.105	11.938	127.903	74.775 - 6.052
2700	4.993	47.286	12.437	127.304	72.821 - 5.684
2800	5.001	47.462	12.936	126.705	70.894 - 5.346
2900	5.011	47.631	13.437	126.102	68.973 - 5.024
3000	5.022	47.796	13.938	125.500	67.078 - 4.729
3100	5.035	47.955	14.441	124.898	65.202 - 4.453
3200	5.050	48.110	14.945	124.295	63.344 - 4.195
3300	5.066	48.261	15.451	123.689	61.502 - 3.954
3400	5.083	48.409	15.959	123.082	59.682 - 3.727
3500	5.107	48.552	16.468	122.450	57.881 - 3.514
3600	5.130	48.692	16.980	121.889	56.100 - 3.314
3700	5.155	48.829	17.494	121.289	54.330 - 3.125
3800	5.181	48.963	18.011	120.686	52.581 - 2.946
3900	5.213	49.095	18.531	120.094	50.838 - 2.776
4000	5.244	49.224	19.054	119.498	49.113 - 2.618
4100	5.278	49.351	19.580	118.903	47.402 - 2.466
4200	5.314	49.476	20.110	118.310	45.704 - 2.323
4300	5.350	49.600	20.643	117.718	44.026 - 2.186
4400	5.390	49.719	21.180	117.131	42.354 - 2.057
4500	5.431	49.838	21.721	116.544	40.699 - 1.934
4600	5.473	49.955	22.266	115.960	39.059 - 1.816
4700	5.517	50.071	22.816	115.378	37.430 - 1.704
4800	5.561	50.186	23.370	114.796	35.816 - 1.596
4900	5.607	50.298	23.928	114.223	34.203 - 1.493
5000	5.654	50.409	24.491	113.648	32.609 - 1.397
5100	5.702	50.520	25.059	113.077	31.021 - 1.304
5200	5.750	50.629	25.631	112.508	29.452 - 1.214
5300	5.801	50.735	26.204	111.940	27.896 - 1.126
5400	5.849	50.844	26.791	111.379	26.338 - 1.047
5500	5.899	50.949	27.379	110.821	24.805 - 0.968
5600	5.949	51.054	27.971	110.263	23.284 - 0.892
5700	6.000	51.158	28.569	109.709	21.786 - 0.819
5800	6.050	51.261	29.171	109.159	20.311 - 0.748
5900	6.100	51.363	29.779	108.609	18.872 - 0.682

Sept. 30, 1965

CARBON UNINEGATIVE ION (C⁻)

AT. WT. = 12.0117

Ground State Configuration 4s² s_{1/2} ΔH_f 0 = 140.8 ± 0.8 kcal. mole⁻¹S_{298.15} = 36.156 cal. deg.⁻¹ mole⁻¹ ΔH_f 298.15 = 140.5 ± 0.8 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E ₁ , cm. ⁻¹	E ₂ , cm. ⁻¹	E ₁	E ₂
0	86223.2	4	4
19223.9	96751.7	6	4
19233.1	96788.2	4	4
28840.0	96864.2	6	6
83285.5	97770.1	2	2
83319.3	97805.8	4	4
83366.0	99653.0	6	10
86131.4		2	

Heat of Formation.

The heat of formation was calculated from the equation: C(g) + e⁻ → C⁻(g) with the JANAP auxiliary value for C(g); using an electron affinity = 1.25 e.v. (28.85 kcal/mole) obtained from M. Senan and L. M. Branacomb, Phys. Rev. 125, 1602 (1962). Other values for the electron affinity are: 1.17 e.v. reported by E. Clementi and A. D. McLean, Phys. Rev. 133, A419 (1964); 1.12 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964); and 1.24 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case nitrogen. The electronic levels above 1 X 10⁵ cm⁻¹ were omitted because their contribution is negligible below 8000°K. The H₂₉₈ value at 0°K. is -1.481 kcal/mole.

Aluminum Carbide (AlC)

(Ideal Gas) Mol. Wt. = 38.991

CAI

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	INFINITE	-	2.134	164.012	164.012	INFINITE
100	6.953	45.523	-	1.439	160.221	-350.146	-
200	7.710	50.540	-	0.000	164.800	-110.996	-
298	7.710	50.540	-	0.000	164.800	-110.996	-
300	7.718	53.428	53.381	.014	164.799	151.224	-110.161
400	8.106	55.705	53.688	.807	164.749	146.705	-80.152
500	8.366	57.534	54.281	1.631	164.627	142.207	-62.156
600	8.540	59.085	54.957	2.477	164.439	137.739	-50.169
700	8.660	60.411	55.644	3.337	164.187	133.308	-41.619
800	8.747	61.574	56.314	4.208	163.883	128.918	-35.217
900	8.813	62.608	56.937	5.086	163.527	124.567	-30.248
1000	8.864	63.539	57.559	5.970	163.133	120.244	-26.322
1100	8.906	64.386	58.151	6.859	162.709	116.440	-23.133
1200	8.940	65.151	58.703	7.751	159.955	112.469	-20.482
1300	8.970	65.879	59.278	8.646	159.601	108.525	-18.244
1400	8.996	66.545	59.727	9.545	159.244	104.612	-16.330
1500	9.019	67.166	60.203	10.445	158.881	100.722	-14.674
1600	9.040	67.749	60.656	11.348	158.513	96.856	-13.229
1700	9.059	68.298	61.050	12.253	158.144	92.913	-11.957
1800	9.077	68.816	61.505	13.160	157.772	89.192	-10.859
1900	9.093	69.307	61.909	14.069	157.399	85.394	-9.822
2000	9.109	69.774	62.285	14.979	157.024	81.614	-8.918
2100	9.125	70.219	62.652	15.890	156.648	77.852	-8.102
2200	9.139	70.644	63.006	16.804	156.271	74.108	-7.362
2300	9.153	71.050	63.347	17.718	155.893	70.383	-6.688
2400	9.167	71.440	63.676	18.634	155.514	66.673	-6.071
2500	9.180	71.815	63.994	19.552	155.136	62.979	-5.505
2600	9.194	72.175	64.302	20.470	154.755	59.299	-4.984
2700	9.206	72.522	64.600	21.390	154.375	55.638	-4.503
2800	9.219	72.857	64.889	22.312	153.992	51.993	-4.064
2900	9.232	73.181	65.169	23.234	153.606	48.368	-3.662
3000	9.244	73.494	65.441	24.158	153.216	44.752	-3.293
3100	9.256	73.797	65.706	25.083	152.822	41.143	-2.958
3200	9.268	74.091	65.964	26.009	152.424	37.540	-2.658
3300	9.280	74.377	66.214	26.937	152.022	33.943	-2.388
3400	9.292	74.654	66.458	27.865	151.616	30.352	-2.146
3500	9.303	74.924	66.696	28.795	151.206	26.766	-1.928
3600	9.315	75.186	66.929	29.724	150.791	23.184	-1.730
3700	9.327	75.441	67.155	30.658	150.371	19.603	-1.552
3800	9.338	75.690	67.377	31.591	149.946	16.026	-1.394
3900	9.350	75.933	67.593	32.526	149.516	12.452	-1.252
4000	9.361	76.170	67.804	33.461	149.081	8.881	-1.121
4100	9.372	76.401	68.011	34.398	148.641	5.312	-1.000
4200	9.384	76.627	68.214	35.336	148.196	1.747	-0.885
4300	9.395	76.848	68.412	36.274	147.746	-1.814	-0.784
4400	9.406	77.064	68.606	37.215	147.291	-5.383	-0.694
4500	9.417	77.275	68.796	38.158	146.831	-8.952	-0.614
4600	9.429	77.483	68.983	39.098	146.366	-12.521	-0.544
4700	9.440	77.685	69.166	40.041	145.896	-16.089	-0.484
4800	9.451	77.884	69.346	40.986	145.421	-19.657	-0.434
4900	9.462	78.079	69.522	41.932	144.941	-23.225	-0.394
5000	9.473	78.271	69.695	42.878	144.456	-26.793	-0.354
5100	9.484	78.458	69.865	43.826	143.966	-30.361	-0.314
5200	9.495	78.643	70.032	44.775	143.471	-33.929	-0.274
5300	9.506	78.824	70.196	45.725	142.971	-37.497	-0.234
5400	9.517	79.001	70.358	46.676	142.466	-41.065	-0.194
5500	9.528	79.176	70.516	47.629	141.956	-44.633	-0.154
5600	9.539	79.348	70.672	48.582	141.441	-48.201	-0.114
5700	9.550	79.517	70.826	49.537	140.921	-51.769	-0.074
5800	9.561	79.683	70.977	50.492	140.396	-55.337	-0.034
5900	9.572	79.847	71.126	51.447	139.866	-58.905	-0.004
6000	9.583	80.007	71.273	52.402	139.331	-62.473	-0.006

Dec. 31, 1960; June 30, 1963

ALUMINUM CARBIDE (AlC)

(IDEAL GAS)

MOL. WT. = 38.991

Ground State Configuration $2\uparrow\uparrow$ $\Delta H_f^0 = [164] \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = [53.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^0 298.15 = [164.8] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

ϵ_i , cm. ⁻¹	g_i
0	4

$$\omega_e x_e = [5.0] \text{ cm.}^{-1}$$

$$b = 1$$

$$\alpha_e = [0.006] \text{ cm.}^{-1}$$

$$r_e = [1.77] \text{ \AA}$$

Heat of Formation.

ΔH_f^0 was calculated from D_0 , 63.0 kcal. mole⁻¹, estimated by J. S. Gordon, AstroSystems International, Livingston, N. J., private communication, June 6, 1963. $\Delta H_f^0 298.15$ was then calculated. P. Zeeman, Can. J. Phys. 32, 9 (1954) reported a $D_0 = 1.6 \pm 0.2 \text{ e.v.}$, 36.9 kcal. mole⁻¹, for a molecule that was apparently AlC(g). However, H. Wooley, Nat'l Bur. Std. Report No. 6928, July 1, 1960, surmised that this D_0 and the reported molecular constants were for the Al_2 molecule. His judgment was accepted.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit.

CAI

(Ideal Gas) Mol. Wt. = 22.831

BORON CARBIDE (BC)

(IDEAL GAS)

MOL. WT. = 22.831

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	g ^o	-(F ^o -H ₂₉₈ °)/T	H ^o -H ₂₉₈ ^o	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0	∞.000	∞.000	∞.000	∞.000	2.080	196.464	196.464	∞.000	∞.000
100	6.957	42.195	56.049	-1.385	197.139	192.948	-421.667	-421.667	19.000
200	6.972	47.020	50.466	-1.689	197.682	188.532	-208.008	-208.008	18.000
300	7.009	48.822	48.822	-2.000	198.000	183.966	-134.844	-134.844	17.000
400	7.102	49.864	49.864	-2.313	198.004	183.970	-132.949	-132.949	16.000
500	7.259	51.942	50.103	-2.736	198.144	179.145	-107.876	-107.876	15.000
600	7.642	53.615	50.644	-3.146	198.155	174.392	-76.223	-76.223	14.000
700	7.895	55.031	51.260	-3.543	198.080	169.645	-61.790	-61.790	13.000
800	8.102	56.265	51.889	-3.930	197.939	164.917	-51.487	-51.487	12.000
900	8.268	57.359	52.518	-4.308	197.722	160.200	-41.184	-41.184	11.000
1000	8.398	58.339	53.100	-4.675	197.519	155.532	-31.767	-31.767	10.000
1100	8.504	59.230	53.669	-5.031	197.257	150.881	-22.350	-22.350	9.000
1200	8.589	60.044	54.212	-5.376	196.966	146.257	-12.933	-12.933	8.000
1300	8.659	60.795	54.730	-5.709	196.650	141.651	-8.512	-8.512	7.000
1400	8.716	61.494	55.221	-6.030	196.182	137.052	-4.091	-4.091	6.000
1500	8.769	62.144	55.694	-6.340	195.598	132.452	-20.691	-20.691	5.000
1600	8.818	62.744	56.144	-6.640	194.900	127.852	-18.654	-18.654	4.000
1700	8.864	63.314	56.575	-6.930	194.100	123.252	-16.617	-16.617	3.000
1800	8.907	63.851	56.987	-7.211	193.200	118.652	-14.580	-14.580	2.000
1900	8.947	64.356	57.381	-7.484	192.200	114.052	-12.543	-12.543	1.000
2000	8.985	64.842	57.763	-7.750	191.100	109.452	-10.506	-10.506	0.000
2100	9.021	65.300	58.128	-8.009	189.900	104.852	-8.469	-8.469	-1.000
2200	9.056	65.738	58.480	-8.261	188.600	100.252	-6.432	-6.432	-2.000
2300	9.089	66.156	58.820	-8.506	187.200	95.652	-4.395	-4.395	-3.000
2400	9.121	66.556	59.144	-8.744	185.700	91.052	-2.358	-2.358	-4.000
2500	9.151	66.940	59.464	-8.976	184.100	86.452	-0.321	-0.321	-5.000
2600	9.179	67.309	59.771	-9.202	182.400	81.852	1.716	1.716	-6.000
2700	9.205	67.664	60.068	-9.422	180.600	77.252	3.753	3.753	-7.000
2800	9.229	68.000	60.356	-9.636	178.700	72.652	5.790	5.790	-8.000
2900	9.251	68.321	60.635	-9.844	176.700	68.052	7.827	7.827	-9.000
3000	9.271	68.629	60.906	-10.047	174.600	63.452	9.864	9.864	-10.000
3100	9.289	68.924	61.169	-10.244	172.400	58.852	11.899	11.899	-11.000
3200	9.305	69.206	61.426	-10.436	170.100	54.252	13.934	13.934	-12.000
3300	9.319	69.475	61.673	-10.622	167.700	49.652	15.969	15.969	-13.000
3400	9.331	69.731	61.910	-10.803	165.200	45.052	17.994	17.994	-14.000
3500	9.342	69.974	62.138	-10.979	162.600	40.452	20.019	20.019	-15.000
3600	9.352	70.205	62.356	-11.150	159.900	35.852	22.044	22.044	-16.000
3700	9.361	70.426	62.564	-11.316	157.100	31.252	24.069	24.069	-17.000
3800	9.369	70.633	62.762	-11.477	154.200	26.652	26.094	26.094	-18.000
3900	9.376	70.827	62.950	-11.633	151.200	22.052	28.119	28.119	-19.000
4000	9.382	71.009	63.128	-11.784	148.100	17.452	30.144	30.144	-20.000
4100	9.387	71.179	63.296	-11.930	144.900	12.852	32.169	32.169	-21.000
4200	9.391	71.336	63.453	-12.071	141.600	8.252	34.194	34.194	-22.000
4300	9.394	71.481	63.599	-12.208	138.200	3.652	36.219	36.219	-23.000
4400	9.396	71.615	63.735	-12.341	134.700	-0.948	38.244	38.244	-24.000
4500	9.397	71.739	63.860	-12.470	131.100	-5.548	40.269	40.269	-25.000
4600	9.398	71.853	63.974	-12.595	127.400	-10.148	42.294	42.294	-26.000
4700	9.398	71.957	64.078	-12.716	123.600	-14.728	44.319	44.319	-27.000
4800	9.398	72.061	64.172	-12.833	119.700	-19.308	46.344	46.344	-28.000
4900	9.397	72.155	64.256	-12.946	115.700	-23.888	48.369	48.369	-29.000
5000	9.396	72.249	64.330	-13.055	111.600	-28.468	50.394	50.394	-30.000
5100	9.394	72.332	64.394	-13.160	107.400	-33.048	52.419	52.419	-31.000
5200	9.391	72.405	64.448	-13.261	103.100	-37.628	54.444	54.444	-32.000
5300	9.387	72.468	64.492	-13.358	98.700	-42.208	56.469	56.469	-33.000
5400	9.382	72.521	64.526	-13.451	94.200	-46.788	58.494	58.494	-34.000
5500	9.376	72.564	64.550	-13.540	89.600	-51.368	60.519	60.519	-35.000
5600	9.369	72.597	64.564	-13.625	84.900	-55.948	62.544	62.544	-36.000
5700	9.361	72.620	64.568	-13.706	80.100	-60.528	64.569	64.569	-37.000
5800	9.352	72.633	64.562	-13.783	75.200	-65.108	66.594	66.594	-38.000
5900	9.342	72.636	64.546	-13.856	70.200	-69.688	68.619	68.619	-39.000
6000	9.331	72.629	64.520	-13.925	65.100	-74.268	70.644	70.644	-40.000

Dec. 31, 1962; June 30, 1963

Ground State Configuration [2P]
 $S_{298.15}^o = [49.822] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 196 \pm 10 \text{ kcal. mole}^{-1}$
 $\Delta F_f^o = 198 \pm 10 \text{ kcal. mole}^{-1}$

$\omega_e = [1350] \text{ cm.}^{-1}$
 $\omega_e x_e = [12.0] \text{ cm.}^{-1}$
 $B_e = [1.555] \text{ cm.}^{-1}$
 $d_e = [0.018] \text{ cm.}^{-1}$
 $\sigma = 1$

Heat of Formation.

The heat of formation at 298.15°K. was calculated from $\Delta H_f^o = 105 \pm 10 \text{ kcal. mole}^{-1}$ for the reaction $BC(g) = B(g) + C(g)$ reported by G. Verhaegen, F. E. Stafford, M. Ackerman, and J. Drowart, *Nature*, **195**, 1280 (1962).

Heat Capacity and Entropy.

All spectroscopic constants were obtained from J. S. Gordon, AstroSystems, International, West Caldwell, New Jersey, private communication, November 2, 1962.

Tetraboron Monocarbide (B₄C)

(Crystal) Mol. Wt. = 55.25515

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	1.212	1.351	13.526	1.343	9.219	9.219	9.219	INFINITE
200	2.391	2.566	13.526	1.346	9.218	9.218	9.218	1.212
298	6.493	6.493	6.493	0.000	9.296	9.296	9.296	10.039
300	12.820	6.562	6.483	1.024	9.296	9.296	9.296	6.666
400	18.250	11.047	7.058	1.566	9.258	9.258	9.258	4.974
500	21.460	15.486	8.304	3.591	9.234	9.234	9.234	3.965
600	23.510	19.591	9.848	5.846	9.257	9.257	9.257	3.291
700	24.780	23.315	11.511	8.263	9.329	9.329	9.329	2.808
800	25.730	26.687	13.200	10.700	9.441	9.441	9.441	2.442
900	26.527	29.764	14.872	13.403	9.579	9.579	9.579	2.154
1000	27.318	32.601	16.505	16.095	9.733	9.733	9.733	1.919
1100	28.044	35.239	18.090	18.864	9.903	9.903	9.903	1.725
1200	28.726	37.708	19.623	21.703	10.076	10.076	10.076	1.559
1300	29.376	40.033	21.104	24.608	10.256	10.256	10.256	1.417
1400	30.003	42.233	22.536	27.577	10.431	10.431	10.431	1.292
1500	30.614	44.324	23.919	30.608	10.608	10.608	10.608	1.185
1600	31.211	46.319	25.257	33.699	10.779	10.779	10.779	1.085
1700	31.799	48.229	26.553	36.850	10.942	10.942	10.942	0.988
1800	32.379	50.063	27.808	40.059	11.092	11.092	11.092	0.920
1900	32.953	51.829	29.026	43.325	11.220	11.220	11.220	0.849
2000	33.522	53.534	30.209	46.649	11.317	11.317	11.317	0.784
2100	34.087	55.183	31.359	50.030	11.383	11.383	11.383	0.724
2200	34.649	56.782	32.479	53.467	11.417	11.417	11.417	0.670
2300	35.207	58.334	33.569	56.959	11.417	11.417	11.417	0.621
2400	35.764	59.844	34.633	60.508	11.383	11.383	11.383	0.576
2500	36.318	61.316	35.671	64.112	11.317	11.317	11.317	0.536
2600	36.871	62.751	36.685	67.771	11.219	11.219	11.219	0.497
2700	37.423	64.153	37.676	71.486	11.092	11.092	11.092	0.465
2800	37.973	65.524	38.547	75.256	10.942	10.942	10.942	0.435
2900	38.523	66.866	39.397	79.081	10.779	10.779	10.779	0.404
3000	39.071	68.181	40.228	82.961	10.608	10.608	10.608	0.375
3100	39.618	69.471	41.040	86.895	10.431	10.431	10.431	0.346
3200	40.165	70.738	41.836	90.884	10.256	10.256	10.256	0.318
3300	40.711	71.982	42.606	94.928	10.076	10.076	10.076	0.291
3400	41.257	73.205	43.357	99.026	9.893	9.893	9.893	0.265
3500	41.802	74.409	44.099	103.179	9.703	9.703	9.703	0.240

MOL. WT. = 55.25515

(CRYSTAL)

TETRABORON MONOCARBIDE (B₄C)

$$\Delta H_f^0 = -9.2 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -9.3 \pm 2.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [25] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 6.483 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 2743 \pm 20^\circ \text{K.}$$

Heat of Formation.

The ΔH_f^0 298.15 was calculated from ΔH_f^0 298.15 = -683.3 ± 2.2 kcal. mole⁻¹ for the reaction B₄C(c) + 4O₂(g) → 2B₂O₃(anorph) + CO₂(g) measured by D. Smith, A. S. Dworkin and E. R. Van Artsdalen, J. Am. Chem. Soc. 77, 2654-6 (1955) and the heat of formation for B₂O₃(anorph) (Dec. 31, 1964) and for CO₂(g) (March 31, 1961) in JANAF Tables.

Heat Capacity and Entropy.

The low temperature heat capacities, 54-294°K., were taken from K. K. Kelley, J. Am. Chem. Soc. 63, 1137 (1941). Above 298°K., C_p was calculated using the equation C_p = 22.89 + 5.40 X 10⁻⁵T - 10.72 X 10⁻⁹T² obtained from the enthalpy data in the range 298 to 1726°K. reported by E. G. King, Ind. Eng. Chem. 41, 1298 (1949). The values from the two sources join smoothly at 298°K. The S_{298.15} was calculated based on the low temperature heat capacities measured by K. K. Kelley, loc. cit., using S_{53.1} = 0.047 cal. deg.⁻¹ mole⁻¹.

Melting Data.

T_m was determined by Dolloff, WADD Tech. Rept. 60-143, 1960 and ΔH_m⁰ was estimated.

$$\Delta H_f^\circ 298.15 = 16.592 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^\circ 298.15 = 16.1 \pm 2.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = [25] \text{ kcal. mole}^{-1}$$

$$T_m = 2743 \pm 20^\circ \text{K.}$$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was obtained from $\Delta H_f^\circ 298.15(c)$ by adding ΔH_m° and the difference between H_m° and H_f° for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1750°K. The heat capacity below 1750°K. was obtained from the heat capacity of the crystal. Above 1750°K. the heat capacity was assumed constant and estimated as 32.50 cal. deg.⁻¹ mole⁻¹ or 6.5 cal. deg.⁻¹ per g-atom.

The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See B₄C(c) table.

Diberyllium Monocarbide Be₂C

(Crystal) Mol. Wt. = 30.037

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0						
100						
200						
298	10.337	3.900	0.000	- 21.700	- 21.098	15.465
300	10.356	3.900	0.019	- 21.699	- 21.094	15.366
400	11.350	4.319	1.106	- 21.796	- 20.991	11.414
500	11.891	5.139	2.270	- 21.899	- 20.862	9.031
600	12.402	6.084	3.484	- 22.147	- 20.794	7.428
700	12.889	7.062	4.835	- 22.365	- 20.682	6.270
800	13.359	8.052	6.339	- 22.510	- 20.746	5.394
900	13.806	9.038	8.037	- 22.633	- 20.793	4.709
1000	14.237	10.010	9.836	- 22.720	- 20.828	4.156
1100	14.652	10.965	11.738	- 22.769	- 20.856	3.706
1200	15.050	11.901	13.742	- 22.779	- 20.871	3.329
1300	15.431	12.818	15.837	- 22.757	- 20.877	3.010
1400	15.796	13.715	18.000	- 22.724	- 20.873	2.737
1500	16.145	14.593	20.234	- 22.702	- 20.860	2.501
1600	16.478	15.449	22.544	- 22.681	- 20.841	2.273
1700	16.796	16.283	24.929	- 22.660	- 20.824	2.047
1800	17.100	17.096	27.389	- 22.640	- 20.810	1.848
1900	17.391	17.887	29.924	- 22.621	- 20.797	1.671
2000	17.668	18.657	32.534	- 22.603	- 20.784	1.513
2100	17.933	19.406	35.219	- 22.586	- 20.772	1.370
2200	18.187	20.134	37.979	- 22.570	- 20.761	1.242
2300	18.430	20.842	40.814	- 22.555	- 20.750	1.125
2400	18.662	21.531	43.724	- 22.540	- 20.740	1.019
2500	18.884	22.201	46.709	- 22.525	- 20.730	0.922
2600	19.096	22.854	49.769	- 22.510	- 20.720	0.832
2700	19.298	23.493	52.904	- 22.496	- 20.710	0.750
2800	19.490	24.119	56.114	- 22.482	- 20.700	0.675
2900	19.672	24.734	59.400	- 22.468	- 20.690	0.608
3000	19.845	25.339	62.764	- 22.454	- 20.680	0.548
3100	20.008	25.934	66.208	- 22.440	- 20.670	0.492
3200	20.161	26.519	69.732	- 22.426	- 20.660	0.440
3300	20.304	27.094	73.336	- 22.412	- 20.650	0.392
3400	20.437	27.659	77.020	- 22.398	- 20.640	0.348
3500	20.560	28.214	80.784	- 22.384	- 20.630	0.308

CBe₂

DIBERYLLIUM MONOCARBIIDE (Be₂C)
(CRYSTAL)
MOL. WT. = 30.037

ΔH_f⁰ = Unknown
ΔH_f⁰ 298.15 = 21.7 ± 2.5 kcal. mole⁻¹
ΔH_f⁰ = [16] kcal. mole⁻¹
S_{298.15} = [3.9 ± 1.0] cal. deg.⁻¹ mole⁻¹
T_m = [2400]°K.

Heat of Formation.
The selected ΔH_f⁰ 298.15 was calculated by the 3rd law method using vapor pressures reported by B. D. Pollock, J. Phys. Chem. 53, 587 (1959). Pressures for the reaction Be₂C(s) → 2Be(g) + C(graphite) were measured by Pollock in the temperature range 1430-1669°K. by Knudsen technique. Vapor pressure data for this decomposition reaction have also been reported by J. Baboin, French Patents 1,193,790 (1959), J. Quirk, Reactor Handbook 3, 88 (1955) and P. Muratov and A. Novoselova, Dokl. Akad. Nauk SSSR 123, 334 (1959). The calculated ΔH_f⁰ 298.15 values are summarized as follows:

Calc. Method	Number of Pressures	T, °K.	ΔH _f ⁰ 298.15 kcal. mole ⁻¹	ΔH _f ⁰ 298.15 kcal. mole ⁻¹	References
3rd law	14	1430-1669	89.117	-21.7	B. D. Pollock
2nd law	14	1430-1669	90.8	-25.1	Least squares fit of Pollock's v.p. to the equation: log P (atm.) = 6.946-19.593/T
3rd law	6	1675-1953	71.411	+13.7	P. Muratov and A. Novoselova
3rd law	8	1900-2600	81.278	- 6.1	J. Quirk
3rd law	8	1800-2300	96.266	-36.0	J. Baboin

H. L. Schick, D. P. Anthrop, P. L. Hanst, R. E. Dreikorn, and M. B. Penish, "Thermodynamics of Certain Refractory Compounds, Part II", 1 March 1963 to 31 May 1963 have listed the measured vapor pressures. The vapor pressures reported by J. Baboin (loc. cit.) used in the 3rd law calculation were those listed by H. L. Schick, et al.

Heat Capacity and Entropy.

The heat capacity values, from 298.15 to 1200°K., were derived from the mean C_p data measured by J. J. Neely, E. Teeter, Jr., and J. B. Price, J. Am. Ceramic Soc. 33, 363 (1950). Neely, et al., estimated an overall error of 1% in their mean heat capacity data. The powdered Be₂C material which was used analyzed 80 to 74% Be₂C. The impurities were mainly oxide and nitride of Be. No corrections were made for the effect of these impurities.

From 1200-2400°K. the C_p was extrapolated so as to approach the value, 22 cal. deg.⁻¹ mole⁻¹ calculated from O. H. Krikorian, "Estimation of High-Temperature Heat Capacities of Carbides," University of California, UCLH 6785, February 6, 1962. The S_{298.15}° 3.9 cal. deg.⁻¹ mole⁻¹, was estimated by Krikorian (loc. cit.).

Melting Data.

H. L. Schick, et al., (loc. cit.) have summarized the available melting data i.e.: Y. Oishi and Y. Hamana, Osaka Kogyo Gijyuan Shikento Kiko 8, 89 (1957) have reported decomposition upon heating as low as 1873°K. L. Brewer, L. Brownley, P. Gilles, and M. Lofgren, "The Chemistry and Metallurgy of Miscellaneous Materials," in "Thermodynamics", McGraw-Hill, New York (1950) and I. S. Guev, AEC TR 3036 Transl. from Zh. Neorg. Khim. 1, 196 (1956) reported melting or dissociation between 2375° and 2423°K.

The melting point is assumed to be 2400°K. as estimated by T. B. Douglas and A. C. Victor, National Bureau of Standards Preliminary Report 6645, 1 January 1960 and H. L. Schick, et al. (loc. cit.). From the estimated melting point, 2400°K., and an estimated 2.5 cal. g. atom⁻¹ deg.⁻¹ for the entropy of melting, the heat of melting was calculated.

Diberyllium Monocarbide (Be₂C)

(Liquid) Mol. Wt. = 30.037

CB₂

DIBERYLLIUM MONOCARBIDE (Be₂C)

(LIQUID)

MOL. WT. = 30.037

T, °K	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100							
200	10.337	11.345	11.345	0.000	3.798	5.416	3.970
300	10.356	11.409	11.345	0.010	3.797	5.426	3.952
400	11.380	11.529	11.764	1.106	3.867	5.467	3.860
500	11.891	11.723	12.584	2.270	3.997	5.483	2.634
600	12.402	12.336	13.529	3.484	4.245	6.059	2.535
700	12.444	12.414	14.507	4.835	4.463	7.392	2.308
800	15.465	23.421	15.497	6.339	4.608	7.800	2.131
900	15.486	25.501	16.483	7.937	4.731	8.192	1.989
1000	17.507	27.091	17.455	9.636	4.818	8.571	1.873
1100	18.529	28.608	18.410	11.438	4.867	8.943	1.777
1200	19.550	30.464	19.346	13.342	4.877	9.313	1.696
1300	20.518	32.060	20.263	15.337	4.895	9.684	1.628
1400	20.860	33.387	21.160	17.398	4.872	10.056	1.570
1500	21.243	35.040	22.038	19.504	4.800	10.431	1.520
1600	22.000	36.421	22.894	21.643	10.309	10.651	1.455
1700	22.000	37.754	23.729	23.843	10.069	10.680	1.373
1800	22.000	39.012	24.544	26.043	9.844	10.752	1.302
1900	22.000	40.501	25.337	28.243	9.632	10.777	1.240
2000	22.000	41.350	26.108	30.443	9.433	10.845	1.189
2100	22.000	42.403	26.859	32.643	9.246	10.916	1.136
2200	22.000	43.427	27.589	34.843	9.073	11.002	1.093
2300	22.000	44.405	28.299	37.043	8.911	11.088	1.054
2400	22.000	45.341	28.990	39.243	8.762	11.186	1.019
2500	22.000	46.239	29.662	41.443	8.626	11.293	0.987
2600	22.000	47.102	30.316	43.643	8.501	11.400	0.958
2700	22.000	47.932	30.953	45.843	8.385	11.515	0.932
2800	22.000	48.732	31.574	48.043	8.276	11.636	0.906
2900	22.000	49.504	32.179	50.243	8.174	11.761	0.881
3000	22.000	50.250	32.769	52.443	8.076	11.889	0.856
3100	22.000	50.971	33.345	54.643	7.981	12.020	0.831
3200	22.000	51.670	33.906	56.843	7.887	12.153	0.806
3300	22.000	52.347	34.455	59.043	7.794	12.288	0.781
3400	22.000	53.004	34.991	61.243	7.702	12.424	0.756
3500	22.000	53.641	35.515	63.443	7.610	12.561	0.731

Dec. 31, 1960; Mar. 31, 1962; June 30, 1963

CB₂

ΔH_f^o 298.15 = [3.798 ± 10] kcal. mole⁻¹

ΔH_f^o = [18] kcal. mole⁻¹

S° 298.15 = [11.345] cal. deg.⁻¹ mole⁻¹

T_m = [2400]°K.

Heat of Formation.

The ΔH_f^o 298.15 was calculated from the heat of formation of the crystal and the estimated heat of melting.

Heat Capacity and Entropy.

The heat capacity was assumed constant and equal to the heat capacity of the solid Be₂C at the estimated melting point.

Melting Data.

The National Bureau of Standards Report 6645, January, 1960, states that Be₂C seems to decompose easily only at temperatures above its reported melting point. For this reason they extended their Be₂C table into the liquid region. For detailed melting data see the Be₂C (c) table.

Carbon Monobromide (CBr)

(Ideal Gas) GFW = 91.92015

CBr

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.0000	.0000	INFINITE	2.266	122.915	122.915	INFINITE
100	7.374	47.282	52.975	1.569	123.264	119.201	260.512
200	7.866	52.446	56.341	.819	123.351	115.096	125.770
298	8.314	55.770	59.770	.000	122.000	111.201	81.513
300	8.421	55.823	59.770	.016	121.995	111.135	80.961
400	8.976	58.344	58.112	.693	118.506	104.239	59.139
500	9.373	60.337	56.764	1.786	118.639	105.656	46.182
600	9.612	61.977	57.501	2.684	118.717	103.059	37.536
700	9.731	63.167	58.242	3.492	118.747	100.437	31.358
800	9.841	64.574	58.960	4.492	118.744	97.821	26.724
900	9.949	65.639	59.644	5.394	118.713	95.207	23.119
1000	10.056	66.593	60.292	6.301	118.662	92.598	20.237
1100	10.162	67.454	60.906	7.207	118.594	89.994	17.880
1200	10.269	68.245	61.484	8.114	118.513	87.391	15.917
1300	10.376	68.971	62.032	9.021	118.418	84.809	14.258
1400	10.483	69.644	62.552	9.929	118.317	82.229	12.836
1500	10.590	70.271	63.046	10.837	118.209	79.654	11.606
1600	10.698	70.858	63.516	11.747	118.093	77.084	10.530
1700	10.805	71.410	63.965	12.657	117.974	74.527	9.560
1800	10.913	71.930	64.393	13.564	117.850	71.976	8.739
1900	11.021	72.423	64.803	14.480	117.724	69.432	7.986
2000	11.129	72.891	65.195	15.392	117.595	66.893	7.310
2100	11.236	73.337	65.573	16.305	117.458	64.361	6.698
2200	11.346	73.762	65.943	17.218	117.314	61.836	6.136
2300	11.454	74.169	66.284	18.131	117.164	59.316	5.636
2400	11.563	74.559	66.621	19.050	117.009	56.802	5.173
2500	11.671	74.933	66.946	19.987	116.851	54.294	4.746
2600	11.780	75.293	67.260	20.935	116.675	51.792	4.356
2700	11.888	75.640	67.560	21.893	116.493	49.292	3.990
2800	11.997	75.974	67.850	22.872	116.304	46.803	3.653
2900	12.106	76.297	68.144	23.862	116.109	44.317	3.340
3000	12.214	76.609	68.421	24.863	115.914	41.836	3.048
3100	12.323	76.911	68.690	25.885	115.721	39.362	2.775
3200	12.432	77.204	68.950	26.928	115.531	36.892	2.519
3300	12.541	77.488	69.206	27.992	115.343	34.421	2.280
3400	12.649	77.764	69.454	29.067	115.156	31.950	2.054
3500	12.758	78.033	69.695	29.162	114.972	29.489	1.842
3600	12.867	78.294	69.930	30.198	114.782	27.034	1.642
3700	12.976	78.548	70.160	31.256	114.587	24.585	1.452
3800	13.085	78.795	70.384	31.963	114.387	22.135	1.274
3900	13.194	79.036	70.603	32.592	114.183	19.716	1.105
4000	13.303	79.272	70.816	33.822	113.972	17.276	.944
4100	13.412	79.502	71.025	34.753	113.753	14.836	.791
4200	13.521	79.726	71.235	35.685	113.528	12.394	.648
4300	13.630	79.946	71.430	36.618	113.298	9.958	.508
4400	13.739	80.160	71.626	37.551	113.063	7.519	.376
4500	13.848	80.370	71.818	38.486	112.823	5.080	.250
4600	13.957	80.576	72.006	39.422	112.578	2.636	.130
4700	14.066	80.778	72.192	40.362	112.328	.189	.028
4800	14.175	80.975	72.372	41.296	112.073	-2.261	.000
4900	14.284	81.169	72.549	42.235	111.813	-4.486	.000
5000	14.393	81.359	72.724	43.175	111.548	-6.585	.001
5100	14.502	81.545	72.895	44.114	111.278	-8.684	.008
5200	14.611	81.728	73.063	45.059	110.999	-10.784	.000
5300	14.720	81.908	73.228	46.002	110.711	-12.884	.000
5400	14.829	82.084	73.390	46.947	110.416	-14.984	.000
5500	14.938	82.258	73.550	47.892	110.116	-17.084	.000
5600	15.047	82.428	73.707	48.840	109.811	-19.184	.008
5700	15.156	82.596	73.861	49.788	109.501	-21.284	.000
5800	15.265	82.761	74.014	50.736	109.186	-23.384	.000
5900	15.374	82.924	74.163	51.684	108.866	-25.484	.000
6000	15.483	83.084	74.311	52.632	108.541	-27.584	.000

June 30, 1967

CARBON MONOBROMIDE (CBr)

Ground State Configuration 2Π

(IDEAL GAS)

GFW = 91.92015

ΔHf° = 123 ± 15 kcal/mol

ΔHf°_{298.15} = 122 ± 15 kcal/molS°_{298.15} = [55.8] gibbs/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	2
465	2
33163	2
33218	2
[400000]	[2]

 $\omega_e = [736] \text{ cm}^{-1}$ $\omega_e x_e = [4.0] \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = [0.0036] \text{ cm}^{-1}$ $r_e = 1.8170 \text{ Å}$ $B_e = 0.4890 \text{ cm}^{-1}$

Heat of Formation

Dixon and Kroto (1) have observed predissociation of CBr(g) which indicates that the dissociation energy (D_0°) is less than 94.7 kcal/mol. They evaluated the kinetic data of Simons and Yarwood (2), obtaining a value of $D_0^\circ = 97 \pm 5$ kcal/mol, based on the heat of formation of bromoform and the dissociation energy of HBr, and concluded that the true value of D_0° is very close to the upper limit of 94.7 kcal/mol. Comparisons of C-X bond energies of CX₄ and CX compounds, however, indicate that this value is too high to be consistent with other carbon halides. Therefore the value of D_0° adopted is 75 ± 15 kcal/mol. The corresponding ΔH_f° for CBr(g) is 122 ± 15 kcal/mol.

Heat Capacity and Entropy

The rotational structure of the near UV spectra of CBr(g) has been investigated by Dixon and Kroto (1) in the 3000 Å region. They assigned the above doublet electronic levels to the ground ($^2\Pi$) and first excited ($^2\Sigma$) states and reported a value of $B_0 = 0.4872 \pm 0.0003 \text{ cm}^{-1}$ for the ground state. An additional electronic level ($^2\Sigma$) is expected to be close to the first excited state by analogy with CF(g) and CCl(g).

The fundamental vibrational frequency ω_e is estimated from Guggenheimer's relation for single bonded molecules (3). The anharmonic vibrational term $\omega_e x_e$ is estimated by assuming $\omega_e x_e = \omega_e^2/(4D_0 + 2\omega_e)$. The value of ω_e is calculated from the Morse potential function. The rotational constant B_e is calculated from $B_e = B_0 + a_e/2$. The bond distance is calculated from B_e .

References

1. R. N. Dixon and H. W. Kroto, Trans. Faraday Soc. 59, 1484 (1963).
2. J. P. Simons and A. J. Yarwood, Trans. Faraday Soc. 57, 2167 (1961).
3. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).

CBr

Bromotrifluoromethane (CBrF₃)

GFW = 148.91535

(Ideal Gas)

Point Group C_{3v} $\Delta H_f^\circ = -152.2 \pm 0.7$ kcal/mol $S_{298.15}^\circ = 71.155 \pm 0.12$ gibbs/mol $\Delta H_f^\circ = -155.1 \pm 0.7$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
1086 (1)	1206 (2)
761 (1)	549 (2)
348 (1)	300 (2)

Bond Distance: C-F = 1.328 Å C-Br = 1.909 Å
 Bond Angle: F-C-F = 108.6 ± 1° F-C-Br = 110.33°
 Product of the Moments of Inertia: $I_A I_B I_C = 2.3403 \times 10^{-113}$ g cm⁶ $\sigma = 3$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₂X (X = H, Cl, Br, I, CF₃), and C₂F₄. Details of the input data and the adjustment are given in (1). Coomber and Whittle (2, 3, 4) have determined equilibrium data for CClF₃(g) + BrCl(g) = CBrF₃(g) + Cl₂(g) and for CF₃X(g) + Br₂(g) = CF₃Br(g) + BrX(g) where X = H, Cl, and CF₃. Equilibrium data for CF₃I(g) + BrI(g) = CBrF₃(g) + I₂(g) were obtained by Lord et al. (5). These data link CBrF₃ with C₂F₆, CHF₃, CClF₃, and CF₃.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Sharbaugh et al. (6), Bowen (7), and Anderson (8) and from microwave data by Sheridan and Gordy (9). The adopted parameters are an average of those reported by (8, 9). Infrared spectra of the gas were observed by several investigators (10, 11, 12) and Raman spectra of the liquid were obtained by Edgell and May (12). The vibrational assignments of (11, 12) are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. The value for ν_6 is taken as 300 cm⁻¹ which is between the values of 305 and 297 ± 3 cm⁻¹ derived from Raman spectra and IR (combination and overtone) spectra, respectively. The thermodynamic functions of this table are essentially the same as those calculated by (11). Uncertainty in the entropy is estimated to vary from 0.12 to 0.5 gibbs/mol over the range from 300 to 1000°K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for CClF₃(g) and CF₄(g). The principal moments of inertia are $I_A = 14.68 \times 10^{-40}$ and $I_B = I_C = 39.93 \times 10^{-40}$ g cm².

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRPL Contract Nr. FV4611-67-C-0009, Dow Chemical Co., July, 1969.
2. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 608 (1967).
3. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 1394 (1967).
4. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 2656 (1967).
5. A. Lord, C. A. Goy and H. O. Pritchard, J. Phys. Chem. **71**, 2705 (1967).
6. A. H. Sharbaugh, B. S. Pritchard and T. C. Madison, Phys. Rev. **77**, 302 (1950).
7. H. J. M. Bowen, Trans. Faraday Soc. **50**, 444 (1954).
8. R. E. Anderson, Dissertation Abstracts **13**, 50 (1958).
9. J. Sheridan and M. Gordy, J. Chem. Phys. **20**, 591 (1952).
10. E. K. Plyler and N. Acquista, J. Res. Nat. Bur. Stand. **48**, 92 (1952).
11. P. R. McGee, F. F. Cleveland, A. G. Meister and C. E. Decker, J. Chem. Phys. **21**, 242 (1953).
12. W. F. Edgell and C. E. May, J. Chem. Phys. **22**, 1808 (1954).

June 30, 1969

Cyanogen Bromide (BrCN)
(Ideal Gas)

GFw = 105.92685

CYANOGEN BROMIDE (BrCN)

(IDEAL GAS)

GFw = 105.92685

CBRN

Point Group $C_{\infty v}$

$S_{298.15}^{\circ} = 59.33 \pm 0.01$ gibbs/mol

Ground State Quantum Weight = 1

$\Delta H_f^{\circ} = 46.1 \pm 1.5$ kcal/mol

$\Delta H_f^{\circ}_{298.15} = 44.5 \pm 1.5$ kcal/mol

Vibrational Frequencies and Degeneracies
 ω_e, cm^{-1}

575 (1)
342.5 (2)
2200 (1)

Bond Distance: C-Br = 1.789 Å C-N = 1.158 Å

Bond Angle: Br-C-N = 180° $\sigma = 1$

Rotational Constants: $B_0 = 0.13705$ $D_0 = 2.829 \times 10^{-8}$ cm^{-1}

Spectroscopic constants used in calculating corrections to rigid-rotator-harmonic oscillator approximation (cm^{-1}).

$\alpha_1 = 5.17 \times 10^{-4}$ $\alpha_{11} = [-3.0]$ $\alpha_{12} = [-4.0]$

$\alpha_2 = -3.84 \times 10^{-4}$ $\alpha_{22} = -0.86$ $\alpha_{23} = -6.19$

$\alpha_3 = 6.77 \times 10^{-4}$ $\alpha_{33} = [-5.0]$ $\alpha_{13} = [-3.0]$

$\delta_{22} = 1.14$

Heat of Formation

The heat of formation is calculated from ΔH_f° (BrCN, c) = 33.58 kcal/mol (1) and $\Delta H_f^{\circ}_{298} = 10.92 \pm 0.1$ kcal/mol.

This latter is obtained from an analysis of the vapor pressure data of Lord and Woolf (2) and Baxter et al. (3).

The heat of formation of the crystal is calculated from $\Delta H_f^{\circ}_{298} = -56.0$ kcal/mol obtained by Lord and Woolf (2)

for the reaction $\text{BrCN(c)} + 2\text{NaOH(56 H}_2\text{O)} = \text{NaCNO(2800 H}_2\text{O)} + \text{NaBr(2800 H}_2\text{O)} + \text{H}_2\text{O(l)}.$

The auxiliary data used were $\Delta H_f^{\circ}(\text{NaOH-56 H}_2\text{O}) = -112.26$ kcal/mol (1, 2), $\Delta H_f^{\circ}(\text{NaCNO-2800 H}_2\text{O}) = -92.25$ kcal/mol (1, 2) and $\Delta H_f^{\circ}(\text{NaBr-2800 H}_2\text{O}) = -70.54$ kcal/mol (1, 2). The uncertainty in the final value reflects the uncertainty in $\Delta H_f^{\circ}(\text{NaCNO-2800 H}_2\text{O})$ which was determined by Lord and Woolf (2) to be -93.5 kcal/mol in excess NaOH-56 H₂O.

Heat Capacity and Entropy

J. S. Gordon (5) used the constants given above to calculate the adopted table, using the method of Pennington and Kobe (6) for anharmonicity, vibration rotation interaction, and centrifugal stretching corrections.

The bond lengths and angle were reported by Tyler and Sheridan (7).

References

1. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
2. G. Lord and A. A. Woolf, J. Chem. Soc. (London), 2546 (1954).
3. G. P. Baxter, T. K. Bezenburger and C. H. Wilson, J. Amer. Chem. Soc. 82, 1386 (1920).
4. V. B. Parker, U. S. Natl. Bur. Std. NBS-2, 1965.
5. J. S. Gordon, J. Chem. Eng. Data, 11, 553 (1966).
6. R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954).
7. J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 58, 2861 (1962).

T, K	C_p°	$S^{\circ} - (C_p^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	INFINITE	2.647	46.071	46.071	INFINITE
100	48.000	48.000	1.047	45.024	45.024	1.047
200	9.970	50.306	1.047	45.965	41.463	25.331
298	11.263	59.334	0.000	44.500	39.462	26.926
300	11.280	59.334	0.021	44.494	39.431	26.725
400	11.983	59.786	1.186	40.944	35.478	21.024
500	12.451	60.660	2.406	41.055	37.846	16.543
600	12.826	67.781	6.1659	41.141	37.198	13.549
700	13.150	69.783	10.650	41.205	36.336	11.407
800	13.433	71.557	15.661	41.256	35.865	9.798
900	13.680	73.154	21.266	41.296	35.188	8.595
1000	13.895	74.607	27.571	41.332	34.308	7.592
1100	14.081	75.940	34.645	41.363	33.823	6.720
1200	14.244	77.173	42.296	41.392	33.137	6.035
1300	14.386	78.318	50.610	41.416	32.448	5.495
1400	14.511	79.389	59.669	41.442	31.758	4.998
1500	14.621	80.394	69.604	41.466	31.066	4.556
1600	14.720	81.341	79.308	41.491	30.371	4.168
1700	14.809	82.236	89.694	41.517	29.675	3.815
1800	14.890	83.085	100.814	41.543	28.977	3.518
1900	14.965	83.892	112.607	41.571	28.281	3.253
2000	15.033	84.661	125.106	41.600	27.579	3.014
2100	15.096	85.396	138.336	41.631	26.878	2.797
2200	15.155	86.100	152.325	41.662	26.173	2.600
2300	15.211	86.775	167.075	41.695	25.470	2.420
2400	15.263	87.423	182.597	41.729	24.764	2.255
2500	15.313	88.047	198.891	41.765	24.056	2.103
2600	15.361	88.649	215.956	41.801	23.347	1.962
2700	15.406	89.230	233.788	41.840	22.635	1.832
2800	15.450	89.791	252.391	41.880	21.924	1.711
2900	15.492	90.334	271.777	41.920	21.211	1.599
3000	15.533	90.859	291.910	41.962	20.496	1.493
3100	15.573	91.369	312.816	42.005	19.780	1.395
3200	15.612	91.864	334.502	42.050	19.063	1.302
3300	15.650	92.345	356.977	42.094	18.341	1.215
3400	15.687	92.813	380.253	42.141	17.623	1.133
3500	15.723	93.268	404.336	42.187	16.896	1.055
3600	15.758	93.712	429.229	42.235	16.175	0.982
3700	15.793	94.144	454.976	42.284	15.451	0.913
3800	15.828	94.566	481.624	42.333	14.728	0.847
3900	15.861	94.977	509.124	42.384	14.002	0.785
4000	15.895	95.379	537.516	42.435	13.272	0.725
4100	15.928	95.772	566.721	42.487	12.540	0.666
4200	15.961	96.156	596.781	42.539	11.812	0.615
4300	15.993	96.532	627.715	42.591	11.080	0.563
4400	16.025	96.900	659.561	42.644	10.345	0.514
4500	16.057	97.261	692.346	42.698	9.608	0.467
4600	16.088	97.614	726.104	42.753	8.876	0.422
4700	16.119	97.960	760.869	42.808	8.139	0.378
4800	16.150	98.300	796.666	42.861	7.401	0.337
4900	16.181	98.633	833.538	42.917	6.660	0.297
5000	16.212	98.961	871.516	42.973	5.922	0.259
5100	16.242	99.282	910.640	43.027	5.172	0.222
5200	16.273	99.596	950.956	43.083	4.431	0.186
5300	16.303	99.908	992.501	43.139	3.691	0.152
5400	16.333	100.213	1035.318	43.194	2.946	0.119
5500	16.363	100.513	1079.436	43.249	2.204	0.088
5600	16.392	100.808	1124.904	43.305	1.454	0.057
5700	16.422	101.098	1171.769	43.360	0.705	0.027
5800	16.452	101.384	1219.984	43.415	0.043	0.002
5900	16.481	101.666	1269.604	43.470	-0.760	0.029
6000	16.510	101.943	1320.684	43.524	-1.546	0.056

CBRN

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	4.4872	19.097	19.097	INFINITE	INFINITE
100	15.456	61.319	8.189	2.034	18.166	11.205	1.244	6.297
200	21.793	85.563	8.563	+0.00	12.000	8.500		
300	21.826	85.698	85.563	+0.00	11.970	8.570		6.243
400	23.204	92.183	86.438	2.208	2.498	10.421	5.694	
500	24.012	97.436	86.131	4.662	2.219	13.618	5.952	
600	24.510	101.681	90.064	7.000	1.945	16.759	6.104	
700	24.834	105.685	92.030	9.559	1.687	19.855	6.190	
800	25.054	109.017	93.949	12.000	1.443	22.915	6.260	
900	25.210	111.977	95.791	14.567	1.213	25.946	6.300	
1000	25.334	114.659	97.545	17.094	0.992	28.953	6.337	
1100	25.409	117.057	99.211	19.631	0.782	31.935	6.345	
1200	25.475	119.271	100.791	22.176	0.579	34.902	6.356	
1300	25.527	121.312	102.292	24.726	0.388	37.852	6.363	
1400	25.569	123.206	103.719	27.281	0.201	40.787	6.367	
1500	25.602	124.971	105.078	29.839	0.023	43.707	6.368	
1600	25.630	126.624	106.374	32.401	-0.151	46.616	6.367	
1700	25.653	128.179	107.611	34.965	-0.321	49.516	6.365	
1800	25.672	129.646	108.795	37.531	-0.486	52.403	6.362	
1900	25.687	131.031	110.029	40.099	-0.648	55.287	6.359	
2000	25.703	132.352	111.017	42.669	-0.805	58.155	6.355	
2100	25.715	133.606	112.004	45.240	-0.961	61.020	6.350	
2200	25.725	134.803	113.070	47.812	-1.110	63.874	6.345	
2300	25.735	135.947	114.040	50.385	-1.257	66.727	6.340	
2400	25.745	137.040	114.917	52.958	-1.402	69.579	6.335	
2500	25.750	138.093	115.680	55.534	-1.541	72.428	6.330	
2600	25.756	139.103	116.754	58.109	-1.677	75.281	6.324	
2700	25.762	140.075	117.599	60.685	-1.811	78.038	6.318	
2800	25.767	141.012	118.419	63.261	-1.944	80.888	6.313	
2900	25.772	141.916	119.216	65.836	-2.077	83.730	6.308	
3000	25.776	142.790	119.983	68.413	-2.201	86.576	6.302	
3100	25.779	143.636	120.735	70.993	-2.311	89.330	6.297	
3200	25.783	144.454	121.463	73.571	-2.429	92.135	6.292	
3300	25.786	145.247	122.172	76.150	-2.542	94.930	6.287	
3400	25.789	146.016	122.862	78.729	-2.653	97.730	6.282	
3500	25.791	146.765	123.534	81.307	-2.759	100.525	6.277	
3600	25.793	147.491	124.190	83.887	-2.863	103.315	6.272	
3700	25.796	148.198	124.829	86.466	-2.964	106.105	6.267	
3800	25.798	148.886	125.453	89.046	-3.061	108.894	6.263	
3900	25.801	149.556	126.063	91.626	-3.154	111.682	6.258	
4000	25.801	150.210	126.658	94.206	-3.244	114.458	6.253	
4100	25.803	150.847	127.240	96.786	-3.330	117.234	6.249	
4200	25.804	151.468	127.810	99.366	-3.412	120.015	6.245	
4300	25.806	152.076	128.367	101.947	-3.491	122.792	6.241	
4400	25.807	152.671	128.917	104.527	-3.566	125.566	6.237	
4500	25.808	153.249	129.447	107.108	-3.639	128.334	6.232	
4600	25.809	153.816	129.971	109.689	-3.706	131.107	6.229	
4700	25.810	154.371	130.484	112.270	-3.771	133.880	6.225	
4800	25.811	154.915	130.987	114.851	-3.839	136.642	6.221	
4900	25.812	155.448	131.482	117.432	-3.906	139.401	6.216	
5000	25.813	155.968	131.966	120.014	-3.969	142.176	6.214	
5100	25.814	156.470	132.441	122.595	-4.028	144.932	6.210	
5200	25.815	156.981	132.908	125.176	-4.031	147.698	6.207	
5300	25.815	157.472	133.367	127.758	-4.073	150.467	6.204	
5400	25.816	157.946	133.819	130.340	-4.118	153.236	6.201	
5500	25.817	158.429	134.261	132.921	-4.141	155.992	6.198	
5600	25.817	158.894	134.697	135.503	-4.169	158.746	6.195	
5700	25.818	159.351	135.126	138.085	-4.192	161.507	6.192	
5800	25.819	159.800	135.547	140.666	-4.212	164.270	6.190	
5900	25.819	160.242	135.967	143.247	-4.237	167.033	6.187	
6000	25.820	160.675	136.370	145.830	-4.258	169.777	6.184	

Dec. 31, 1963

$$\Delta H_f^0 = [19] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = [12] \text{ kcal. mole}^{-1}$$

$$S^0_{298.15} = 85.563 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

$$\text{Ground State Quantum Weight} = [1]$$

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
267.2 (1)	670.7 (3)
122.5 (2)	182.5 (3)

$$\text{Bond Distance: C-Br} = 1.942 \text{ \AA}$$

$$\text{Bond Angle: Br-C-Br} = 109^\circ 28'$$

$$\text{Product of Moments of Inertia: } I_A I_B I_C = 2.3756 \times 10^{-111} \text{ g. cm.}^6$$

$$\sigma = 12$$

Heat of Formation.

The heat of formation, ΔH_f^0 298.15, was calculated and reported by P. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", National Bureau of Standards Circular 500, 1952.

Heat Capacity and Entropy.

The molecular constants, bond distances, and bond angle were determined by electron diffraction by C. Finbak, O. Hassel, and B. Ottar, Arch. Math. Naturv B44, No. 13 (1941) and C. Finbak, O. Hassel, and O. Olavsen, Tidsskr. Kjemi Bergv. 3, 13 (1943). The constants reported by C. Finbak, et al., in 1943 were selected. These constants are listed in, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society (London), 1958. The principal moments of inertia calculated from these constants were $I_A = I_B = I_C = 1.3343 \times 10^{-37} \text{ g. cm.}^2$.

The vibrational frequencies used were assigned by A. G. Meister, S. E. Roesser, and F. P. Cleveland, J. Chem. Phys. 18, 346 (1950). They measured the infrared and Raman spectrum, considered the previous literature, calculated force constants and made most probable value assignments for the frequencies. A more recent paper by B. Morzynska and J. P. Mathieu, Compt. Rend 255, 2820 (1963) made assignments from Raman and infrared spectra which agreed with all of Meister, et al.'s assignments except ν_2 which they found was 126 cm⁻¹ rather than 122 cm⁻¹.

GF_W = 47.46415

$\Delta H^{\circ}_0 = 119.1 \pm 5 \text{ kcal/mol}$

$\Delta H^{\circ}_{298.15} = 120 \pm 5 \text{ kcal/mol}$

(IDEAL GAS)

CARBON MONOCHLORIDE (CCl)

$S^{\circ}_{298.15} = 53.63 \pm 0.1 \text{ gibbs/mol}$

Carbon Monochloride (CCl)

(Ideal Gas) GF_W = 47.46415

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o - H ^o ₂₉₈)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	2.245	119.104	119.104	INFINITE
100	7.760	45.342	60.362	119.485	117.229	256.204
200	7.488	50.612	54.330	119.802	114.840	125.491
298	7.709	53.634	0.000	120.000	112.358	82.361
300	7.715	53.681	0.014	120.003	112.311	81.818
400	8.029	55.945	53.940	120.129	109.726	59.952
500	8.278	57.764	54.529	120.200	107.117	46.821
600	8.459	59.291	55.199	120.295	104.497	38.063
700	8.568	60.605	55.879	120.213	101.876	31.807
800	8.644	61.758	56.543	120.175	99.259	27.116
900	8.757	62.785	57.181	120.115	96.647	23.469
1000	8.814	63.711	57.768	120.041	94.043	20.553
1100	8.859	64.553	58.346	119.953	91.446	18.160
1200	8.897	65.326	58.914	119.855	88.850	15.784
1300	8.929	66.039	59.435	119.746	86.281	13.505
1400	8.957	66.702	59.931	119.633	83.712	11.306
1500	8.981	67.321	60.403	119.513	81.151	9.182
1600	9.003	67.901	60.854	119.388	78.594	7.136
1700	9.023	68.448	61.284	119.261	76.051	5.177
1800	9.041	68.964	61.697	119.129	73.512	3.306
1900	9.058	69.453	62.092	118.996	70.983	1.526
2000	9.074	69.918	62.472	118.860	68.459	0.000
2100	9.089	70.361	62.837	118.728	65.943	-1.483
2200	9.103	70.784	63.189	118.594	63.431	-2.970
2300	9.118	71.169	63.528	118.463	60.930	-4.463
2400	9.131	71.578	63.855	118.300	58.432	-5.959
2500	9.145	71.951	64.172	118.156	55.939	-7.459
2600	9.159	72.310	64.478	118.010	53.454	-8.963
2700	9.172	72.656	64.774	117.862	50.973	-10.471
2800	9.186	72.989	65.062	117.714	48.500	-11.982
2900	9.200	73.312	65.341	117.563	46.030	-13.496
3000	9.215	73.624	65.612	117.410	43.565	-15.013
3100	9.229	73.926	65.879	117.257	41.107	-16.532
3200	9.245	74.220	66.131	117.103	38.653	-18.053
3300	9.260	74.504	66.381	116.944	36.202	-19.575
3400	9.277	74.781	66.624	116.787	33.760	-21.098
3500	9.294	75.050	66.861	116.627	31.317	-22.622
3600	9.311	75.312	67.092	116.467	28.883	-24.147
3700	9.329	75.568	67.318	116.305	26.453	-25.672
3800	9.348	75.817	67.538	116.142	24.028	-27.197
3900	9.368	76.060	67.753	115.979	21.607	-28.722
4000	9.388	76.297	67.964	115.815	19.190	-30.247
4100	9.409	76.529	68.170	115.650	16.773	-31.772
4200	9.431	76.756	68.372	115.484	14.356	-33.297
4300	9.453	76.979	68.569	115.318	11.939	-34.822
4400	9.476	77.196	68.763	115.152	9.528	-36.347
4500	9.500	77.409	68.953	114.985	7.117	-37.872
4600	9.524	77.618	69.139	114.819	4.704	-39.397
4700	9.549	77.825	69.320	114.656	2.292	-40.922
4800	9.574	78.025	69.501	114.496	-0.122	-42.447
4900	9.600	78.222	69.677	114.330	-2.535	-43.972
5000	9.626	78.417	69.850	114.155	-4.948	-45.497
5100	9.653	78.608	70.019	113.989	-7.356	-47.022
5200	9.680	78.795	70.186	113.824	-9.764	-48.547
5300	9.708	78.980	70.351	113.661	-12.172	-50.072
5400	9.736	79.162	70.512	113.498	-14.580	-51.597
5500	9.764	79.341	70.671	113.334	-16.988	-53.122
5600	9.793	79.517	70.827	113.173	-19.396	-54.647
5700	9.822	79.690	70.981	113.010	-21.804	-56.172
5800	9.851	79.861	71.133	112.849	-24.212	-57.697
5900	9.880	80.030	71.282	112.689	-26.620	-59.222
6000	9.909	80.196	71.429	112.529	-29.028	-60.747

Electronic Levels and Quantum Weights

State	ϵ_i , cm ⁻¹	g_i
$\chi^{\circ}\Pi$	0	2
	134.92	2
4Σ	[20000]	4
$A^2\Delta$	36004	4

$\omega_e = 876.4 \text{ cm}^{-1}$

$\omega_e x_e = 6.15 \text{ cm}^{-1}$

$\alpha_e = [0.0066] \text{ cm}^{-1}$

$r_e = 1.642 \text{ \AA}$

Heat of Formation

The data of Hiller and Palmer (1) provide a value of $D_0(\text{CCl}) = 80 \pm 5 \text{ kcal/mol}$, which appears to be reasonably substantiated. They studied the chemiluminescence from flames of CHCl_3 and CCl_4 burning in potassium vapor. These flames exhibit C_2 Swan band radiation with major departures from vibrational and rotational equilibrium. The spectra are interpreted as due to the reaction $\text{C} + \text{CCl} + C_2^* + \text{Cl}$ where the carbon atom is either 3D ground state or 1D first excited state. The separation between the ground and first excited state of the carbon atom is matched closely by the difference in preferential population of the excited C_2 levels. The assumption is made that all the exothermicity of the reaction is retained as vibrational excitation of the C_2 , thus the populated levels are measures of the heat of reaction. In this manner we obtain a heat of reaction of $87 \pm 2.5 \text{ kcal}$ for the reaction $\text{C} + \text{CCl} + C_2 + \text{Cl}$ which, using JANAF auxiliary data, gives $\Delta H^{\circ}(\text{CCl}, g) = 124 \pm 2.5 \text{ kcal/mol}$; however, this represents the initial state of the CCl which in the flame is presumed to have about 4 kcal of vibrational energy at roughly 2000°K. Thus, we obtain $\Delta H^{\circ}_{298}(\text{CCl}, g) = 120 \pm 5 \text{ kcal/mol}$, which is adopted.

The heat of formation can also be estimated from the dissociation energy calculated from the linear Birge-Sponer extrapolation of the ground state vibrational constants. This yields $D_0 = 89 \text{ kcal}$ or $\Delta H^{\circ}_{298} = 111 \text{ kcal/mol}$. There are several indications that this dissociation energy is probably a maximum value, for example, Hildenbrand (2) has applied an ionic-covalent correction to the linear extrapolation which gives $D_0 = 72 \text{ kcal}$. We would expect this heat of formation to be a minimum value. A real minimum for the dissociation energy can be obtained from the knowledge that the first vibrational level of the $^2\Delta$ state is occupied and so the dissociation energy of this state must be greater than 850 cm^{-1} . This yields a minimum dissociation energy of the ground state of 76 kcal, assuming the dissociation products are $C(^1\Delta)$ and $\text{Cl}(^2P)$, and $\Delta H^{\circ}_{298}(\text{CCl}, g) = 124 \text{ kcal/mol}$ which is the maximum value of the heat of formation.

Heat Capacity and Entropy

The rotational and electronic constants are those of Verma and Mulliken (2). The vibrational constants are those derived by Ovcharenko et al. (3) from the data of Gordon and King (4). The anharmonicity constants listed by Verma and Mulliken are not used, since these are based only on the 0,0 and 0,1 transitions. The u_2 level is estimated by analogy with $\text{CF}(g)$. The value for a_e was obtained from the other constants assuming a Morse potential function.

References

1. W. J. Miller and R. B. Palmer, J. Chem. Phys. **40**, 3701 (1964).
2. R. D. Verma and H. S. Mulliken, J. Mol. Spectry. **5**, 413 (1961).
3. I. E. Ovcharenko, Yu. Ya. Kuzyskov, and V. M. Tat'yevskii, Opt. Spectry. (Eng. Transl.) **13**, 294 (1965).
4. R. D. Gordon and G. W. King, Can. J. Phys. **39**, 252 (1961).
5. D. L. Hildenbrand, Douglas Advanced Research Laboratories, Huntington Beach, Calif., private communication, Dec. 30, 1965.

Carbonyl Chloride Fluoride (COClF)

Mol. Wt. = 82.47

(Ideal Gas)

CARBONYL CHLORIDE FLUORIDE (COClF)

(IDEAL GAS)

MOL. WT. = 82.47

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	0.000	INFINITE	2.845	-101.404	-101.404	INFINITE
100	8.223	55.353	2.046	2.046	-101.404	-101.404	-101.404	220.321
200	12.539	41.624	1.000	1.000	-102.000	-102.000	-102.000	159.815
298	12.539	41.624	1.000	1.000	-102.000	-102.000	-102.000	72.460
300	12.559	66.261	66.104	0.023	-102.002	-102.002	-102.002	71.999
400	14.159	70.111	66.698	1.366	-102.060	-102.060	-102.060	53.417
500	15.300	73.415	67.719	2.648	-102.093	-102.093	-102.093	42.263
600	16.273	76.303	68.914	4.433	-102.114	-102.114	-102.114	34.829
700	17.041	78.664	70.156	6.096	-102.130	-102.130	-102.130	29.511
800	17.633	81.161	71.390	7.616	-102.143	-102.143	-102.143	25.826
900	18.050	83.200	72.552	9.582	-102.155	-102.155	-102.155	22.825
1000	18.163	85.138	73.754	11.584	-102.162	-102.162	-102.162	19.945
1100	18.413	86.691	74.869	13.213	-102.171	-102.171	-102.171	17.915
1200	18.613	88.492	75.936	15.065	-102.177	-102.177	-102.177	16.223
1300	18.777	89.969	76.962	16.934	-102.186	-102.186	-102.186	14.792
1400	18.912	91.395	77.943	18.619	-102.194	-102.194	-102.194	13.565
1500	19.024	92.694	78.863	20.716	-102.210	-102.210	-102.210	12.501
1600	19.118	93.925	79.785	22.623	-102.223	-102.223	-102.223	11.570
1700	19.198	95.056	80.651	24.539	-102.234	-102.234	-102.234	10.749
1800	19.266	96.165	81.464	26.462	-102.246	-102.246	-102.246	10.019
1900	19.324	97.229	82.266	28.392	-102.253	-102.253	-102.253	9.365
2000	19.374	98.221	83.056	30.327	-102.259	-102.259	-102.259	8.777
2100	19.418	99.168	83.803	32.267	-102.317	-102.317	-102.317	8.245
2200	19.457	100.072	84.522	34.210	-102.346	-102.346	-102.346	7.761
2300	19.491	100.937	85.217	36.158	-102.376	-102.376	-102.376	7.319
2400	19.521	101.768	85.869	38.108	-102.411	-102.411	-102.411	6.913
2500	19.547	102.565	86.540	40.062	-102.450	-102.450	-102.450	6.540
2600	19.571	103.332	87.172	42.018	-102.492	-102.492	-102.492	6.199
2700	19.592	104.071	87.764	43.976	-102.539	-102.539	-102.539	5.877
2800	19.611	104.784	88.378	45.936	-102.586	-102.586	-102.586	5.560
2900	19.628	105.473	88.956	47.896	-102.643	-102.643	-102.643	5.264
3000	19.644	106.136	89.516	49.856	-102.702	-102.702	-102.702	4.986
3100	19.658	106.783	90.064	51.827	-102.764	-102.764	-102.764	4.804
3200	19.671	107.407	90.597	53.793	-102.831	-102.831	-102.831	4.578
3300	19.683	108.012	91.115	55.761	-102.903	-102.903	-102.903	4.365
3400	19.694	108.600	91.621	57.730	-102.978	-102.978	-102.978	4.165
3500	19.704	109.171	92.114	59.700	-103.056	-103.056	-103.056	3.976
3600	19.713	109.726	92.596	61.671	-103.141	-103.141	-103.141	3.797
3700	19.721	110.267	93.066	63.642	-103.230	-103.230	-103.230	3.627
3800	19.729	110.793	93.526	65.615	-103.322	-103.322	-103.322	3.467
3900	19.736	111.305	93.975	67.588	-103.419	-103.419	-103.419	3.314
4000	19.743	111.805	94.415	69.562	-103.519	-103.519	-103.519	3.169
4100	19.749	112.293	94.845	71.536	-103.624	-103.624	-103.624	3.032
4200	19.755	112.769	95.266	73.512	-103.733	-103.733	-103.733	2.900
4300	19.760	113.233	95.678	75.487	-103.847	-103.847	-103.847	2.774
4400	19.765	113.686	96.082	77.464	-103.965	-103.965	-103.965	2.654
4500	19.770	114.132	96.479	79.440	-104.087	-104.087	-104.087	2.540
4600	19.774	114.567	96.867	81.417	-104.213	-104.213	-104.213	2.429
4700	19.778	114.992	97.248	83.395	-104.342	-104.342	-104.342	2.324
4800	19.782	115.408	97.622	85.373	-104.477	-104.477	-104.477	2.223
4900	19.786	115.816	97.989	87.351	-104.615	-104.615	-104.615	2.126
5000	19.789	116.216	98.330	89.330	-104.757	-104.757	-104.757	2.032
5100	19.792	116.606	98.704	91.309	-104.905	-104.905	-104.905	1.943
5200	19.795	116.992	99.052	93.289	-105.055	-105.055	-105.055	1.856
5300	19.798	117.369	99.394	95.268	-105.209	-105.209	-105.209	1.773
5400	19.801	117.739	99.730	97.248	-105.366	-105.366	-105.366	1.692
5500	19.803	118.103	100.061	99.228	-105.531	-105.531	-105.531	1.615
5600	19.806	118.460	100.387	101.209	-105.699	-105.699	-105.699	1.540
5700	19.808	118.810	100.707	103.190	-105.870	-105.870	-105.870	1.467
5800	19.810	119.155	101.022	105.171	-106.046	-106.046	-106.046	1.397
5900	19.812	119.493	101.332	107.152	-106.225	-106.225	-106.225	1.329
6000	19.814	119.826	101.638	109.133	-106.408	-106.408	-106.408	1.264

June 30, 1961

Moments of inertia: $I_A = [7.480 \times 10^{-59}] \text{ g cm}^2$ $I_B = [16.008 \times 10^{-59}] \text{ g cm}^2$ $I_C = [23.31 \times 10^{-59}] \text{ g cm}^2$
 $\sigma = 1$

Heat of Formation

The heats of formation of COCl₂ and COF₂ have been averaged to obtain that of COClF.

Heat Capacity and Entropy

The molecular constants are from R. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys. 22, 1953 (1954).

(IDEAL GAS)

CHLOROTRIFLUOROMETHANE (CClF₃)

GFW = 104.45935

Point Group C_{3v} $\Delta H_f^\circ = -168.0 \pm 0.8$ kcal/mol $S_{298.15}^\circ = 68.174 \pm 0.1$ gibbs/mol $\Delta H_f^\circ = -169.2 \pm 0.8$ kcal/mol

Ground State Quantum Weight = 1

Chlorotrifluoromethane (CClF₃)
(Ideal Gas) GFW = 104.45935

T, °K	C _p ^o	S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	3.294	-167.980	-167.980	INFINITE	
100	8.799	55.209	60.045	-166.578	-166.578	362.164	
200	12.679	62.465	69.536	-165.966	-165.966	177.753	
300	15.986	66.174	76.567	-165.200	-165.200	116.924	
400	16.040	68.273	81.724	-164.904	-164.904	116.159	
500	18.531	73.247	88.335	-163.184	-163.184	66.836	
600	21.590	81.400	95.432	-161.695	-161.695	34.504	
700	24.498	88.810	103.263	-160.483	-160.483	13.491	
800	27.159	95.617	111.878	-159.408	-159.408	3.907	
900	29.500	101.925	120.263	-158.459	-158.459	0.889	
1000	31.582	107.328	128.426	-157.682	-157.682	0.266	
1100	33.387	111.965	136.390	-157.022	-157.022	0.089	
1200	34.925	115.874	144.194	-156.554	-156.554	0.034	
1300	36.239	119.076	151.878	-156.336	-156.336	0.019	
1400	37.316	121.503	158.590	-156.308	-156.308	0.011	
1500	38.108	123.140	164.366	-156.437	-156.437	0.007	
1600	38.670	124.011	169.246	-156.683	-156.683	0.004	
1700	39.050	124.165	173.273	-157.006	-157.006	0.003	
1800	39.282	124.505	176.519	-157.396	-157.396	0.002	
1900	39.398	124.924	179.944	-157.844	-157.844	0.001	
2000	39.400	125.410	183.524	-158.344	-158.344	0.000	
2100	39.380	125.950	187.244	-158.884	-158.884	0.000	
2200	39.339	126.540	191.094	-159.464	-159.464	0.000	
2300	39.269	127.170	195.064	-160.084	-160.084	0.000	
2400	39.170	127.830	199.144	-160.744	-160.744	0.000	
2500	39.044	128.520	203.334	-161.444	-161.444	0.000	
2600	38.884	129.230	207.634	-162.184	-162.184	0.000	
2700	38.690	129.960	212.044	-162.964	-162.964	0.000	
2800	38.464	130.710	216.564	-163.784	-163.784	0.000	
2900	38.208	131.480	221.194	-164.644	-164.644	0.000	
3000	37.924	132.260	225.924	-165.544	-165.544	0.000	
3100	37.610	133.050	230.754	-166.484	-166.484	0.000	
3200	37.270	133.850	235.684	-167.464	-167.464	0.000	
3300	36.904	134.660	240.714	-168.484	-168.484	0.000	
3400	36.514	135.480	245.844	-169.544	-169.544	0.000	
3500	36.094	136.310	251.074	-170.644	-170.644	0.000	
3600	35.644	137.150	256.404	-171.784	-171.784	0.000	
3700	35.164	138.000	261.834	-172.964	-172.964	0.000	
3800	34.654	138.860	267.364	-174.184	-174.184	0.000	
3900	34.114	139.730	272.994	-175.444	-175.444	0.000	
4000	33.544	140.610	278.724	-176.744	-176.744	0.000	
4100	32.944	141.500	284.554	-178.084	-178.084	0.000	
4200	32.314	142.400	290.484	-179.464	-179.464	0.000	
4300	31.654	143.310	296.514	-180.884	-180.884	0.000	
4400	30.964	144.230	302.644	-182.344	-182.344	0.000	
4500	30.244	145.160	308.874	-183.844	-183.844	0.000	
4600	29.494	146.100	315.204	-185.384	-185.384	0.000	
4700	28.714	147.050	321.634	-186.964	-186.964	0.000	
4800	27.904	148.010	328.164	-188.584	-188.584	0.000	
4900	27.064	148.980	334.794	-190.244	-190.244	0.000	
5000	26.194	149.960	341.524	-191.944	-191.944	0.000	
5100	25.294	150.950	348.354	-193.684	-193.684	0.000	
5200	24.364	151.950	355.284	-195.464	-195.464	0.000	
5300	23.404	152.960	362.314	-197.284	-197.284	0.000	
5400	22.414	153.980	369.444	-199.144	-199.144	0.000	
5500	21.394	155.010	376.674	-201.044	-201.044	0.000	
5600	20.344	156.050	384.004	-202.984	-202.984	0.000	
5700	19.264	157.100	391.534	-204.964	-204.964	0.000	
5800	18.154	158.160	399.264	-206.984	-206.984	0.000	
5900	17.014	159.230	407.094	-209.044	-209.044	0.000	
6000	15.844	160.310	415.024	-211.144	-211.144	0.000	

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1966

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
1106 (1)	1217 (2)
782 (1)	560 (2)
474 (1)	350 (2)

Bond Distance: C-F = 1.328 Å C-Cl = 1.751 Å

Bond Angle: F-C-F = 108.6 ± 0.5° F-C-Cl = 110.33° σ = 3

Product of the Moments of Inertia: I_AI_BI_C = 9.4425 × 10⁻¹¹⁴ g³ cm⁶

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₄. Details of the input data and the adjustment are given in (1). Coomber and Whittle (2) have determined equilibrium data for CClF₃(g) + BrX(g) = CBrF₃(g) + ClX(g) where X = Cl and Br. Lord et al. (3) studied the analogous equilibria CF₃I(g) + ClI(g) = CClF₃(g) + I₂(g). These data link CClF₃ with CBrF₃ and CF₃I.

Other data which were omitted from the adjustment include those of Baibuz (4, 5), Meers (6), Kolesov (7), Kimbriide (8), and von Wartenberg (9). Baibuz (4, 5) derived ΔH° = -166.2 ± 2.2 kcal/mol by applying the method of estimate in a spherical bomb to mixtures of H₂, O₂ and CClF₃. By comparison with similar data for CF₄ and CCl₄, we estimate the Baibuz' value to be about +2 kcal/mol. Meers (6) gave a preliminary report of values of ΔH° at 300°C for reactions involving HF, HCl and CCl₃F_n (n = 1, 2, 3, 4). We derive ΔH° = -172 and -173 kcal/mol from two different combinations of reactions; however, no detailed account of the data has been published. The other authors (7, 8, 9) measured ΔH° for reaction of CClF₃ with an alkali metal (Na or K) to form amorphous carbon and mixtures of the fluoride and chloride. Discrepancies of many kcal/mol exist in these studies, presumably due to inadequate characterization of the thermochemical reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen (10) and Bartell (11). Results from Bartell are adopted. These parameters are consistent with the microwave data of Coles (12). Principal moments of inertia are I_A = 14.58 × 10⁻³⁹ and I_B = I_C = 25.37 × 10⁻³⁹ g cm². Vibrational assignments are based on the work of Claassen (13) and the gas-phase Raman spectra observed by Holzer and Moser (14).

The largest uncertainty in Cp° and S° probably results from the neglect of anharmonicity. Baibuz (15) and Albright (16) have given estimates for the anharmonic contributions. These vary from 0.1 to 0.3 gibbs/mol in both Cp° and S° over the range from 300 to 1000°K, respectively. Somewhat larger contributions are possible based on the anharmonic functions calculated by McBride (17) for CF₄(g). We estimate the overall uncertainty in the entropy of this JANAF table to be 0.1 eu at 300°K and 0.4 eu at 1000°K. Cp° is consistent with Cv° measured at 300°K by the wire-ribbon method (18).

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFPL Contract Nr. F04611-67-C-0009, Dow Chemical Co., J. W. Coomber and E. Whittle, Trans. Faraday Soc. 63, 2656 (1967).
2. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 63, 2656 (1967).
3. A. Lord, C. A. Goy and H. O. Pritchard, J. Phys. Chem. 71, 2705 (1967).
4. V. F. Baibuz, Dokl. Akad. Nauk SSSR 140 (6), 1388 (1961); English translation, 786 (1961).
5. V. F. Baibuz and V. A. Medvedev, Tr. Gos. Inst. Prikl. Khim. No. 43, 84 (1962).
6. W. H. Meers and R. F. Stahl, I.U.P.A.C. Thermochemical Bulletin 2, 5 (1956).
7. V. P. Kolesov, I. D. Zenkov and S. M. Skuratov, Russ. J. Phys. Chem. (English Translation) 36 (9), 1120 (1962); 37 (3), 378 (1963).
8. F. W. Kirkbride and F. G. Davidson, Nature 174, 79 (1954).
9. H. von Wartenberg and J. Schiefer, Z. Anorg. Allg. Chem. 278, 326 (1955).
10. H. J. M. Bowen, Trans. Faraday Soc. 50, 444 (1954).
11. L. S. Bartell and L. O. Brockway, J. Chem. Phys. 23, 1860 (1955).
12. D. K. Coles and R. H. Hughes, Phys. Rev. 75, 858 (1949); recalculated by J. Sheridan and W. Gordy, J. Chem. Phys. 20, 591 (1952).
13. H. H. Claassen, J. Chem. Phys. 22, 50 (1954).
14. W. Holzer and H. Moser, J. Mol. Spectrosc. 20, 188 (1966).
15. W. Baibuz, Kältetechnik 17, 219 (1965).
16. L. Albright, W. C. Callegar and K. K. Innes, J. Am. Chem. Soc. 76, 8017 (1954).
17. B. J. McBride, S. Heimes, J. G. Ehlers and S. Gordon, NASA SP-3001, 156 (1963).
18. W. N. Vanderkooi and T. DeVries, J. Phys. Chem. 50, 636 (1956).

(Ideal Gas) GFW = 61.47085

CYANOGEN CHLORIDE (ClCN)

(IDEAL GAS)

QFW = 61.47085

T, °K	Cp	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	0.000	INFINITE	-	2.584	32.801	INFINITE
100	7.468	46.084	-	32.797	32.325	-70.646
200	10.860	52.389	-	32.858	31.838	-34.794
298	12.850	56.459	-	32.970	31.309	-22.950
300	10.838	56.426	+0.20	32.972	31.299	-22.901
400	11.644	58.760	56.695	33.069	30.723	-16.786
500	12.195	62.420	7.742	33.185	30.120	-13.166
600	12.637	66.483	58.719	33.258	29.500	-10.765
700	12.991	68.657	68.711	33.311	28.869	-9.013
800	13.302	68.613	60.691	33.353	28.232	-7.712
900	13.571	68.095	61.638	33.385	27.589	-6.700
1000	13.802	71.437	68.860	33.414	26.943	-5.868
1100	13.983	72.761	63.616	33.438	26.294	-5.324
1200	14.150	73.985	64.247	33.458	25.645	-4.871
1300	14.304	75.124	65.040	33.475	24.992	-4.202
1400	14.444	76.189	65.799	33.494	24.341	-3.800
1500	14.570	77.190	66.525	33.514	23.686	-3.451
1600	14.687	78.134	67.222	33.534	23.038	-3.145
1700	14.797	79.026	67.890	33.555	22.371	-2.876
1800	14.843	79.872	68.532	33.576	21.712	-2.636
1900	14.923	80.676	69.151	33.600	21.056	-2.422
2000	14.997	81.444	69.746	33.624	20.393	-2.228
2100	15.060	82.177	70.321	33.652	19.732	-2.054
2200	15.120	82.879	70.876	33.678	19.066	-1.894
2300	15.178	83.552	71.412	33.707	18.405	-1.749
2400	15.233	84.199	71.932	33.736	17.739	-1.615
2500	15.285	84.822	72.435	33.766	17.070	-1.492
2600	15.332	85.423	72.923	33.797	16.401	-1.379
2700	15.378	86.002	73.397	33.829	15.731	-1.273
2800	15.423	86.562	73.857	33.862	15.062	-1.176
2900	15.466	87.104	74.305	33.895	14.390	-1.084
3000	15.508	87.629	74.740	33.929	13.716	-0.999
3100	15.547	88.138	75.164	33.963	13.043	-0.919
3200	15.586	88.633	75.577	33.997	12.365	-0.845
3300	15.624	89.113	75.980	34.030	11.687	-0.774
3400	15.661	89.580	76.373	34.064	11.012	-0.708
3500	15.698	90.034	76.757	34.098	10.331	-0.645
3600	15.733	90.477	77.132	34.132	9.652	-0.586
3700	15.768	90.909	77.499	34.166	8.971	-0.530
3800	15.802	91.329	77.857	34.201	8.294	-0.477
3900	15.836	91.740	78.208	34.235	7.614	-0.427
4000	15.870	92.142	78.551	34.269	6.937	-0.376
4100	15.902	92.534	78.887	34.304	6.261	-0.333
4200	15.935	92.918	79.217	34.338	5.587	-0.289
4300	15.967	93.293	79.540	34.372	4.912	-0.248
4400	15.998	93.660	79.857	34.407	4.188	-0.208
4500	16.030	94.020	80.167	34.441	3.467	-0.170
4600	16.061	94.373	80.472	34.477	2.611	-0.134
4700	16.093	94.719	80.772	34.513	2.121	-0.099
4800	16.124	95.058	81.066	34.548	1.433	-0.065
4900	16.154	95.391	81.355	34.584	0.740	-0.033
5000	16.185	95.717	81.639	34.621	0.054	-0.002
5100	16.215	96.038	81.918	34.658	-0.644	-0.028
5200	16.246	96.353	82.193	34.696	-1.332	-0.056
5300	16.276	96.663	82.463	34.734	-2.027	-0.084
5400	16.305	96.967	82.729	34.772	-2.717	-0.110
5500	16.335	97.267	82.990	34.810	-3.413	-0.136
5600	16.364	97.562	83.248	34.849	-4.113	-0.161
5700	16.394	97.851	83.501	34.888	-4.807	-0.184
5800	16.423	98.137	83.751	34.927	-5.505	-0.207
5900	16.451	98.418	83.998	34.966	-6.201	-0.230
6000	16.480	98.694	84.240	35.006	-6.898	-0.251

Dec. 31, 1960; June 30, 1961; June 30, 1962

Point Group C_{∞v}S_{298.15} = 56.459 gibbs/mol

Ground State Quantum Weight = 1

 $\Delta H^\circ_0 = 32.8 \text{ kcal/mol}$ $\Delta H^\circ_{298.15} = 32.97 \text{ kcal/mol}$

Vibrational Frequencies and Degeneracies

 $\omega_1 \text{ cm}^{-1}$

714.52 (1)

378.3 (2)

2215.5 (1)

C-N = 1.162 Å

C-Cl = 1.631 Å

Cl-C-N = 180°

Cl-C-Cl = 180°

D₀ = 5.503 X 10⁻⁸ cm⁻¹C₁ = 1Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm⁻¹),C₁ = 8.25 X 10⁻⁴C₂ = -5.46 X 10⁻⁴C₃ = 1.06 X 10⁻³C₄ = [-4]C₅ = [-7]C₆ = [-6.8]C₇ = -0.65C₈ = -7.236C₉ = -2.8C₁₀ = 0.95C₁₁ = [-4]C₁₂ = [-6.8]C₁₃ = -2.8C₁₄ = 0.95C₁₅ = -7.236C₁₆ = -2.8C₁₇ = 0.95C₁₈ = [-4]C₁₉ = [-6.8]C₂₀ = -2.8C₂₁ = 0.95C₂₂ = [-4]C₂₃ = [-6.8]C₂₄ = -2.8C₂₅ = 0.95C₂₆ = [-4]C₂₇ = [-6.8]C₂₈ = -2.8C₂₉ = 0.95C₃₀ = [-4]C₃₁ = [-6.8]C₃₂ = -2.8C₃₃ = 0.95C₃₄ = [-4]C₃₅ = [-6.8]C₃₆ = -2.8C₃₇ = 0.95C₃₈ = [-4]C₃₉ = [-6.8]C₄₀ = -2.8C₄₁ = 0.95C₄₂ = [-4]C₄₃ = [-6.8]C₄₄ = -2.8C₄₅ = 0.95C₄₆ = [-4]C₄₇ = [-6.8]C₄₈ = -2.8C₄₉ = 0.95C₅₀ = [-4]

Heat of Formation.

The heat of formation was taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties" NES Technical Note 270-1, Washington, 1965.

Heat Capacity and Entropy.

J. S. Gordon, AstroSystems International Inc., Fairfield, N. J., (private communication, Feb., 1966), has used the constants listed above to calculate C from 298.15 to 6000°K using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants B₀ and D₀ were taken from C. A. Burrus and W. Gordy, Phys. Rev. 101, 599 (1956); ω₁, ω₂, ω₃, ω₄, ω₅, ω₆, ω₇, ω₈, ω₉, ω₁₀, ω₁₁, ω₁₂, ω₁₃, ω₁₄, ω₁₅, ω₁₆, ω₁₇, ω₁₈, ω₁₉, ω₂₀, ω₂₁, ω₂₂, ω₂₃, ω₂₄, ω₂₅, ω₂₆, ω₂₇, ω₂₈, ω₂₉, ω₃₀, ω₃₁, ω₃₂, ω₃₃, ω₃₄, ω₃₅, ω₃₆, ω₃₇, ω₃₈, ω₃₉, ω₄₀, ω₄₁, ω₄₂, ω₄₃, ω₄₄, ω₄₅, ω₄₆, ω₄₇, ω₄₈, ω₄₉, ω₅₀, ω₅₁, ω₅₂, ω₅₃, ω₅₄, ω₅₅, ω₅₆, ω₅₇, ω₅₈, ω₅₉, ω₆₀, ω₆₁, ω₆₂, ω₆₃, ω₆₄, ω₆₅, ω₆₆, ω₆₇, ω₆₈, ω₆₉, ω₇₀, ω₇₁, ω₇₂, ω₇₃, ω₇₄, ω₇₅, ω₇₆, ω₇₇, ω₇₈, ω₇₉, ω₈₀, ω₈₁, ω₈₂, ω₈₃, ω₈₄, ω₈₅, ω₈₆, ω₈₇, ω₈₈, ω₈₉, ω₉₀, ω₉₁, ω₉₂, ω₉₃, ω₉₄, ω₉₅, ω₉₆, ω₉₇, ω₉₈, ω₉₉, ω₁₀₀, ω₁₀₁, ω₁₀₂, ω₁₀₃, ω₁₀₄, ω₁₀₅, ω₁₀₆, ω₁₀₇, ω₁₀₈, ω₁₀₉, ω₁₁₀, ω₁₁₁, ω₁₁₂, ω₁₁₃, ω₁₁₄, ω₁₁₅, ω₁₁₆, ω₁₁₇, ω₁₁₈, ω₁₁₉, ω₁₂₀, ω₁₂₁, ω₁₂₂, ω₁₂₃, ω₁₂₄, ω₁₂₅, ω₁₂₆, ω₁₂₇, ω₁₂₈, ω₁₂₉, ω₁₃₀, ω₁₃₁, ω₁₃₂, ω₁₃₃, ω₁₃₄, ω₁₃₅, ω₁₃₆, ω₁₃₇, ω₁₃₈, ω₁₃₉, ω₁₄₀, ω₁₄₁, ω₁₄₂, ω₁₄₃, ω₁₄₄, ω₁₄₅, ω₁₄₆, ω₁₄₇, ω₁₄₈, ω₁₄₉, ω₁₅₀, ω₁₅₁, ω₁₅₂, ω₁₅₃, ω₁₅₄, ω₁₅₅, ω₁₅₆, ω₁₅₇, ω₁₅₈, ω₁₅₉, ω₁₆₀, ω₁₆₁, ω₁₆₂, ω₁₆₃, ω₁₆₄, ω₁₆₅, ω₁₆₆, ω₁₆₇, ω₁₆₈, ω₁₆₉, ω₁₇₀, ω₁₇₁, ω₁₇₂, ω₁₇₃, ω₁₇₄, ω₁₇₅, ω₁₇₆, ω₁₇₇, ω₁₇₈, ω₁₇₉, ω₁₈₀, ω₁₈₁, ω₁₈₂, ω₁₈₃, ω₁₈₄, ω₁₈₅, ω₁₈₆, ω₁₈₇, ω₁₈₈, ω₁₈₉, ω₁₉₀, ω₁₉₁, ω₁₉₂, ω₁₉₃, ω₁₉₄, ω₁₉₅, ω₁₉₆, ω₁₉₇, ω₁₉₈, ω₁₉₉, ω₂₀₀, ω₂₀₁, ω₂₀₂, ω₂₀₃, ω₂₀₄, ω₂₀₅, ω₂₀₆, ω₂₀₇, ω₂₀₈, ω₂₀₉, ω₂₁₀, ω₂₁₁, ω₂₁₂, ω₂₁₃, ω₂₁₄, ω₂₁₅, ω₂₁₆, ω₂₁₇, ω₂₁₈, ω₂₁₉, ω₂₂₀, ω₂₂₁, ω₂₂₂, ω₂₂₃, ω₂₂₄, ω₂₂₅, ω₂₂₆, ω₂₂₇, ω₂₂₈, ω₂₂₉, ω₂₃₀, ω₂₃₁, ω₂₃₂, ω₂₃₃, ω₂₃₄, ω₂₃₅, ω₂₃₆, ω₂₃₇, ω₂₃₈, ω₂₃₉, ω₂₄₀, ω₂₄₁, ω₂₄₂, ω₂₄₃, ω₂₄₄, ω₂₄₅, ω₂₄₆, ω₂₄₇, ω₂₄₈, ω₂₄₉, ω₂₅₀, ω₂₅₁, ω₂₅₂, ω₂₅₃, ω₂₅₄, ω₂₅₅, ω₂₅₆, ω₂₅₇, ω₂₅₈, ω₂₅₉, ω₂₆₀, ω₂₆₁, ω₂₆₂, ω₂₆₃, ω₂₆₄, ω₂₆₅, ω₂₆₆, ω₂₆₇, ω₂₆₈, ω₂₆₉, ω₂₇₀, ω₂₇₁, ω₂₇₂, ω₂₇₃, ω₂₇₄, ω₂₇₅, ω₂₇₆, ω₂₇₇, ω₂₇₈, ω₂₇₉, ω₂₈₀, ω₂₈₁, ω₂₈₂, ω₂₈₃, ω₂₈₄, ω₂₈₅, ω₂₈₆, ω₂₈₇, ω₂₈₈, ω₂₈₉, ω₂₉₀, ω₂₉₁, ω₂₉₂, ω₂₉₃, ω₂₉₄, ω₂₉₅, ω₂₉₆, ω₂₉₇, ω₂₉₈, ω₂₉₉, ω₃₀₀, ω₃₀₁, ω₃₀₂, ω₃₀₃, ω₃₀₄, ω₃₀₅, ω₃₀₆, ω₃₀₇, ω₃₀₈, ω₃₀₉, ω₃₁₀, ω₃₁₁, ω₃₁₂, ω₃₁₃, ω₃₁₄, ω₃₁₅, ω₃₁₆, ω₃₁₇, ω₃₁₈, ω₃₁₉, ω₃₂₀, ω₃₂₁, ω₃₂₂, ω₃₂₃, ω₃₂₄, ω₃₂₅, ω₃₂₆, ω₃₂₇, ω₃₂₈, ω₃₂₉, ω₃₃₀, ω₃₃₁, ω₃₃₂, ω₃₃₃, ω₃₃₄, ω₃₃₅, ω₃₃₆, ω₃₃₇, ω₃₃₈, ω₃₃₉, ω₃₄₀, ω₃₄₁, ω₃₄₂, ω₃₄₃, ω₃₄₄, ω₃₄₅, ω₃₄₆, ω₃₄₇, ω₃₄₈, ω₃₄₉, ω₃₅₀, ω₃₅₁, ω₃₅₂, ω₃₅₃, ω₃₅₄, ω₃₅₅, ω₃₅₆, ω₃₅₇, ω₃₅₈, ω₃₅₉, ω₃₆₀, ω₃₆₁, ω₃₆₂, ω₃₆₃, ω₃₆₄, ω₃₆₅, ω₃₆₆, ω₃₆₇, ω₃₆₈, ω₃₆₉, ω₃₇₀, ω₃₇₁, ω₃₇₂, ω₃₇₃, ω₃₇₄, ω₃₇₅, ω₃₇₆, ω₃₇₇, ω₃₇₈, ω₃₇₉, ω₃₈₀, ω₃₈₁, ω₃₈₂, ω₃₈₃, ω₃₈₄, ω₃₈₅, ω₃₈₆, ω₃₈₇, ω₃₈₈, ω

Carbonyl Monochloride (COCl₂)

(Ideal Gas) Mol. Wt. = 63.46355

CC10

CARBONYL MONOCHLORIDE (COCl₂) (IDEAL GAS) MOL. WT. = 63.46355

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _f
0	8.000	0.000	INFINITE	2.361	15.374	15.374	INFINITE
100	9.000	59.401	64.505	1.021	15.134	15.134	18.628
200	9.951	64.505	64.505	0.000	15.000	15.000	18.628
298	10.773	63.542	63.542				13.467
300	10.784	63.609	63.593	1.020	14.998	14.998	13.339
400	11.267	69.331	69.331	2.275	14.809	14.809	10.616
500	11.690	73.512	73.512	3.462	14.674	14.674	8.989
600	12.022	77.387	77.387	4.578	14.510	14.510	7.906
700	12.294	80.864	80.864	5.521	14.396	14.396	7.131
800	12.514	83.320	83.320	6.286	14.296	14.296	6.548
900	12.682	84.951	84.951	6.851	14.208	14.208	6.093
1000	12.806	86.000	86.000	7.245	14.126	14.126	5.727
1100	13.041	87.245	87.245	7.466	14.057	14.057	5.426
1200	13.152	88.409	88.409	7.593	14.000	14.000	5.173
1300	13.245	89.498	89.498	7.646	13.954	13.954	4.957
1400	13.326	90.538	90.538	7.691	13.916	13.916	4.771
1500	13.399	91.540	91.540	7.729	13.884	13.884	4.609
1600	13.465	92.500	92.500	7.761	13.857	13.857	4.466
1700	13.523	93.426	93.426	7.788	13.834	13.834	4.339
1800	13.573	94.320	94.320	7.810	13.814	13.814	4.225
1900	13.618	95.186	95.186	7.828	13.796	13.796	4.122
2000	13.659	96.026	96.026	7.843	13.780	13.780	4.028
2100	13.696	96.843	96.843	7.856	13.766	13.766	3.943
2200	13.729	97.636	97.636	7.867	13.753	13.753	3.865
2300	13.758	98.406	98.406	7.875	13.741	13.741	3.793
2400	13.783	99.154	99.154	7.881	13.730	13.730	3.727
2500	13.805	99.882	99.882	7.885	13.720	13.720	3.665
2600	13.824	100.590	100.590	7.888	13.711	13.711	3.608
2700	13.840	101.282	101.282	7.890	13.703	13.703	3.554
2800	13.853	101.958	101.958	7.891	13.696	13.696	3.504
2900	13.864	102.618	102.618	7.892	13.690	13.690	3.456
3000	13.873	103.264	103.264	7.893	13.685	13.685	3.412
3100	13.880	103.897	103.897	7.894	13.681	13.681	3.370
3200	13.885	104.518	104.518	7.895	13.678	13.678	3.330
3300	13.889	105.126	105.126	7.896	13.675	13.675	3.292
3400	13.892	105.722	105.722	7.897	13.673	13.673	3.256
3500	13.895	106.306	106.306	7.898	13.671	13.671	3.222
3600	13.898	106.878	106.878	7.899	13.669	13.669	3.189
3700	13.900	107.438	107.438	7.900	13.667	13.667	3.158
3800	13.902	107.986	107.986	7.901	13.665	13.665	3.128
3900	13.904	108.522	108.522	7.902	13.663	13.663	3.099
4000	13.906	109.046	109.046	7.903	13.661	13.661	3.071
4100	13.908	109.558	109.558	7.904	13.659	13.659	3.045
4200	13.910	110.059	110.059	7.905	13.657	13.657	3.019
4300	13.912	110.550	110.550	7.906	13.655	13.655	2.995
4400	13.914	111.031	111.031	7.907	13.653	13.653	2.971
4500	13.916	111.502	111.502	7.908	13.651	13.651	2.948
4600	13.918	111.963	111.963	7.909	13.649	13.649	2.926
4700	13.920	112.415	112.415	7.910	13.647	13.647	2.904
4800	13.922	112.858	112.858	7.911	13.645	13.645	2.883
4900	13.924	113.292	113.292	7.912	13.643	13.643	2.863
5000	13.926	113.717	113.717	7.913	13.641	13.641	2.843
5100	13.928	114.133	114.133	7.914	13.639	13.639	2.825
5200	13.930	114.540	114.540	7.915	13.637	13.637	2.806
5300	13.932	114.938	114.938	7.916	13.635	13.635	2.788
5400	13.934	115.327	115.327	7.917	13.633	13.633	2.770
5500	13.936	115.707	115.707	7.918	13.631	13.631	2.753
5600	13.938	116.078	116.078	7.919	13.629	13.629	2.736
5700	13.940	116.440	116.440	7.920	13.627	13.627	2.720
5800	13.942	116.793	116.793	7.921	13.625	13.625	2.704
5900	13.944	117.138	117.138	7.922	13.623	13.623	2.688
6000	13.946	117.474	117.474	7.923	13.621	13.621	2.673

Dec. 31, 1965

Point Group C_{2v}

S_{298.15} = [64] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 2

ΔH_f⁰ = [-15 ± 10] kcal. mole⁻¹

ΔH_f⁰ 298.15 = [-15 ± 10] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

(ω, cm.⁻¹)

570 (1)

281 (1)

1880 (1)

C-Cl = [1.78] Å

C-Cl-C = [120] °

Product of the Moments of Inertia: I_AI_BI_C = [1.27603 × 10⁻¹¹⁵] g.³ cm.⁶

Heat of Formation.

The enthalpy change (ΔH_f⁰) for the reaction COCl₂(g) = CO(g) + 2Cl(g) is calculated to be 82 kcal. mole⁻¹, which is the sum of two bond energies, i.e. D(Cl-COCl) + D(Cl-CO). By comparison with the values, D(H₃C-COCH₃)/D(H₃C-CO) = 72/18 = 4.0 for CH₃COC(CH₃)₂ and D(H₃C-COCl)/D(Cl-CO) = 4.3 for CH₃COCl(g), the ratio of D(Cl-COCl)/D(Cl-CO) is estimated to be 4.0 for COCl₂(g). Hence the enthalpy change for the reaction COCl₂(g) = COCl(g) + Cl(g) is calculated as 82 × (4/5) = 65.6 kcal. mole⁻¹. Using the ΔH_f⁰ value obtained, the heat of formation for COCl(g) is derived to be -15 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational frequencies were reported by M. E. Jécox and D. E. Milligan, J. Chem. Phys. 43, 886 (1965). The bond distances and angle were estimated by Jécox and Milligan, loc. cit. Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I_A = 1.29887 × 10⁻³⁶, I_B = 7.1580 × 10⁻⁴⁰, and I_C = 1.37145 × 10⁻³⁸ g. cm.²

CC10

CARBON DICHLORIDE (CCl₂)

(IDEAL GAS)

GFW = 82.91715

Point Group C_{2v}

$\Delta H_f^\circ = 56.7 \pm 5 \text{ kcal/mol}$

$S_{298.15}^\circ = 63.4 \pm 0.5 \text{ gibbs/mol}$

$\Delta H_f^\circ_{298.15} = 57.0 \pm 5 \text{ kcal/mol}$

Ground State Quantum Weight = 1

Carbon Dichloride (CCl₂)

(Ideal Gas)

GFW = 82.91715

T, °K	C _p ^a	S ^b - (C ^a - H ²⁹⁸⁰)/T	H ^c - H ²⁹⁸⁰	ΔH ^f	Log K _p
0	6.900	INFINITE	- 2.1722	56.724	INFINITE
100	8.292	53.066	72.287	56.816	- 122.482
200	9.720	59.250	84.363	56.856	- 122.482
298	11.054	63.392	90.000	56.895	- 122.482
300	11.075	63.461	90.200	56.900	- 122.482
400	11.984	66.781	101.777	57.001	- 122.482
500	12.559	68.522	110.406	57.139	- 122.482
600	12.949	71.068	116.710	57.169	- 122.482
700	13.259	73.668	121.734	57.176	- 122.482
800	13.466	75.657	125.674	57.172	- 122.482
900	13.635	77.269	128.711	57.164	- 122.482
1000	13.772	78.641	130.910	57.162	- 122.482
1100	13.878	80.003	132.331	57.170	- 122.482
1200	13.953	81.371	133.882	57.181	- 122.482
1300	14.005	82.745	135.557	57.191	- 122.482
1400	14.045	84.125	137.347	57.204	- 122.482
1500	14.075	85.509	139.251	57.222	- 122.482
1600	14.105	86.889	141.275	57.245	- 122.482
1700	14.135	88.265	143.419	57.273	- 122.482
1800	14.165	89.637	145.683	57.306	- 122.482
1900	14.195	91.005	148.067	57.344	- 122.482
2000	14.225	92.369	150.571	57.387	- 122.482
2100	14.255	93.729	153.205	57.435	- 122.482
2200	14.285	95.085	155.969	57.487	- 122.482
2300	14.315	96.437	158.863	57.544	- 122.482
2400	14.345	97.785	161.887	57.606	- 122.482
2500	14.375	99.129	165.041	57.674	- 122.482
2600	14.405	100.469	168.325	57.747	- 122.482
2700	14.435	101.805	171.739	57.825	- 122.482
2800	14.465	103.137	175.283	57.908	- 122.482
2900	14.495	104.465	178.957	57.996	- 122.482
3000	14.525	105.789	182.761	58.089	- 122.482
3100	14.555	107.109	186.695	58.187	- 122.482
3200	14.585	108.425	190.659	58.290	- 122.482
3300	14.615	109.737	194.753	58.398	- 122.482
3400	14.645	111.045	198.887	58.511	- 122.482
3500	14.675	112.349	203.061	58.629	- 122.482
3600	14.705	113.649	207.275	58.752	- 122.482
3700	14.735	114.945	211.529	58.880	- 122.482
3800	14.765	116.237	215.823	59.013	- 122.482
3900	14.795	117.525	220.157	59.151	- 122.482
4000	14.825	118.809	224.531	59.294	- 122.482
4100	14.855	120.089	228.945	59.442	- 122.482
4200	14.885	121.365	233.399	59.595	- 122.482
4300	14.915	122.637	237.893	59.753	- 122.482
4400	14.945	123.905	242.427	59.916	- 122.482
4500	14.975	125.169	247.001	60.084	- 122.482
4600	15.005	126.429	251.615	60.257	- 122.482
4700	15.035	127.685	256.269	60.435	- 122.482
4800	15.065	128.937	260.963	60.618	- 122.482
4900	15.095	130.185	265.697	60.806	- 122.482
5000	15.125	131.429	270.471	61.000	- 122.482
5100	15.155	132.669	275.285	61.200	- 122.482
5200	15.185	133.905	280.139	61.405	- 122.482
5300	15.215	135.137	285.033	61.616	- 122.482
5400	15.245	136.365	290.000	61.832	- 122.482
5500	15.275	137.589	295.041	62.054	- 122.482
5600	15.305	138.809	300.165	62.282	- 122.482
5700	15.335	140.025	305.371	62.516	- 122.482
5800	15.365	141.237	310.659	62.756	- 122.482
5900	15.395	142.445	316.029	63.002	- 122.482
6000	15.425	143.649	321.483	63.254	- 122.482

Mar. 31, 1965; Dec. 31, 1968

Electronic Levels and Quantum Weights

ϵ_1 , cm ⁻¹	$\frac{g_1}{O}$
0	1
(4000)	(3)
(17500)	(1)

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	$\frac{g_1}{O}$
721 (1)	1
(350)	(1)
748 (1)	1

Bond Distance: C-Cl = [1.76] Å

Bond Angle: Cl-C-Cl = [100 ± 10]°

Product of Moments of Inertia: $I_A I_B I_C = [1.1017] \times 10^{-114} \text{ g}^3 \text{ cm}^6$

Heat of Formation

Shapiro and Jaccoc (2) have measured mass-spectrometrically the appearance potentials 12.2 and 14.7 eV for the processes $\text{CHCl}_3(g) + e^- \rightarrow \text{CCl}_2(g) + \text{HCl}(g) + 2e^-$ and $\text{C}_2\text{Cl}_4(g) + e^- \rightarrow \text{CCl}_2(g) + \text{CCl}_2(g) + 2e^-$, respectively. The difference in these two processes gives $\Delta H_f^\circ = 2.5 \text{ eV}$ (57.65 kcal/mol) for the reaction $\text{C}_2\text{Cl}_4(g) + \text{HCl}(g) \rightarrow \text{CCl}_2(g) + \text{CHCl}_3(g)$ which leads to $\Delta H_f^\circ(\text{CCl}_2, g) = 57.32 \text{ kcal/mol}$, using JANAF $\Delta H_f^\circ(298) = -2.97, -22.063$ and -24.7 kcal/mol for $\text{C}_2\text{Cl}_4(g)$, $\text{HCl}(g)$ and $\text{CHCl}_3(g)$, respectively. Since the authors claimed that the experimental error was probably 5 kcal/mol, the value, 57 ± 5 kcal/mol, is adopted for the heat of formation.

Heat Capacity and Entropy

Milligan and Jaccoc (2) have found two stretching fundamentals (721 and 748 cm⁻¹) for the CCl₂ radical in the infrared and ultraviolet spectra by matrix-isolation, and proposed a bent molecular structure (the valence angle = 100 ± 10°) with a ground singlet state which was based on the analogy with the electronic absorption spectrum of CF₂. L. Andrews (3) has confirmed all these observations in his infrared spectrometric studies of dichlorocarbene in solid argon, and made vibrational assignment to the fundamentals and also eliminated the possibility of a linear molecular structure for CCl₂. The bending frequency (350 cm⁻¹) is estimated by the valence force method (4), using the same ratio of bending over stretching force constants from CF₂(g) (5). The bond distance is estimated to be the same as that of CCl₄(g) measured by Bartell et al. (6). The three principal moments of inertia are $I_A = 2.1828 \times 10^{-39}$, $I_B = 21.4013 \times 10^{-39}$, and $I_C = 23.5840 \times 10^{-39} \text{ g cm}^2$.

The triplet low lying electronic level of 4000 cm⁻¹ is estimated by analogy with that of CF₂(g). The other level of 17,500 cm⁻¹ is also estimated based on a weak band appearing between 4400 and 5600 Å in the spectra of CCl₂ observed by Milligan and Jaccoc (2).

References

- (1) J. S. Shapiro and F. P. Lossing, *J. Phys. Chem.* **72**, 1552 (1968).
- (2) D. E. Milligan and M. E. Jaccoc, *J. Chem. Phys.* **47**, 703 (1967).
- (3) L. Andrews, *J. Chem. Phys.* **48**, 979 (1968).
- (4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co. Inc., New York, 1945.
- (5) JANAF CF₂(g) table dated Sept. 30, 1965.
- (6) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.* **23**, 1854 (1955).

$$\Delta H_f^\circ = -116.5 \pm 2 \text{ kcal/mol}$$

Point Group C_{2v}

$$\Delta H_f^\circ = -117.5 \pm 2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 71.91 \pm 0.05 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Dichlorodifluoromethane (CCl₂F₂)

(Ideal Gas) GFW = 120.9140

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	9.473	57.674	84.928	-2.725	-116.497	INFINITE
100	14.005	56.665	73.396	-1.546	-117.074	249.663
200	17.307	71.911	49.000	-0.000	-117.399	121.266
298	17.358	72.018	48.932	-0.032	-117.500	79.315
300	17.358	72.018	48.932	-0.032	-117.501	78.784
400	19.463	77.351	42.623	1.691	-117.488	57.383
500	21.276	81.926	37.037	3.994	-117.484	44.348
600	22.371	85.907	32.691	6.130	-117.307	35.998
700	23.136	89.417	29.106	8.706	-117.052	29.326
800	23.687	91.558	26.170	10.700	-116.750	24.707
900	24.087	93.358	23.758	13.140	-116.415	21.775
1000	24.369	97.912	20.828	15.664	-116.776	18.938
1100	24.621	100.248	18.871	18.015	-116.637	16.020
1200	24.802	102.396	17.266	20.697	-116.486	14.069
1300	24.943	104.343	15.906	23.661	-116.325	12.583
1400	25.063	106.243	14.846	26.875	-116.231	11.661
1500	25.158	107.975	14.038	27.966	-116.101	10.452
1600	25.237	109.601	13.425	30.506	-115.974	9.396
1700	25.303	111.133	12.972	33.033	-115.846	8.464
1800	25.358	112.584	12.646	35.559	-115.716	7.640
1900	25.406	113.954	12.416	38.105	-115.586	6.898
2000	25.446	115.256	12.244	40.667	-115.451	6.234
2100	25.482	116.500	12.116	43.194	-115.376	5.633
2200	25.512	117.686	12.024	45.743	-115.289	5.080
2300	25.538	118.809	11.959	48.312	-115.191	4.574
2400	25.561	119.869	11.910	50.897	-115.081	4.134
2500	25.583	120.952	11.875	53.488	-114.965	3.715
2600	25.602	121.956	11.850	55.968	-114.872	3.329
2700	25.619	122.923	11.825	58.459	-114.784	2.971
2800	25.634	123.854	11.809	60.894	-114.704	2.638
2900	25.647	124.754	11.794	63.355	-114.624	2.331
3000	25.659	125.624	11.781	66.621	-114.552	2.043
3100	25.670	126.466	11.769	69.787	-114.485	1.774
3200	25.678	127.281	11.759	72.894	-114.424	1.522
3300	25.685	128.074	11.750	75.948	-114.368	1.283
3400	25.691	128.838	11.740	78.962	-114.320	1.062
3500	25.705	129.583	11.730	81.934	-114.278	0.853
3600	25.712	130.307	11.721	84.863	-114.239	0.654
3700	25.718	131.012	11.712	87.754	-114.207	0.467
3800	25.723	131.696	11.704	90.609	-114.180	0.291
3900	25.728	132.366	11.696	93.430	-114.149	0.137
4000	25.735	133.018	11.690	96.223	-114.115	0.039
4100	25.739	133.653	11.685	99.487	-114.135	3.583
4200	25.744	134.274	11.681	102.701	-114.132	6.456
4300	25.748	134.881	11.677	105.865	-114.128	9.336
4400	25.752	135.471	11.673	108.979	-114.120	12.201
4500	25.755	136.050	11.670	112.042	-114.110	15.066
4600	25.759	136.616	11.667	115.055	-114.107	17.940
4700	25.762	137.170	11.664	118.018	-114.100	20.814
4800	25.765	137.714	11.661	120.931	-114.094	23.688
4900	25.767	138.244	11.658	123.794	-114.084	26.564
5000	25.770	138.764	11.655	126.607	-114.078	29.435
5100	25.772	139.275	11.652	129.360	-114.070	32.304
5200	25.775	139.775	11.650	132.063	-114.060	35.166
5300	25.778	140.266	11.647	134.716	-114.049	38.022
5400	25.779	140.748	11.645	137.319	-114.036	40.871
5500	25.781	141.221	11.642	140.000	-114.021	43.618
5600	25.783	141.686	11.640	142.659	-114.004	46.366
5700	25.785	142.142	11.638	145.298	-113.985	49.114
5800	25.786	142.583	11.636	147.827	-113.964	51.862
5900	25.788	143.031	11.634	150.246	-113.941	54.610
6000	25.789	143.465	11.632	152.555	-113.916	57.358

Dec. 31, 1980; June 30, 1961; Mar. 31, 1984; June 30, 1970

Vibrational Frequencies and Degeneracies

ω_1 , cm ⁻¹	ω_2 , cm ⁻¹	ω_3 , cm ⁻¹
1099 (1)	457.5 (1)	436 (1)
261.5 (1)	322 (1)	1162 (1)
667.2 (1)	922 (1)	446 (1)

Bond Distance: C-Cl = 1.77 ± 0.02 Å C-F = 1.33 ± 0.02 Å

Bond Angle: F-C-F = 109.5 ± 3° Cl-C-Cl = 108.5 ± 2°

Product of the Moments of Inertia: I_AB_C = 2.5841 × 10⁻¹¹³ g³cm⁻⁶

Heat of Formation

Hears and Stahl (1) investigated several heats of reaction involving CF₄, CF₃Cl, CF₂Cl₂, CFC₃, CCl₄, HF and HCl. Using JANAF values for all compounds except CF₂Cl₂ and CFC₃ we obtain the following observations:

1. ΔH_f²⁹⁸(CCl₃F, g) = -70.12 ± 1.1 kcal/mol2. ΔH_f²⁹⁸(CCl₂F₂, g) = -116.53 ± 1.5 kcal/mol3. ΔH_f²⁹⁸(CCl₂F₂, g) - ΔH_f²⁹⁸(CCl₃F, g) = -49.39 ± 1.0 kcal/mol4. ΔH_f²⁹⁸(CCl₂F₂, g) - 2ΔH_f²⁹⁸(CCl₃F, g) = 20.34 ± 1.0 kcal/mol5. ΔH_f²⁹⁸(CCl₂F₂, g) - 2ΔH_f²⁹⁸(CCl₃F, g) = 165.47 ± 1.0 kcal/mol

The sum of the squares of the deviations is smallest when ΔH_f²⁹⁸(CCl₂F₂, g) = -117.5 kcal/mol and ΔH_f²⁹⁸(CCl₃F, g) = -69 kcal/mol, and all the values are within their uncertainty ranges.

Petersen and Pitzer (2) obtained an approximate equilibrium constant for the reaction 2CCl₃F(g) + CCl₄(g) = 3CCl₂F₂(g) of log K₄₀₀ = -3.0. This on 3rd law reduction gives ΔH_r²⁹⁸ = 7.64 kcal and with ΔH_f²⁹⁸(CCl₃F, g) = -117.9 kcal/mol. ΔH_f²⁹⁸(CCl₄, g) = -22.94 kcal/mol this yields ΔH_f²⁹⁸(CCl₂F₂, g) = -117.9 kcal/mol.

Kirkbride and Davidson (3) investigated the reaction of potassium with the chlorofluoromethanes and obtained

ΔH_f²⁹⁸(CCl₂F₂, g) = -115.1 ± 2 kcal/mol and ΔH_f²⁹⁸(CCl₃F, g) = -72.9 ± 4 kcal/mol after correction with JANAF

auxiliary data. Wartenberg and Schiefer (3) investigated the same reaction and we obtain, after correction with JANAF auxiliary data, ΔH_f²⁹⁸(CCl₂F₂, g) = -117.7 kcal/mol and ΔH_f²⁹⁸(CCl₃F, g) = -63.1 kcal/mol. Kolesov et al. (4) have reported analogous data for the reaction with sodium which, after correction with JANAF auxiliary data, yields ΔH_f²⁹⁸(CCl₂F₂, g) = -114.4 ± 3.5 kcal/mol.

We adopt the values calculated above from Hears and Stahl (1), since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF₄ to CCl₄. With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5 and 36.0 kcal.

Heat Capacity and Entropy

Claisen (5) chose the frequencies given above from his own gas-phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict (6). Masi (g) has measured the gas phase heat capacities at 243, 273, 318 and 363°K, within this range our adopted heat capacities are from .3 to .7% high. The entropies agree to within 0.05% and further adjustment to obtain better fits was not considered necessary. The molecular structure was determined from the microwave measurements of Long et al. (7). The individual moments of inertia were: I_A = 31.929 × 10⁻³⁹ g cm², I_B = 21.216 × 10⁻³⁹ g cm², and I_C = 38.148 × 10⁻³⁹ g cm².

References

1. W. H. Hears and R. F. Stahl, IUPAC Thermochemical Bulletin **2**, 5 (1956).
2. F. W. Kirkbride and F. G. Davidson, Nature **174**, 79 (1954).
3. H. Wartenberg and J. Schiefer, Z. Anorg. Chem. **228**, 326 (1955).
4. V. P. Kolesov, I. D. Zankov, and S. M. Skuratov, Russ. J. Phys. Chem. (English Trans.) **37**, 378 (1963).
5. H. H. Claisen, J. Chem. Phys. **22**, 50 (1954).
6. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **47**, 202 (1951).
7. M. W. Long, Q. Williams, and T. L. Weatherly, J. Chem. Phys. **33**, 508 (1960).
8. D. E. Petersen and K. S. Pitzer, J. Phys. Chem. **61**, 1252 (1957).
9. J. F. Masi, J. Amer. Chem. Soc. **74**, 4738 (1952) and **75**, 2276 (1953).

T, °K.	C _p	S°	(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	8.000	55.000	INF INITE	3.073	52.182	52.182	INF INITE
150	11.539	62.734	69.012	1.232	52.579	50.331	54.994
200	13.700	67.816	67.816	1.000	52.600	49.221	56.078
250	13.823	67.861	67.816	1.026	52.600	49.200	56.840
300	13.853	67.861	67.816	1.026	52.600	49.200	56.840
350	13.876	67.861	67.816	1.026	52.600	49.200	56.840
400	13.893	67.861	67.816	1.026	52.600	49.200	56.840
450	13.906	67.861	67.816	1.026	52.600	49.200	56.840
500	13.916	67.861	67.816	1.026	52.600	49.200	56.840
600	13.931	67.861	67.816	1.026	52.600	49.200	56.840
700	13.943	67.861	67.816	1.026	52.600	49.200	56.840
800	13.953	67.861	67.816	1.026	52.600	49.200	56.840
900	13.961	67.861	67.816	1.026	52.600	49.200	56.840
1000	13.967	67.861	67.816	1.026	52.600	49.200	56.840
1100	13.971	67.861	67.816	1.026	52.600	49.200	56.840
1200	13.974	67.861	67.816	1.026	52.600	49.200	56.840
1300	13.976	67.861	67.816	1.026	52.600	49.200	56.840
1400	13.978	67.861	67.816	1.026	52.600	49.200	56.840
1500	13.979	67.861	67.816	1.026	52.600	49.200	56.840
1600	13.980	67.861	67.816	1.026	52.600	49.200	56.840
1700	13.981	67.861	67.816	1.026	52.600	49.200	56.840
1800	13.982	67.861	67.816	1.026	52.600	49.200	56.840
1900	13.983	67.861	67.816	1.026	52.600	49.200	56.840
2000	13.984	67.861	67.816	1.026	52.600	49.200	56.840
2100	13.985	67.861	67.816	1.026	52.600	49.200	56.840
2200	13.986	67.861	67.816	1.026	52.600	49.200	56.840
2300	13.987	67.861	67.816	1.026	52.600	49.200	56.840
2400	13.988	67.861	67.816	1.026	52.600	49.200	56.840
2500	13.989	67.861	67.816	1.026	52.600	49.200	56.840
2600	13.990	67.861	67.816	1.026	52.600	49.200	56.840
2700	13.991	67.861	67.816	1.026	52.600	49.200	56.840
2800	13.992	67.861	67.816	1.026	52.600	49.200	56.840
2900	13.993	67.861	67.816	1.026	52.600	49.200	56.840
3000	13.994	67.861	67.816	1.026	52.600	49.200	56.840
3100	13.995	67.861	67.816	1.026	52.600	49.200	56.840
3200	13.996	67.861	67.816	1.026	52.600	49.200	56.840
3300	13.997	67.861	67.816	1.026	52.600	49.200	56.840
3400	13.998	67.861	67.816	1.026	52.600	49.200	56.840
3500	13.999	67.861	67.816	1.026	52.600	49.200	56.840
3600	14.000	67.861	67.816	1.026	52.600	49.200	56.840
3700	14.001	67.861	67.816	1.026	52.600	49.200	56.840
3800	14.002	67.861	67.816	1.026	52.600	49.200	56.840
3900	14.003	67.861	67.816	1.026	52.600	49.200	56.840
4000	14.004	67.861	67.816	1.026	52.600	49.200	56.840
4100	14.005	67.861	67.816	1.026	52.600	49.200	56.840
4200	14.006	67.861	67.816	1.026	52.600	49.200	56.840
4300	14.007	67.861	67.816	1.026	52.600	49.200	56.840
4400	14.008	67.861	67.816	1.026	52.600	49.200	56.840
4500	14.009	67.861	67.816	1.026	52.600	49.200	56.840
4600	14.010	67.861	67.816	1.026	52.600	49.200	56.840
4700	14.011	67.861	67.816	1.026	52.600	49.200	56.840
4800	14.012	67.861	67.816	1.026	52.600	49.200	56.840
4900	14.013	67.861	67.816	1.026	52.600	49.200	56.840
5000	14.014	67.861	67.816	1.026	52.600	49.200	56.840
5100	14.015	67.861	67.816	1.026	52.600	49.200	56.840
5200	14.016	67.861	67.816	1.026	52.600	49.200	56.840
5300	14.017	67.861	67.816	1.026	52.600	49.200	56.840
5400	14.018	67.861	67.816	1.026	52.600	49.200	56.840
5500	14.019	67.861	67.816	1.026	52.600	49.200	56.840
5600	14.020	67.861	67.816	1.026	52.600	49.200	56.840
5700	14.021	67.861	67.816	1.026	52.600	49.200	56.840
5800	14.022	67.861	67.816	1.026	52.600	49.200	56.840
5900	14.023	67.861	67.816	1.026	52.600	49.200	56.840
6000	14.024	67.861	67.816	1.026	52.600	49.200	56.840

June 30, 1961

CARBONYL DICHLORIDE (COCl₂)

(IDEAL GAS)

MOL. WT. = 98.925

ΔH_f⁰ = -52.2 ± 0.8 kcal. mole⁻¹
Point group C_{2v}
ΔH_f⁰ 298.15 = -52.5 ± 0.8 kcal. mole⁻¹
S_{298.15} = 67.816 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(J, cm. ⁻¹)	(570) (1)
1827 (1)	285 (1)
849 (1)	440 (1)
[585] (1)	

Interatomic distances: C-O 1.166 ± 0.002 Å
C1-O 2.589 ± 0.001
C1-Cl 2.884 ± 0.001
C-Cl 1.746 ± 0.004
Cl-C-Cl angle 111.3 ± 0.1°

Moments of inertia: I_A = 1.0690 X 10⁻³⁸ g. cm.² I_B = 2.4469 X 10⁻³⁸ I_C = 3.5291 X 10⁻³⁸ σ = 2
Heat of Formation
J. Thomsen, Thermochemische Untersuchungen, Barth, Leipzig, 1882, Vol. 2, p. 361, reports the heat of alkali line hydrolysis of COCl₂ from which ΔH_f⁰ 298.15 is calculated to be -54.4 ± 0.3 kcal. mole⁻¹. From the heat of combustion of COCl₂ in O₂ and H₂, reported by Thomsen, op. cit., p. 363, ΔH_f⁰ 298.15 is calculated to be -51.73 ± 0.43 kcal. mole⁻¹. M. Bodenstein and H. Plaut, Z. phys. Chem. 110, 399 (1924), J. A. Christiansen, ibid. 103, 99 (1923), and M. Bodenstein and G. Dnaut, ibid. 61, 437 (1908), report 10 values of K_p from 647° to 876°K for the reaction CO + Cl₂ ⇌ COCl₂. These yield -25.91 ± 0.04 kcal. for ΔH_f⁰ 298.15, whence ΔH_f⁰ 298.15 for COCl₂ is -52.33 ± 0.62 kcal. mole⁻¹. The average of the 3 foregoing values of ΔH_f⁰ 298.15, weighted for the uncertainties, is adopted here. Values calculated from the degree of dissociation of COCl₂ from 374° to 778°K, reported by R. H. Atkinson, C. T. Heycock, and W. J. Pope, J. Chem. Soc. 117, 1410 (1920), range from -47.06 to -53.11 kcal. mole⁻¹ and are ignored.

Heat Capacity and Entropy

The vibrational frequencies were assigned by E. Catalano and K. S. Pitzer, J. Am. Chem. Soc. 80, 1054 (1958), on the basis of their own infra-red spectra and other data. The molecular dimensions listed above were deduced from microwave spectra by G. W. Robinson, J. Chem. Phys. 21, 1741 (1953), and are confirmed by electron-diffraction values compiled by P. W. Allen and L. E. Sutton, Acta Cryst. 2, 46 (1950). The moments of inertia are weighted for the isotopes and were calculated from Robinson's dimensions by M. P. Glaque and J. B. Ott, J. Am. Chem. Soc., 82, 2669 (1960). Glaque and Ott, loc. cit., determined S_{298.15} experimentally to be 67.61 cal. deg.⁻¹ mole⁻¹, with which the value calculated here agrees.

CCl₂ 20

GFV = 118.37015

(IDEAL GAS)

 $\Delta H_f^\circ = 19.15 \pm 2 \text{ kcal/mol}$ $\Delta H_f^\circ = 19 \pm 2 \text{ kcal/mol}$ TRICHLOROMETHYL (CCl₃)Point Group D_{3h} $S_{298.15}^\circ = 70.92 \pm 1.5 \text{ gibbs/mol}$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

wavenumber

[450] (1)

[480] (1)

838 (2)

[240] (2)

Bond Distance: C-Cl = [1.74] Å

Bond Angle: Cl-C-Cl = [120°]

Product of the Moments of Inertia: $I_A I_B I_C = [3.8215 \times 10^{-113}] \text{ g cm}^2$ $\sigma = 6$

Heat of Formation

Benson (1) has reanalysed the kinetic data of Sullivan and Davidson (2) for the reaction $\text{Br}_2(\text{g}) + \text{CHCl}_3(\text{g}) =$ $\text{HBr}(\text{g}) + \text{CH}_2\text{Cl}_2(\text{g})$ and has obtained from it the heat of the initial step, $\text{Br}(\text{g}) + \text{CHCl}_3(\text{g}) = \text{CHCl}_2(\text{g}) + \text{HBr}(\text{g})$, as $8.2 \pm 1 \text{ kcal/mol}$. Substituting this value and $\Delta H_f^\circ(\text{Br}) = 26.74 \text{ kcal/mol}$, $\Delta H_f^\circ(\text{CHCl}_2) = -24.66 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{HBr}) = -8.71 \text{ kcal/mol}$, we obtain $\Delta H_f^\circ(\text{CCl}_3, \text{g}) = 19 \pm 2 \text{ kcal/mol}$, which is adopted here.

Heat Capacity and Entropy

Walsh (3) has predicted that CCl₃ is non-planar on the basis of his orbital correlation diagram. Andrews (4)

indicates that his matrix infrared observations of the symmetric and antisymmetric stretches are consistent with a

non-planar C_{3v} structure and a near tetrahedral angle. The antisymmetric stretch has been confirmed by Current andBurdett (5). They rationalize the absence of the symmetric stretch and claim support of the C_{3v} structure. Rogers

et al. (6) have made a thorough search for the symmetric stretch and did not find it in the region where it was reported

by Andrews (4). Thus, they conclude that since only the antisymmetric stretch has been confirmed, the possibility of a

planar D_{3h} molecule cannot be excluded. Wagat et al. (7) have observed the NMR spectrum of trapped CCl₃ and find it

consistent with a planar molecule. The absence of the symmetric stretch strongly implies a planar configuration, and we

adopt such a configuration until more definitive proof of the non-planarity can be obtained. The remaining vibrational

frequencies are estimated by comparison with those of BCl₃. The bond length was estimated as 1.74 Å by Andrews (4) froma correlation with related molecules. The individual moments of inertia are $I_A = I_B = 2.6734 \times 10^{-38} \text{ g cm}^2$ and $I_C =$ $5.3468 \times 10^{-38} \text{ g cm}^2$.

References

1. S. W. Benson, J. Chem. Phys. **43**, 2044 (1965).2. J. H. Sullivan and N. Davidson, J. Chem. Phys. **19**, 143 (1951).3. A. D. Walsh, J. Chem. Soc. (London) **1953**, 2301 (1953).4. L. Andrews, J. Chem. Phys. **48**, 972 (1968).5. J. H. Current and J. K. Burdett, J. Phys. Chem. **73**, 3504 (1969).6. E. E. Rogers, S. Abramowitz, M. E. Jacob and D. E. Milligan, J. Chem. Phys. **52**, 2188 (1970).

7. M. Hagat, N. Leray and J. Rencin, Vysokomolekulyarnye Soedineniya, Vsesoyuz. Khim. Obshch. D. I. Mandaleeva,

11, 223 (1966).Trichloromethyl (CCl₃)

GFV = 118.37015

(Ideal Gas)

T, °K	C _p ^o	S ^o - (C _p ^o - H _{298.15})/T	H ^o - H _{298.15}	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	3.392	19.151	INFINITE	
100	9.795	57.405	62.694	19.989	43.686	
200	13.070	56.271	72.246	18.923	21.060	
298	15.212	70.918	70.918	19.000	22.093	
300	15.245	71.012	70.918	19.002	22.112	
400	16.658	75.606	71.535	19.111	23.133	
500	17.564	79.428	72.742	19.227	24.126	
600	18.156	82.686	74.135	19.333	25.095	
700	18.555	85.517	75.563	19.428	26.048	
800	18.895	87.944	77.020	19.514	26.987	
900	19.035	90.244	78.500	19.592	27.917	
1000	19.184	92.258	79.615	19.667	28.836	
1100	19.297	94.092	80.449	19.702	29.755	
1200	19.385	95.775	82.023	19.751	30.667	
1300	19.458	97.307	83.361	19.807	31.581	
1400	19.509	98.713	84.507	19.857	32.494	
1500	19.555	100.121	85.424	19.902	33.398	
1600	19.592	101.584	86.195	19.943	34.293	
1700	19.623	102.973	87.123	19.980	35.185	
1800	19.652	104.298	88.017	19.996	36.076	
1900	19.672	105.568	88.861	19.998	36.962	
2000	19.691	106.768	89.687	19.991	37.847	
2100	19.708	107.929	90.476	19.961	38.773	
2200	19.722	109.066	91.235	19.965	39.687	
2300	19.735	110.183	91.975	19.965	40.586	
2400	19.745	111.283	92.700	19.965	41.473	
2500	19.755	112.369	93.359	19.958	42.355	
2600	19.764	113.444	94.021	19.947	43.252	
2700	19.772	114.509	94.661	19.932	44.147	
2800	19.780	115.561	95.282	19.917	45.043	
2900	19.785	116.604	95.893	19.902	45.941	
3000	19.791	117.774	96.470	19.887	46.841	
3100	19.796	118.823	97.039	19.872	47.742	
3200	19.800	119.852	97.592	19.858	48.643	
3300	19.805	120.861	98.131	19.843	49.544	
3400	19.810	121.853	98.656	19.828	50.445	
3500	19.812	122.827	99.166	19.824	51.352	
3600	19.815	123.785	99.664	19.822	52.262	
3700	19.816	124.728	100.151	19.820	53.173	
3800	19.817	125.657	100.625	19.819	54.083	
3900	19.818	126.571	101.089	19.818	54.993	
4000	19.826	127.473	101.543	19.820	55.914	
4100	19.828	128.363	101.986	19.817	56.827	
4200	19.830	129.241	102.420	19.810	57.748	
4300	19.832	130.109	102.844	19.803	58.669	
4400	19.834	130.963	103.260	19.796	59.589	
4500	19.836	131.803	103.667	19.788	60.517	
4600	19.837	132.629	104.066	19.781	61.449	
4700	19.839	133.442	104.456	19.774	62.382	
4800	19.840	134.244	104.836	19.767	63.313	
4900	19.841	135.034	105.209	19.760	64.244	
5000	19.842	135.811	105.568	19.753	65.189	
5100	19.843	136.576	105.951	19.746	66.130	
5200	19.845	137.329	106.307	19.739	67.075	
5300	19.846	138.071	106.657	19.731	68.019	
5400	19.847	138.801	107.000	19.724	68.961	
5500	19.847	139.519	107.340	19.717	69.921	
5600	19.848	140.226	107.672	19.710	70.870	
5700	19.849	140.921	108.000	19.703	71.819	
5800	19.850	141.604	108.325	19.696	72.763	
5900	19.851	142.276	108.645	19.689	73.703	
6000	19.851	142.938	108.950	19.683	74.643	

Trichlorofluoromethane (CCl₃F)

GFW = 137.3686

(Ideal Gas)

Point Group C_{3v} $\Delta H_f^\circ = -68.24 \pm 1.5 \text{ kcal/mol}$ $S_{298.15}^\circ = 74.00 \pm 0.05 \text{ gibbs/mol}$ $\Delta H_f^\circ = -69.0 \pm 1.5 \text{ kcal/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}
349.5 (1)	241 (2)	
535.3 (1)	398 (2)	
1095 (1)	847 (2)	

Bond Distance: C-Cl = 1.76 Å C-F = 1.33 Å

Bond Angle: Cl-C-Cl = 109°40' F-C-Cl = 109°28'

Product of the Moments of Inertia: $I_{AB}I_C = 5.73499 \times 10^{-113} \text{ g cm}^{-6}$ $\sigma = 3$

Heat of Formation

Weare and Stahl (1) investigated several heats of reaction involving CF₄, CF₃Cl, CF₂Cl₂, CFCI₃, CCl₄, HF and HCl. Using JANAF values for all compounds except CF₂Cl₂ and CFCI₃, we obtain the following observations:

1. $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -70.12 \pm 1.1 \text{ kcal/mol}$
2. $\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) = -116.53 \pm 1.5 \text{ kcal/mol}$
3. $\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) - \Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -49.39 \pm 1.0 \text{ kcal/mol}$
4. $\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) - 2\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = 20.34 \pm 1.0 \text{ kcal/mol}$
5. $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) - 2\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) = 165.47 \pm 1.0 \text{ kcal/mol}$

The sum of the squares of the deviations is smallest when $\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) = -117.5 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -69 \text{ kcal/mol}$, and all the values are within their uncertainty ranges.

Petersen and Pitzer (2) obtained an approximate equilibrium constant for the reaction $\text{CCl}_3\text{F}(g) + 2\text{CCl}_4(g) = 3\text{CCl}_3\text{F}(g)$ of $\log K_{1400} = -4.5$. This on 3rd law reduction gives $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -169.2 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{CCl}_4, g) = -22.94 \text{ kcal/mol}$ this yields $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -68.2 \text{ kcal/mol}$.

Kirkbride and Davidson (2) investigated the reaction of potassium with the chlorofluoromethanes and obtained $\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) = -115.1 \pm 2 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -72.9 \pm 4 \text{ kcal/mol}$ after correction with JANAF auxiliary data. Wartenberg and Schiefer (3) investigated the same reaction and we obtain, after correction with JANAF

auxiliary data, $\Delta H_f^\circ(\text{CCl}_2\text{F}_2, g) = -112.7 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -63.1 \text{ kcal/mol}$. Baibuz (4) has reported $\Delta H_f^\circ(\text{CCl}_3\text{F}, g) = -66.4 \pm 2.1 \text{ kcal/mol}$ from heat of explosion measurements. A correlation of his other results would indicate that this value is not negative enough, possibly by as much as 3 kcal.

We adopt the values calculated above from Weare and Stahl (1), since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF₄ to CCl₄. With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5 and 36.0 kcal.

Heat Capacity and Entropy

Claassen (5) chose the frequencies given above from his own gas phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict (6), and the matrix studies of King (7). The molecular structure was determined from the microwave measurements of Long et al. (8). The individual moments of inertia were: $I_A = I_C = 34.301 \times 10^{-39} \text{ g cm}^2$ and $I_B = 46.744 \times 10^{-39} \text{ g cm}^2$.

References

1. W. H. Mears and R. F. Stahl, IUPAC Thermochemical Bulletin **2**, 5 (1956).
2. F. W. Kirkbride and F. G. Davidson, Nature **174**, 79 (1954).
3. H. Wartenberg and J. Schiefer, Z. Anorg. Chem. **218**, 326 (1955).
4. V. F. Baibuz, Dokl. Akad. Nauk SSSR, **140** 1358 (1961).
5. H. H. Claassen, J. Chem. Phys. **22**, 50 (1954).
6. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **47**, 202 (1951).
7. S. T. King, J. Chem. Phys. **48**, 1321 (1968).
8. H. W. Long, O. Williams, and T. L. Weatherly, J. Chem. Phys. **33**, 508 (1960).
9. D. E. Petersen and K. S. Pitzer, J. Phys. Chem. **51**, 1252 (1957).

Dec. 31, 1960; June 30, 1961; Mar. 31, 1964; June 30, 1970

Carbon Monofluoride (CF)

GFW = 31.0096

Ground State Configuration $2^1\Pi_F$

CF

$$\Delta H_F^\circ = 80.1 \pm 2 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 61 \pm 2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 50.889 \pm 0.01 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	2
77.11	2
[25000]	4
42705	2
49452	2

$\omega_e = 1308.1 \text{ cm}^{-1}$
 $\sigma = 1$
 $\alpha_e = 0.0184 \text{ cm}^{-1}$
 $x_e = 1.2667 \text{ \AA}$

Heat of Formation

M. Farber et al. (1) have studied the weight change of graphite in CF₄ at high temperatures. Our reanalysis of their data uses the equilibrium constants for CF₄, CF₃ and CF₂ from the JANAF Tables (2); the only other C-F species considered is assumed to be CF. This treatment yields negative values for the CF pressure except at the highest temperature, where 3rd law analysis of the equilibrium constant yields $\Delta H_{298}^\circ(\text{CF}, g) = 59.4 \text{ kcal/mol}$. Farber et al. also investigated mass-spectrometrically the vapor species present at equilibrium and followed the intensities of CF⁺ and F⁺. From a second law treatment of the intensities they report $\Delta H_{298}^\circ(\text{CF}, g) = 62.0 \text{ kcal/mol}$, or $\Delta H_{298}^\circ(\text{CF}, g) = 64 \text{ kcal/mol}$. From an analytical extrapolation of the 10 observed levels they reported a dissociation energy of $126.9 \pm 2.9 \text{ kcal/mol}$, which yields $\Delta H_{298}^\circ(\text{CF}, g) = 61.9 \pm 2.9 \text{ kcal/mol}$. Porter et al. (3) have investigated the A-X band system under high dispersion. From an analytical extrapolation of the 10 observed levels they reported a dissociation energy of $126.9 \pm 2.9 \text{ kcal/mol}$, which yields $\Delta H_{298}^\circ(\text{CF}, g) = 61.9 \pm 2.9 \text{ kcal/mol}$. Porter et al. (3) have investigated the A-X band system under high dispersion. From an analytical extrapolation of the 10 observed levels they reported a dissociation energy of $126.9 \pm 2.9 \text{ kcal/mol}$, which yields $\Delta H_{298}^\circ(\text{CF}, g) = 61.9 \pm 2.9 \text{ kcal/mol}$.

The predissociation limit of CF(g) has been reported by Thrush and Zwolenik (4) as $\leq 132 \text{ kcal/mol}$; Kuzakov and Tatiievsky (5) determined the same quantity as $\leq 133 \text{ kcal/mol}$. These results yield $\Delta H_{298}^\circ(\text{CF}, g) \geq 56 \text{ kcal/mol}$. Thrush and Zwolenik (4) also report a predissociation limit for the reaction $\text{CF}_2 \rightarrow \text{CF} + \text{F}$ which is $\leq 140 \text{ kcal/mol}$. This value has now been shown to be erroneous (see the CF₂(g) table for details).

Modica (6) has studied the equilibrium $\text{CF}_2 \rightarrow \text{CF} + \text{F}$ in a shock tube in the range 2680° to 3400°K . Since functions for CF₂, CF and F are well established, the data were analyzed using 2nd and 3rd law treatments. The 2nd law analysis gives $\Delta H_{298}^\circ = 107.2 \pm 7.6 \text{ kcal/mol}$, in agreement with the value reported by Modica. The 3rd law analysis yields $\Delta H_{298}^\circ = 134.9 \pm 7.2 \text{ kcal/mol}$ and a drift of $9.7 \pm 2.5 \text{ eu}$. The excessive drift indicates that the reported equilibrium constants do not represent the stated reaction.

Andrews and Barrow (7) report a dissociation energy of 114 kcal from an extrapolation of four B state levels. This extrapolation is considered unreliable by Porter et al. (3) since this state is formed from an avoided crossing and is likely to be perturbed.

The adopted value of $\Delta H_{298}^\circ(\text{CF}, g)$ is $61 \pm 2 \text{ kcal/mol}$, which is within the uncertainties and ranges of the acceptable investigations.

Heat Capacity and Entropy

The vibrational and rotational constants are from Porter et al. (3); the higher electronic levels are those reported by Andrews and Barrow (7), except that the B state is now considered to be $^2\Sigma$. The estimated level at 25000 cm^{-1} is proposed in order to explain the low bond dissociation energy of C₂F₂ by analogy with the reasoning used by Simons (8) for C₂F₄. This level would be a $^2\Sigma$ level and could correlate with the ground state atoms.

References

1. M. Farber, M. A. Frisch, and H. C. Ko, Trans. Faraday Soc. **55**, 3202 (1959).
2. JANAF Thermochemical Tables; CF₄ dated 6-30-69; CF₃ dated 6-30-69; CF₂ dated 6-30-70.
3. T. L. Porter, D. E. Mann and N. Acquista, J. Mol. Spectry. **15**, 228 (1965).
4. B. A. Thrush and J. J. Zwolenik, Trans. Faraday Soc. **53**, 582 (1957).
5. Yu. Ya. Kuzakov and V. M. Tatiievsky, Opt. i. Spektroskopiya **5**, 699 (1958).
6. A. P. Modica, J. Chem. Phys. **44**, 1585 (1966).
7. E. B. Andrews and R. F. Barrow, Proc. Phys. Soc. (London), **64A**, 481 (1951).
8. J. P. Simons, Nature **205**, 1308 (1965).

T, °K	Cp°	$-\frac{G^\circ - H_{298}^\circ}{T}$	$H^\circ - H_{298}^\circ$	ΔH_F°	ΔG_F°	Log Kp
0	∞	INFINITE	2.171	60.136	60.136	INFINITE
100	7.413	43.028	57.245	60.524	58.277	127.364
200	7.414	43.028	57.245	60.524	58.277	127.364
298	7.114	50.889	50.889	61.000	53.455	93.183
300	7.188	50.934	50.889	61.002	53.408	93.007
400	7.432	53.033	51.174	61.102	50.860	87.789
500	7.709	54.721	51.501	61.136	48.294	81.109
600	7.954	56.149	52.342	61.126	45.726	74.656
700	8.154	57.391	52.976	61.081	43.163	68.476
800	8.312	58.490	53.598	61.013	40.607	62.493
900	8.438	59.477	54.197	60.925	38.061	56.742
1000	8.538	60.371	54.760	60.826	35.525	51.264
1100	8.619	61.189	55.318	60.715	33.000	45.956
1200	8.686	61.942	55.839	60.596	30.487	40.702
1300	8.742	62.639	56.335	60.467	27.983	35.500
1400	8.789	63.289	56.809	60.334	25.490	30.352
1500	8.829	63.897	57.261	60.195	23.006	25.256
1600	8.864	64.468	57.694	60.052	20.530	20.204
1700	8.895	65.006	58.109	59.907	18.065	15.192
1800	8.923	65.515	58.506	59.758	15.607	10.219
1900	8.947	65.998	58.888	59.608	13.159	5.284
2000	8.970	66.458	59.255	59.455	10.719	0.391
2100	8.991	66.896	59.609	59.301	8.286	-4.552
2200	9.010	67.315	59.949	59.144	5.858	-9.482
2300	9.027	67.716	60.278	58.986	3.442	-14.402
2400	9.044	68.100	60.596	58.826	1.030	-19.312
2500	9.060	68.470	60.904	58.664	-1.376	-24.212
2600	9.075	68.825	61.202	58.501	-3.774	-29.102
2700	9.089	69.168	61.490	58.336	-6.167	-33.982
2800	9.103	69.499	61.771	58.172	-8.552	-38.852
2900	9.117	69.819	62.043	58.004	-10.931	-43.712
3000	9.130	70.128	62.307	57.834	-13.307	-48.562
3100	9.143	70.427	62.564	57.665	-15.674	-53.402
3200	9.156	70.718	62.814	57.493	-18.037	-58.232
3300	9.168	71.000	63.058	57.320	-20.397	-63.052
3400	9.181	71.274	63.296	57.146	-22.748	-67.862
3500	9.193	71.540	63.528	56.970	-25.096	-72.662
3600	9.206	71.799	63.754	56.793	-27.436	-77.452
3700	9.219	72.052	63.975	56.614	-29.775	-82.242
3800	9.232	72.298	64.190	56.435	-32.105	-87.032
3900	9.245	72.538	64.401	56.253	-34.433	-91.822
4000	9.259	72.772	64.608	56.072	-36.755	-96.612
4100	9.272	73.001	64.810	55.888	-39.077	-101.402
4200	9.286	73.224	65.007	55.702	-41.388	-106.192
4300	9.301	73.443	65.201	55.515	-43.686	-110.982
4400	9.316	73.657	65.391	55.327	-45.984	-115.772
4500	9.331	73.866	65.577	55.136	-48.282	-120.562
4600	9.346	74.072	65.759	54.947	-50.580	-125.352
4700	9.362	74.273	65.938	54.756	-52.878	-130.142
4800	9.379	74.470	66.114	54.562	-55.160	-134.932
4900	9.395	74.664	66.286	54.368	-57.442	-139.722
5000	9.413	74.854	66.456	54.172	-59.724	-144.512
5100	9.430	75.040	66.622	53.975	-62.028	-149.302
5200	9.448	75.223	66.786	53.776	-64.297	-154.092
5300	9.467	75.404	66.947	53.577	-66.564	-158.882
5400	9.486	75.581	67.105	53.376	-68.839	-163.672
5500	9.505	75.755	67.261	53.174	-71.100	-168.462
5600	9.525	75.926	67.414	52.971	-73.348	-173.252
5700	9.545	76.095	67.565	52.766	-75.605	-178.042
5800	9.565	76.261	67.713	52.560	-77.854	-182.832
5900	9.586	76.425	67.860	52.353	-80.099	-187.622
6000	9.607	76.586	68.004	52.145	-82.346	-192.412

Dec. 31, 1950; Mar. 31, 1961; Sept. 30, 1966; Dec. 31, 1967; June 30, 1970

CF

Cyanogen Fluoride (FCN)

(Ideal Gas)

GFW = 45.01625

CYANOGEN FLUORIDE (FCN)

(IDEAL GAS)

GFW = 45.01625

Point Group $C_{\infty v}$ $\Delta H_f^\circ = 8.5 \pm 4$ kcal/mol

CFN

 $S^\circ_{298.15} = 53.85 \pm 0.2$ gibbs/mol $\Delta H^\circ_{298.15} = 8.6 \pm 4$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 ω_e, cm^{-1}

1077 (1)	2290 (1)
[420] (2)	

Bond Distances: C-F = 1.262 \AA C-N = 1.159 \AA Bond Angle: F-C-N = 180° Rotational Constants: $B_0 = 0.3531 \text{ cm}^{-1}$

Heat of Formation

Davis and Okabe (1) have determined the dissociation energy of FCN to F(g) and CN(g) by measuring the threshold energies of incident photon radiation to produce F^\bullet CN which is monitored by its fluorescence. The dissociation energy determined by this technique is ≤ 111 kcal/mol with an uncertainty of about 1 kcal in the determination of the limit.

Dibeler and Liston (2) have reported a dissociation energy of ≤ 115.6 kcal/mol from the threshold of the CN^+ ion as determined by photoionization.

We adopt a median value of 113.1 ± 2.5 kcal/mol which leads to $\Delta H^\circ_{298}(\text{FCN}, g) = 8.6 \pm 4$ kcal/mol with auxiliary JANAF values for F(g) and CN(g).

Heat Capacity and Entropy

The molecular structure and bond lengths and angle were determined using microwave spectroscopy by Tyler and Sheridan (3). The vibrational frequencies were reported by Aynsley et. al. (4) from the infra-red spectrum, except for the bending frequency which is estimated from the values for ClCN, BrCN and ICN, by comparison of bending force constants. The reasonable limits for this value as calculated from generous limits on the bending force constant are $405\text{--}450 \text{ cm}^{-1}$.

References:

1. D. D. Davis and H. Okabe, J. Chem. Phys. **49**, 5526 (1968).
2. V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).
3. J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).
4. E. E. Aynsley, R. E. Dodd, and R. Little, Proc. Chem. Soc. (London), **1959**, 265 (1959).

T, °K	C_p	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔC_p	Log Kp
0	0.000	INFINITE	INFINITE	0.000	0.000	INFINITE
100	7.161	52.432	52.432	1.728	6.519	6.262
200	8.900	50.037	50.037	0.000	6.597	5.129
298	10.113	53.846	53.846	0.000	6.601	5.089
300	10.130	53.908	53.846	0.019	6.601	5.089
400	10.934	56.939	54.254	1.074	6.437	3.517
500	11.582	59.447	55.049	2.199	6.266	2.566
600	12.031	61.596	55.945	3.379	6.089	1.929
700	12.438	63.482	56.907	4.603	5.915	1.473
800	12.779	65.166	57.836	5.864	5.745	1.131
900	13.066	66.688	58.736	7.157	5.580	0.864
1000	13.306	68.077	59.602	8.476	5.427	0.652
1100	13.508	69.355	60.431	9.817	5.283	0.479
1200	13.677	70.538	61.225	11.176	5.148	0.335
1300	13.820	71.639	61.984	12.551	5.026	0.213
1400	13.942	72.668	62.711	13.940	4.915	0.109
1500	14.045	73.633	63.407	15.339	4.812	0.030
1600	14.133	74.542	64.075	16.748	4.716	0.000
1700	14.210	75.402	64.716	18.165	4.634	0.000
1800	14.275	76.216	65.333	19.590	4.562	0.000
1900	14.333	76.989	65.926	21.020	4.500	0.000
2000	14.383	77.726	66.498	22.456	4.446	0.000
2100	14.427	78.428	67.049	23.896	4.399	0.000
2200	14.465	79.100	67.582	25.341	4.356	0.000
2300	14.500	79.744	68.097	26.789	4.316	0.000
2400	14.530	80.362	68.595	28.241	4.279	0.000
2500	14.556	80.956	69.078	29.695	4.244	0.000
2600	14.582	81.527	69.545	31.152	4.211	0.000
2700	14.604	82.078	69.999	32.612	4.180	0.000
2800	14.624	82.609	70.440	34.073	4.150	0.000
2900	14.642	83.123	70.869	35.536	4.121	0.000
3000	14.658	83.620	71.286	37.002	4.093	0.000
3100	14.673	84.100	71.691	38.468	4.066	0.000
3200	14.687	84.567	72.086	39.936	4.040	0.000
3300	14.699	85.019	72.472	41.405	4.015	0.000
3400	14.711	85.456	72.847	42.876	4.000	0.000
3500	14.721	85.884	73.213	44.348	3.976	0.000
3600	14.731	86.299	73.571	45.820	3.952	0.000
3700	14.740	86.703	73.921	47.294	3.928	0.000
3800	14.748	87.096	74.262	48.768	3.904	0.000
3900	14.756	87.479	74.596	50.243	3.880	0.000
4000	14.763	87.853	74.923	51.719	3.856	0.000
4100	14.769	88.217	75.243	53.196	3.832	0.000
4200	14.776	88.573	75.556	54.673	3.808	0.000
4300	14.781	88.921	75.863	56.151	3.784	0.000
4400	14.787	89.261	76.163	57.629	3.760	0.000
4500	14.792	89.593	76.456	59.108	3.736	0.000
4600	14.797	89.919	76.747	60.588	3.712	0.000
4700	14.801	90.237	77.031	62.068	3.688	0.000
4800	14.805	90.549	77.309	63.548	3.664	0.000
4900	14.809	90.854	77.583	65.029	3.640	0.000
5000	14.813	91.153	77.851	66.510	3.616	0.000
5100	14.816	91.446	78.115	67.991	3.592	0.000
5200	14.819	91.734	78.374	69.473	3.568	0.000
5300	14.823	92.016	78.629	70.955	3.544	0.000
5400	14.825	92.294	78.879	72.438	3.520	0.000
5500	14.828	92.566	79.126	73.920	3.496	0.000
5600	14.831	92.833	79.368	75.403	3.472	0.000
5700	14.833	93.095	79.606	76.886	3.448	0.000
5800	14.836	93.353	79.841	78.370	3.424	0.000
5900	14.838	93.607	80.072	79.854	3.400	0.000
6000	14.840	93.856	80.300	81.337	3.376	0.000

Dec. 31, 1960; June 30, 1961; June 30, 1969

CFN

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	-2.484	-41.139	-41.139	INFINITE
100	7.969	50.185	67.074	-1.689	-41.062	-41.949	91.675
200	8.476	55.826	60.187	-0.872	-41.014	-42.857	46.830
298	9.305	59.363	59.363	0.000	-41.000	-43.766	32.080
300	9.320	59.420	59.363	0.017	-41.000	-43.784	31.895
400	10.078	64.782	60.778	2.034	-41.058	-44.629	19.944
500	10.768	68.541	60.472	2.034	-41.058	-44.629	19.944
600	11.310	71.310	66.554	61.322	-41.124	-46.538	16.951
700	11.748	73.631	62.199	4.293	-41.210	-47.433	14.809
800	12.093	75.365	63.066	5.408	-41.308	-48.315	13.199
900	12.407	76.682	63.783	6.460	-41.408	-49.187	11.946
1000	12.697	77.682	64.472	7.460	-41.528	-50.043	10.936
1100	12.971	78.492	65.501	8.230	-41.666	-50.890	10.110
1200	13.240	79.012	66.248	10.517	-41.768	-51.724	9.420
1300	13.505	79.402	66.907	11.727	-41.897	-52.549	8.859
1400	13.765	79.682	67.482	12.872	-42.047	-53.364	8.399
1500	13.921	79.936	68.003	14.450	-42.161	-54.167	7.932
1600	13.323	78.794	68.932	15.779	-42.298	-54.965	7.508
1700	13.394	79.603	69.536	17.151	-42.436	-55.751	7.167
1800	13.448	80.360	70.117	18.465	-42.580	-56.532	6.864
1900	13.486	81.079	70.682	20.000	-42.728	-57.308	6.594
2000	13.521	81.700	71.214	21.151	-42.874	-58.065	6.345
2100	13.555	82.431	71.734	22.505	-43.024	-58.821	6.121
2200	13.578	83.082	72.230	23.222	-43.181	-59.574	5.910
2300	13.601	83.666	72.702	24.200	-43.345	-60.324	5.710
2400	13.624	84.206	73.169	25.584	-43.501	-61.040	5.559
2500	13.655	84.823	73.644	27.949	-43.667	-61.774	5.400
2600	13.674	85.359	74.084	29.315	-43.837	-62.494	5.253
2700	13.690	85.915	74.511	30.683	-44.011	-63.208	5.116
2800	13.705	86.489	74.924	32.050	-44.189	-63.916	4.989
2900	13.719	86.895	75.329	33.424	-44.369	-64.616	4.869
3000	13.731	87.320	75.721	34.797	-44.554	-65.313	4.758
3100	13.742	87.770	76.102	36.171	-44.742	-66.009	4.653
3200	13.752	88.237	76.474	37.545	-44.935	-66.684	4.554
3300	13.761	88.721	76.840	38.919	-45.132	-67.356	4.460
3400	13.770	89.041	77.189	40.297	-45.332	-68.030	4.373
3500	13.778	89.440	77.533	41.675	-45.537	-68.696	4.289
3600	13.785	89.829	77.869	43.053	-45.744	-69.356	4.210
3700	13.791	90.206	78.199	44.432	-45.956	-70.006	4.133
3800	13.797	90.574	78.519	45.812	-46.171	-70.646	4.059
3900	13.803	90.933	78.832	47.191	-46.391	-71.296	3.995
4000	13.808	91.282	79.139	48.572	-46.613	-71.929	3.930
4100	13.813	91.623	79.440	49.953	-46.840	-72.561	3.868
4200	13.818	91.956	79.734	51.334	-47.071	-73.184	3.808
4300	13.822	92.281	80.024	52.715	-47.304	-73.804	3.750
4400	13.826	92.599	80.304	54.099	-47.543	-74.418	3.696
4500	13.829	92.910	80.581	55.482	-47.784	-75.029	3.644
4600	13.833	93.214	80.852	56.865	-48.029	-75.629	3.593
4700	13.836	93.511	81.124	58.248	-48.276	-76.224	3.544
4800	13.839	93.803	81.379	59.631	-48.530	-76.814	3.497
4900	13.842	94.088	81.636	61.016	-48.785	-77.403	3.452
5000	13.845	94.368	81.888	62.400	-49.044	-77.987	3.409
5100	13.847	94.642	82.135	63.785	-49.308	-78.567	3.367
5200	13.849	94.911	82.371	65.170	-49.576	-79.144	3.326
5300	13.852	95.175	82.617	66.555	-49.844	-79.709	3.286
5400	13.854	95.434	82.852	67.940	-50.117	-80.263	3.248
5500	13.856	95.688	83.083	69.326	-50.394	-80.815	3.211
5600	13.858	95.938	83.311	70.711	-50.675	-81.369	3.175
5700	13.860	96.183	83.534	72.097	-50.957	-81.919	3.140
5800	13.862	96.424	83.754	73.483	-51.247	-82.454	3.107
5900	13.863	96.661	83.971	74.870	-51.538	-82.988	3.074
6000	13.865	96.894	84.185	76.256	-51.833	-83.522	3.042

Dec. 31, 1985

CARBONYL MONOFLUORIDE (COF)

(IDEAL GAS)

MOL. WT. = 47.00895

Point Group C_{∞v}ΔH_f° = [-41 ± 15] kcal. mole⁻¹ΔF_f° 298.15 = [59] cal. deg.⁻¹ mole⁻¹ΔF_f° 298.15 = [-41 ± 15] kcal. mole⁻¹

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω_e, cm.⁻¹

1018 (1)

626 (1)

1655 (1)

C-O = [1.18] Å

F-C-O = [135] °

Product of the Moments of Inertia: I_AI_BI_C = [2.186 × 10⁻¹¹⁶] g.³ cm.⁶O⁻ = 1

Heat of Formation.

The enthalpy change (ΔH_f°) for the reaction COF₂(g) = CO(g) + 2F(g) was calculated as 160.5 kcal. mole⁻¹. By analogy with D(Cl-COCl)/D(Cl-CO), the value of D(F-COF)/D(F-CO) was taken to be 4. Based on ΔH_f° = 160.5 x (4/5) = 128.4 kcal. mole⁻¹ for the reaction COF₂(g) = CO(g) + F(g), the heat of formation for COF(g) was derived as -41 ± 15 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational frequencies were reported by D. E. Milligen, M. E. Jacox, A. M. Bass, J. J. Cornford and D. E. Mann, J. Chem. Phys. 42, 3187 (1965). The bond distances and angle were estimated by comparison with those for HFCO (g). Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The three principal moments of inertia are: I_A = 7.8757 x 10⁻³⁹, I_B = 3.3880 x 10⁻⁴⁰, and I_C = 8.2155 x 10⁻³⁹ g. cm.²

Point Group C_{2v}

$$\Delta H_f^\circ = -152.0 \pm 0.4 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -152.7 \pm 0.4 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 61.85 \pm 0.02 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Carbonyl Fluoride (COF₂)

CFW = 66.0074

(Ideal Gas)

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log Kp
0	0.000	INFINITE	INFINITE	2.657	-151.958	-151.958	INFINITE
100	6.004	51.617	70.536	1.682	-152.218	-152.218	330.556
200	9.296	57.767	62.820	-1.011	-152.481	-152.481	168.100
298	11.294	61.851	61.851	-0.000	-152.700	-152.700	109.710
300	11.330	61.921	61.921	0.021	-152.704	-152.704	108.520
400	13.092	65.432	62.318	1.285	-152.651	-152.651	86.695
500	14.860	68.507	63.255	2.626	-152.661	-152.661	63.947
600	15.695	71.240	64.342	4.137	-153.048	-153.047	52.841
700	16.305	73.693	65.362	5.719	-153.121	-153.120	44.974
800	16.924	75.912	66.645	7.382	-153.162	-153.165	38.698
900	17.406	77.935	67.824	9.099	-153.235	-153.033	34.247
1000	17.786	79.789	68.929	10.860	-153.279	-153.675	30.526
1100	18.089	81.499	69.995	12.654	-153.310	-153.313	27.040
1200	18.334	83.084	71.021	14.475	-153.335	-153.946	24.041
1300	18.533	84.559	72.006	16.319	-153.391	-153.577	22.793
1400	18.697	85.939	72.952	18.181	-153.425	-153.204	20.950
1500	18.834	87.234	73.862	20.058	-153.488	-152.830	19.353
1600	18.949	88.453	74.736	21.947	-153.492	-153.456	17.946
1700	19.046	89.605	75.577	23.847	-153.526	-153.076	16.722
1800	19.129	90.696	76.387	25.756	-153.562	-152.697	15.626
1900	19.201	91.732	77.168	27.672	-153.590	-152.314	14.644
2000	19.262	92.719	77.921	29.596	-153.638	-151.939	13.761
2100	19.316	93.660	78.648	31.525	-153.678	-152.562	12.941
2200	19.365	94.559	79.351	33.459	-153.724	-152.186	12.234
2300	19.404	95.421	80.011	35.397	-153.771	-151.763	11.570
2400	19.441	96.248	80.690	37.339	-153.823	-152.370	10.941
2500	19.474	97.042	81.328	39.285	-153.878	-151.978	10.401
2600	19.503	97.806	81.947	41.234	-153.937	-151.579	9.883
2700	19.529	98.543	82.548	43.186	-153.990	-151.180	9.404
2800	19.552	99.253	83.132	45.140	-154.046	-150.778	8.959
2900	19.573	99.940	83.700	47.096	-154.137	-150.371	8.544
3000	19.592	100.604	84.252	49.054	-154.213	-150.000	8.157
3100	19.609	101.247	84.790	51.014	-154.291	-150.556	7.794
3200	19.625	101.869	85.314	52.976	-154.376	-150.144	7.454
3300	19.639	102.473	85.825	54.939	-154.464	-149.733	7.135
3400	19.653	103.060	86.323	56.904	-154.537	-149.313	6.834
3500	19.665	103.630	86.810	58.870	-154.655	-148.893	6.550
3600	19.676	104.184	87.285	60.837	-154.756	-148.469	6.281
3700	19.686	104.723	87.749	62.805	-154.863	-148.042	6.027
3800	19.696	105.248	88.202	64.774	-154.974	-147.610	5.786
3900	19.704	105.760	88.646	66.744	-155.080	-147.181	5.556
4000	19.713	106.259	89.080	68.715	-155.209	-146.755	5.341
4100	19.720	106.746	89.505	70.686	-155.334	-146.309	5.136
4200	19.727	107.221	89.921	72.659	-155.463	-145.866	4.946
4300	19.734	107.685	90.329	74.632	-155.596	-145.419	4.768
4400	19.740	108.139	90.729	76.605	-155.735	-144.975	4.598
4500	19.746	108.583	91.121	78.580	-155.877	-144.537	4.437
4600	19.751	109.017	91.505	80.555	-156.023	-144.097	4.282
4700	19.756	109.442	91.882	82.530	-156.175	-143.652	4.136
4800	19.761	109.858	92.252	84.506	-156.331	-143.204	3.992
4900	19.765	110.265	92.616	86.482	-156.491	-142.753	3.857
5000	19.769	110.665	92.973	88.459	-156.656	-142.301	3.734
5100	19.773	111.056	93.323	90.436	-156.826	-141.846	3.604
5200	19.777	111.440	93.666	92.413	-156.996	-141.389	3.479
5300	19.780	111.817	94.007	94.391	-157.167	-140.930	3.329
5400	19.784	112.187	94.340	96.369	-157.341	-140.468	3.182
5500	19.787	112.550	94.665	98.348	-157.518	-140.004	3.033
5600	19.790	112.906	94.991	100.327	-157.690	-139.538	2.902
5700	19.793	113.256	95.308	102.306	-157.861	-139.072	2.794
5800	19.795	113.601	95.620	104.285	-158.037	-138.604	2.699
5900	19.798	113.939	95.928	106.265	-158.215	-138.132	2.608
6000	19.800	114.272	96.231	108.245	-158.392	-137.658	2.500

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Mar. 31, 1965; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
965 (1)	1249 (1)
1928 (1)	584 (1)
626 (1)	774 (1)

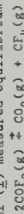
Bond Distances: C-F = 1.312 Å C-O = 1.174 Å

Bond Angles: F-C-F = 108° F-C-O = 128° 1'

Product of the Moments of Inertia: $I_A I_B I_C = 7.243 \times 10^{-115} \text{ g}^3 \text{ cm}^6$

Heat of Formation

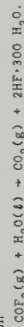
Ruff and Li (1) measured equilibrium constants for the reaction



in the temperature range 573-1273°K. These equilibrium data were recently analyzed by Stull, Westrum, and Sinke (2).

Their third law analysis of the data clearly indicates that the three low temperature points are in error and should not be used in calculating ΔH_f° . They reported, $\Delta H_f^\circ = -12 \pm 3 \text{ kcal/mol}$, based upon an average of the five high temperature points. Combining this result with the heat of formation of carbon dioxide and carbon tetrafluoride (3), we derive,

$$\Delta H_f^\circ(\text{COF}_2, \text{g}) = -152.5 \pm 3.3 \text{ kcal/mol.}$$

Wartenberg and Riteris (4) measured the heat of hydrolysis of CF_2O . They reported, $\Delta H_r = -26.7 \pm 0.2 \text{ kcal/mol}$, for the reactionCombining this result with heat of formation data for carbon dioxide and HF ($\Delta H_f^\circ(\text{HF} \cdot 300 \text{ H}_2\text{O}) = -76.84 \text{ kcal/mol}$ (5)), we derive,

$$\Delta H_f^\circ(\text{COF}_2, \text{g}) = -152.7 \pm 0.4 \text{ kcal/mol.}$$

Armstrong, Coyle, and Krueger (6) measured the heats of combustion of CH_4 in O_2 -F₂ mixtures and found $\Delta H_f^\circ(\text{COF}_2, \text{g}) =$

$$-154.8 \text{ kcal/mol. The value calculated from Wartenberg's data is adopted here.}$$

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Hopper et al. (7) and are in good agreement with the results of Lovell et al. (8) and Nielsen et al. (9). The molecular constants are from the microwave studies of

Laurie et al. (10) and are in reasonable agreement with the electron-diffraction work of Brown and Livingston (11).

Individual moments of inertia calculated from the rotational constants of Laurie et al. (10) are $I_A = 7.105 \times 10^{-39}$

$$\text{g cm}^2, I_B = 7.144 \times 10^{-39} \text{ g cm}^2, \text{ and } I_C = 14.27 \times 10^{-39} \text{ g cm}^2.$$

References

- O. Ruff and S. Li, Z. Anorg. Chem., **242**, 272 (1939).
- D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, Inc., New York, 1969, p. 80.
- JANAF Thermochemical Tables, The Dow Chemical Co., June 30, 1969.
- H. von Wartenberg and G. Riteris, Z. Anorg. Chem., **258**, 358 (1949).
- Ref. 3, Dec. 31, 1968.
- G. T. Armstrong, C. F. Coyle, and L. A. Krueger, WADC TR 58-543, October, 1958.
- M. J. Hopper, J. W. Russell, and J. Overend, J. Chem. Phys., **48**, 3765 (1968).
- R. J. Lovell, C. V. Stephenson, E. A. Jones, J. Chem. Phys., **22**, 1853 (1954).
- A. H. Nielsen, T. G. Burke, P. J. H. Voltz, and E. A. Jones, J. Chem. Phys., **20**, 596 (1952).
- V. W. Laurie, D. T. Pence, and R. H. Jackson, J. Chem. Phys., **37**, 2395 (1962).
- T. T. Brown and R. L. Livingston, J. Amer. Chem. Soc., **74**, 6084 (1952).

Trifluoromethyl (CF₃)

(Ideal Gas)

CFW = 69.00635

Point Group C_{3v}S_{298.15} = 63.329 ± 1.0 gibbs/mol

Ground State Quantum Weight = 2

ΔH_F⁰ = -111.7 ± 1.0 kcal/molΔH_F⁰_{298.15} = -112.4 ± 1.0 kcal/molCF₃

T, °K	C _p ^a	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _F ^b	Log K _p
0	8.000	INF	INF	2.754	-111.737	INF
100	52.000	52.000	52.000	-111.737	-111.737	11.737
200	9.655	59.007	64.352	-112.237	-110.231	12.045
298	11.903	63.329	67.731	-109.689	-109.210	80.053
300	11.940	63.403	67.799	-109.689	-109.210	79.545
400	13.735	67.072	70.315	-108.786	-108.307	59.063
500	15.135	70.315	72.500	-107.986	-107.507	46.764
600	16.172	73.170	75.126	-107.258	-106.779	36.559
700	16.936	75.724	77.480	-106.666	-106.187	28.695
800	17.503	78.024	79.582	-106.145	-105.666	22.266
900	17.928	80.111	81.466	-105.689	-105.210	16.445
1000	18.253	82.018	83.166	-105.286	-104.807	11.172
1100	18.506	83.770	84.716	-104.936	-104.457	6.994
1200	18.706	85.389	86.146	-104.616	-104.137	3.301
1300	18.865	86.893	87.496	-104.326	-103.847	1.600
1400	18.995	88.296	88.796	-104.056	-103.577	0.791
1500	19.102	89.616	90.066	-103.806	-103.327	0.429
1600	19.190	90.846	91.316	-103.566	-103.087	0.243
1700	19.265	92.011	92.466	-103.336	-102.857	0.146
1800	19.328	93.114	93.566	-103.116	-102.637	0.092
1900	19.382	94.161	94.616	-102.906	-102.427	0.063
2000	19.428	95.156	95.616	-102.706	-102.227	0.044
2100	19.468	96.105	96.566	-102.516	-102.037	0.032
2200	19.503	97.012	97.476	-102.336	-101.847	0.024
2300	19.533	97.879	98.343	-102.166	-101.667	0.018
2400	19.560	98.711	99.175	-102.006	-101.497	0.013
2500	19.584	99.510	99.975	-101.856	-101.347	0.009
2600	19.606	100.279	100.744	-101.716	-101.207	0.006
2700	19.625	101.019	101.484	-101.586	-101.077	0.004
2800	19.642	101.733	102.198	-101.466	-100.957	0.003
2900	19.657	102.422	102.898	-101.356	-100.847	0.002
3000	19.671	103.089	103.575	-101.256	-100.747	0.001
3100	19.683	103.734	104.230	-101.166	-100.657	0.000
3200	19.695	104.359	104.865	-101.086	-100.567	0.000
3300	19.705	104.966	105.472	-101.016	-100.487	0.000
3400	19.715	105.554	106.060	-100.956	-100.417	0.000
3500	19.724	106.122	106.628	-100.906	-100.357	0.000
3600	19.732	106.681	107.177	-100.866	-100.307	0.000
3700	19.739	107.222	107.716	-100.836	-100.267	0.000
3800	19.746	107.749	108.243	-100.816	-100.237	0.000
3900	19.752	108.262	108.756	-100.806	-100.217	0.000
4000	19.758	108.762	109.256	-100.806	-100.207	0.000
4100	19.763	109.250	109.744	-100.816	-100.207	0.000
4200	19.768	109.726	110.222	-100.836	-100.217	0.000
4300	19.773	110.191	110.685	-100.866	-100.247	0.000
4400	19.778	110.646	111.130	-100.906	-100.297	0.000
4500	19.782	111.090	111.556	-100.956	-100.357	0.000
4600	19.786	111.525	111.972	-101.016	-100.427	0.000
4700	19.789	111.951	112.379	-101.086	-100.507	0.000
4800	19.793	112.367	112.774	-101.166	-100.597	0.000
4900	19.796	112.775	113.159	-101.256	-100.697	0.000
5000	19.799	113.175	113.526	-101.356	-100.807	0.000
5100	19.802	113.566	113.882	-101.466	-100.927	0.000
5200	19.804	113.952	114.229	-101.586	-101.057	0.000
5300	19.806	114.329	114.566	-101.716	-101.197	0.000
5400	19.809	114.697	114.894	-101.856	-101.347	0.000
5500	19.811	115.063	115.211	-101.996	-101.497	0.000
5600	19.813	115.420	115.548	-102.146	-101.657	0.000
5700	19.815	115.771	115.875	-102.306	-101.827	0.000
5800	19.817	116.115	116.192	-102.476	-101.997	0.000
5900	19.819	116.454	116.510	-102.656	-102.177	0.000
6000	19.821	116.787	116.847	-102.846	-102.367	0.000

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1964; June 30, 1969

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
1090 (1)	1259 (2)
701 (1)	5001 (2)

Bond Distance: C-F = [1.33] Å

Bond Angle: F-C-F = [112.7]°

Product of the Moments of Inertia: I_AI_BI_C = [9.608 × 10⁻¹¹⁵] g³ cm⁶

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃). Details of the input data and the adjustment are given in (1). Kinetic data provide the most consistent paths to ΔH_F⁰ of CF₃(g). Forward and reverse activation energies for the reactions CHF₃(g) + X(g) → CF₃(g) + HX(g) have been reported for X = Cl by Coomber (2), for X = Br by Amphlett (3), and for X = I by Goy (4). Increases of about 0.3 kcal/mol in the reverse activation energies for X = Cl and Br were proposed by Arthur (5) on the basis of additional data. Combining these values and reducing to 298.15°K, we get ΔH_F⁰ = 2.93 ± 0.7 (X = Cl), 18.89 ± 0.7 (X = Br), and 35.5 ± 3 kcal/mol at 298.15°K for X = I. Coomber (2) reviewed data for the analogous reactions with X = CH₃ and CD₃; these yield ΔH_F⁰ = 0.6 ± 2 kcal/mol at 298.15°K for X = CH₃. Activation energies have also been reported (6) for CF₃I(g) + I₂(g) → CF₃I(g) + I₂(g) from which we derive the average value ΔH_F⁰ = 17.1 ± 2 kcal/mol. The data of Tschukou-Roux (7) for C₂F₆(g) + 2CF₃(g), recalculated as suggested by Coomber (8) but with JANAF functions, yield ΔH_F⁰ = 97.6 ± 6 kcal/mol. Differences between the calculated and observed values of ΔH_F⁰ are all less than half of the uncertainties assigned to the observed values.

The thorough discussion of photoionization data by Noutary (9) emphasized that CF₃⁺ is formed with large amounts of excess energy both during ionization of CF₃ and during fragmentation of other fluorides. The amount of excess energy varies with the parent molecule. This may also be involved in electron-impact studies and could account for some of the discrepancies in bond-dissociation energies derived from appearance potentials and ionization potentials. Such data have been summarized by Coomber (10). Ionization data were omitted from the simultaneous adjustment due to uncertainty in the amounts of excess energy.

Also omitted was the mass-spectrometric study of 3C₂F₄(g) + 4CF₃(g) → 2C₂F₆(g) + 2C₂F₄(g) by Ehler (11) which gave ΔH_F⁰ = -102 ± 3 kcal/mol. The discrepancy of 10 kcal/mol suggests that the data may not represent equilibrium for the above reaction. This reaction was one of many which resulted from heating MnF₃ in an effusion cell made of graphite.

Heat Capacity and Entropy

The bond length is assumed to be 1.33 Å by comparison with the molecules CF₃X, and the bond angle is estimated from molecular-orbital calculations of Morokuma (12) and Pople and coworkers (13). The nonplanar structure is consistent with electron-spin-resonance spectra (14) of CF₃ in krypton and xenon matrices, with infrared spectra of CF₃ in various matrices (15) and in the gaseous phase (16), and with photoionization spectra (17). The observed vibrational fundamentals of Carlson (18) are confirmed by the matrix spectra of Milligan (19). The latter estimated ν₄ to be in the range of 500 to 800 cm⁻¹. We choose the lower value by comparison with CF₃H, SiF₃H and SiF₃ (18).

The uncertainty in ν₄ corresponds to an uncertainty in the entropy of 0.4 eu at 300°K and 0.7 eu at 1000°K. Coomber (2) and Amphlett (3) used kinetic data to derive entropies of 63.2 eu at 350°K and 71.5 eu at 600°K. The calculated entropies from this table are higher by 2.0 and 1.7 eu, respectively. These differences are only slightly larger than our estimate of the uncertainty in the kinetic results. We estimate the overall uncertainty in the calculated entropies as 1.0 eu at 298°K and 1.6 eu at 1000°K.

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFPRC Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 52, 2183 (1956).
3. J. C. Amphlett and E. Whittle, Trans. Faraday Soc. 52, 2130 (1956).
4. N. A. Goy, A. Lord, and H. P. Fritchard, J. Phys. Chem. 65, 1086 (1961).
5. N. A. Goy, A. Lord, and H. P. Fritchard, J. Phys. Chem. 65, 1086 (1961).
6. Reference (4) Table III, G. S. Laurence, Trans. Faraday Soc. 53, 1155 (1957).
7. E. Tschukou-Roux, J. Chem. Phys. 43, 2251 (1965).
8. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 53, 1394 (1957).
9. C. J. Noutary, J. Res. Nat. Bur. Stand. 72A, 479 (1968).
10. J. W. Coomber and E. Whittle, Trans. Faraday Soc. 53, 2656 (1957).
11. T. C. Ehler, J. Phys. Chem. 65, 1086 (1961).
12. D. L. Beveridge, P. A. Dobosh and J. A. Pople, J. Chem. Phys. 48, 4801 (1968).
13. D. L. Beveridge, P. A. Dobosh and J. A. Pople, J. Chem. Phys. 48, 4803 (1968); M. S. Gordon and J. A. Pople, J. Chem. Phys. 49, 4643 (1968).
14. R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965).
15. G. E. Milligan, H. E. Cox, and J. J. Cornford, J. Chem. Phys. 24, 4058 (1956).
16. G. E. Milligan, H. E. Cox, and J. J. Cornford, J. Chem. Phys. 24, 4058 (1956).
17. C. Lifshitz and W. A. Chupka, J. Chem. Phys. 47, 3439 (1967).
18. D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 5330 (1965).
19. J. C. Amphlett and E. Whittle, Trans. Faraday Soc. 53, 2656 (1957).

CF₃

$$\Delta H_f^\circ = -139.4 \pm 0.8 \text{ kcal/mol}$$

$$\Delta H_f^{298.15} = -140.8 \pm 0.8 \text{ kcal/mol}$$

Point Group C_{3v}

$$S_{298.15}^\circ = 73.498 \pm 0.15 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	g , cm ⁻¹
1074 (1)	1185 (2)
742 (1)	539 (2)
284 (1)	260 (2)

$$\text{Bond Distance: C-F} = 1.332 \text{ \AA} \quad \text{C-I} = 2.130 \text{ \AA}$$

$$\text{Bond Angle: F-C-F} = 108.3 \pm 1^\circ \quad \text{F-C-I} = 110.62^\circ$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = 4.4095 \times 10^{-113} \text{ g}^3 \text{ cm}^6 \quad \sigma = 3$$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₆. Details of the input data and the adjustment are given in (1). Lord, Goy and Fritchard (2, 3) report equilibrium data for the reactions CF₃X(g) + I₂(g) = CF₃I(g) + XI(g) where X = H, Cl, and Br. In addition to these prime links, there is a weak link to CF₃ through kinetic studies of CF₃I(g) + I(g) = CF₃(g) + I₂(g). Data for this reaction (3, 12) yield the average value $\Delta H_f^\circ = 17.1 \pm 2 \text{ kcal/mol}$ at 298.15°K.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen (4), Anderson (5), and Wong and Schomaker (6). Differences among the data are small. The results of Anderson are adopted since they are intermediate between the others. Microwave data (7) are consistent with the adopted parameters. Infrared spectra of the gas were observed by several investigators (8, 9, 10) and Raman spectra of the liquid were obtained by Edgell and May (10). The vibrational assignments of (8, 10) are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. In particular, ν_6 is taken as 260 cm⁻¹ (from overtone and combination bands of the gas) rather than 265 cm⁻¹ (from the Raman spectra of the liquid). The approximate values of ν_2 , ν_3 and ν_6 have been confirmed by analysis (11) of absorption spectra in the UV.

The thermodynamic functions of this table are essentially the same as those calculated by (9). Uncertainty in the entropy is estimated to vary from 0.15 to 0.6 gibbs/mol over the range from 300 to 1000°K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for CCl₃(g) and CF₃(g). The principal moments of inertia are $I_A = 14.71 \times 10^{-39}$ and $I_B = I_C = 54.75 \times 10^{-39} \text{ g cm}^2$.

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. A. Lord, C. A. Goy and H. O. Pritchard, J. Phys. Chem. **71**, 2705 (1967).
3. C. A. Goy, A. Lord and H. O. Pritchard, J. Phys. Chem. **71**, 1086 (1967).
4. H. J. M. Bowen, Trans. Faraday Soc. **50**, 444 (1954).
5. R. E. Anderson, Dissertation Abstracts **13**, 60 (1969).
6. C. Wong and V. Schomaker, J. Chem. Phys. **28**, 1010 (1958).
7. J. Sheridan and M. Gordy, J. Chem. Phys. **20**, 591 (1952).
8. E. K. Plyler and N. Acquista, J. Res. Nat. Bur. Stand. **18**, 92 (1952).
9. F. R. McGee, F. F. Cleveland, A. G. Meister and C. E. Decker, J. Chem. Phys. **21**, 242 (1953).
10. W. F. Edgell and C. E. May, J. Chem. Phys. **22**, 1808 (1954).
11. L. H. Sutcliffe and A. D. Walsh, Trans. Faraday Soc. **57**, 873 (1961).
12. G. S. Laurence, Trans. Faraday Soc. **53**, 1155 (1957).

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	kcal/mol	ΔG ^c	Log K ^p
0	10.000	59.000	INFINITE	= 3.957	= 139.393		= 139.393	INFINITE
100	14.036	67.363	73.960	1.927	140.471	139.550	137.950	150.645
200	16.955	73.468	73.468	.000	140.800	138.503	136.503	100.040
300	17.002	73.603	73.466	.031	140.806	136.477	136.477	99.423
400	19.230	76.615	74.194	1.649	142.975	138.721	137.721	97.676
500	20.646	81.250	75.376	3.857	146.258	142.413	139.413	97.476
600	21.968	87.198	77.194	6.002	148.187	129.250	129.250	97.079
700	22.819	90.654	78.675	8.245	148.095	126.100	126.100	39.370
800	23.418	92.743	80.544	10.559	147.990	122.866	122.866	33.553
900	23.862	94.486	82.187	12.745	147.876	119.565	119.565	29.102
1000	24.196	95.900	83.732	15.358	147.760	116.737	116.737	25.153
1100	24.457	101.379	85.233	17.617	147.642	113.442	113.442	22.579
1200	24.661	103.516	86.669	20.217	147.521	110.354	110.354	20.135
1300	24.824	105.497	88.042	22.692	147.405	107.478	107.478	17.609
1400	24.955	107.352	89.361	25.161	147.296	104.810	104.810	16.250
1500	25.063	109.108	90.617	27.602	147.174	102.351	102.351	14.867
1600	25.152	110.687	91.817	30.193	147.063	99.302	99.302	13.427
1700	25.227	112.215	92.972	32.712	146.953	95.257	95.257	12.246
1800	25.290	113.656	94.002	35.236	146.847	92.221	92.221	11.187
1900	25.341	115.020	95.115	37.760	146.743	89.186	89.186	10.245
2000	25.381	116.326	96.175	40.307	146.641	86.160	86.160	9.415
2100	25.431	117.568	97.165	42.848	146.543	83.139	83.139	8.652
2200	25.466	118.752	98.119	45.392	146.450	80.125	80.125	7.960
2300	25.486	119.895	99.041	47.941	146.358	77.108	77.108	7.327
2400	25.501	120.991	99.922	50.488	146.268	74.088	74.088	6.748
2500	25.507	122.013	100.775	53.045	146.186	71.059	71.059	6.215
2600	25.568	123.015	101.630	55.601	146.111	68.093	68.093	5.724
2700	25.587	123.981	102.440	58.159	146.036	65.094	65.094	5.269
2800	25.600	124.810	103.200	60.710	145.962	62.067	62.067	4.847
2900	25.608	125.600	103.920	63.256	145.889	59.007	59.007	4.457
3000	25.633	126.679	104.732	65.882	145.836	56.115	56.115	4.088
3100	25.648	127.520	105.453	68.406	145.776	53.123	53.123	3.785
3200	25.647	128.334	106.156	70.971	145.723	50.134	50.134	3.424
3300	25.656	129.118	106.840	73.536	145.678	47.150	47.150	3.153
3400	25.666	129.876	107.500	76.100	145.634	44.178	44.178	2.871
3500	25.686	130.635	108.157	78.673	145.589	41.178	41.178	2.571
3600	25.694	131.356	108.791	81.242	145.553	38.195	38.195	2.319
3700	25.701	132.062	109.411	83.812	145.523	35.214	35.214	2.080
3800	25.708	132.748	110.016	86.382	145.496	32.242	32.242	1.859
3900	25.716	133.416	110.607	88.952	145.476	29.272	29.272	1.654
4000	25.720	134.067	111.186	91.525	145.459	26.271	26.271	1.435
4100	25.726	134.702	111.751	94.097	145.449	23.293	23.293	1.242
4200	25.731	135.322	112.305	96.670	145.443	20.311	20.311	1.037
4300	25.736	135.926	112.846	99.242	145.437	17.329	17.329	0.853
4400	25.740	136.519	113.379	101.817	145.441	14.345	14.345	0.691
4500	25.744	137.098	113.900	104.391	145.457	11.378	11.378	0.553
4600	25.748	137.664	114.410	106.966	145.471	8.396	8.396	0.439
4700	25.751	138.217	114.911	109.541	145.491	5.416	5.416	0.352
4800	25.753	138.758	115.400	112.112	145.512	2.451	2.451	0.289
4900	25.758	139.290	115.886	114.682	145.537	3.531	3.531	0.245
5000	25.761	139.811	116.357	117.268	145.584	1.584	1.584	0.214
5100	25.763	140.321	116.822	119.844	145.626	6.503	6.503	0.279
5200	25.766	140.822	117.278	122.420	145.674	1.495	1.495	0.399
5300	25.768	141.314	117.724	124.992	145.728	1.485	1.485	0.539
5400	25.771	141.794	118.160	127.574	145.785	1.464	1.464	0.696
5500	25.773	142.267	118.603	130.151	145.850	1.452	1.452	0.733
5600	25.775	142.731	119.030	132.729	145.920	21.440	21.440	0.837
5700	25.777	143.188	119.450	135.306	145.977	24.427	24.427	0.937
5800	25.779	143.638	119.861	137.878	146.035	27.414	27.414	1.037
5900	25.781	144.077	120.268	140.462	146.165	30.410	30.410	1.126
6000	25.783	144.510	120.670	143.041	146.258	33.400	33.400	1.217

Carbon Tetrafluoride (CF₄)

(Ideal Gas) GFW = 88.00475

CARBON TETRAFLUORIDE (CF₄)

(IDEAL GAS)

GFW = 88.00475

Point Group T_d $\Delta H_f^\circ = -221.61 \pm 0.3 \text{ kcal/mol}$ $S_{298.15}^\circ = 62.454 \pm 0.05 \text{ gibbs/mol}$ $\Delta H_f^\circ = -221.61 \pm 0.3 \text{ kcal/mol}$

Ground State Quantum Weight = 1

 $\Delta H_f^\circ = -221.61 \pm 0.3 \text{ kcal/mol}$

T, °K	C _p ^a	S ^b	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	6.300	0.000	INF INITE	3.043	-221.611	-221.611	-221.611	INF INITE
100	6.300	50.729	73.154	2.242	-222.212	-222.212	-222.212	478.902
200	11.322	57.306	63.686	1.276	-222.726	-222.726	-222.726	235.643
298	14.592	62.454	62.454	0.000	-223.040	-223.040	-223.040	155.669
300	14.648	62.454	62.454	0.027	-223.045	-223.045	-223.045	154.661
400	17.304	67.139	63.042	1.631	-223.227	-223.227	-223.227	114.021
500	19.290	71.225	64.294	3.465	-223.326	-223.326	-223.326	89.623
600	20.741	74.877	65.759	5.471	-223.362	-223.362	-223.362	73.352
700	21.599	77.122	67.300	7.600	-223.380	-223.380	-223.380	62.955
800	22.159	78.581	68.454	9.754	-223.386	-223.386	-223.386	55.648
900	23.166	83.617	70.362	12.110	-223.280	-223.280	-223.280	46.235
1000	23.613	86.282	71.632	14.450	-223.216	-223.216	-223.216	40.614
1100	23.960	88.550	73.250	16.829	-223.144	-223.144	-223.144	36.340
1200	24.234	90.687	74.614	19.239	-223.064	-223.064	-223.064	32.985
1300	24.463	92.633	75.783	21.683	-222.976	-222.976	-222.976	29.954
1400	24.631	94.414	77.179	24.129	-222.882	-222.882	-222.882	26.684
1500	24.777	96.119	78.366	26.599	-222.815	-222.815	-222.815	24.544
1600	24.899	97.722	79.585	29.083	-222.731	-222.731	-222.731	22.536
1700	25.001	99.234	80.859	31.576	-222.644	-222.644	-222.644	20.746
1800	25.086	100.661	82.111	34.081	-222.554	-222.554	-222.554	19.179
1900	25.161	102.024	83.359	36.595	-222.462	-222.462	-222.462	17.735
2000	25.224	103.317	84.599	39.115	-222.401	-222.401	-222.401	16.455
2100	25.279	104.549	85.740	41.640	-222.323	-222.323	-222.323	15.299
2200	25.327	105.726	86.848	44.170	-222.250	-222.250	-222.250	14.247
2300	25.369	106.853	87.916	46.704	-222.179	-222.179	-222.179	13.281
2400	25.406	107.933	88.945	49.244	-222.109	-222.109	-222.109	12.407
2500	25.439	108.971	89.938	51.786	-222.045	-222.045	-222.045	11.599
2600	25.468	109.969	90.972	54.332	-221.994	-221.994	-221.994	10.852
2700	25.494	110.934	91.964	56.860	-221.976	-221.976	-221.976	10.150
2800	25.516	111.869	92.918	59.383	-221.961	-221.961	-221.961	9.497
2900	25.539	112.754	93.841	61.981	-221.922	-221.922	-221.922	8.892
3000	25.556	113.620	94.738	64.538	-221.774	-221.774	-221.774	8.335
3100	25.575	114.459	95.615	67.095	-221.735	-221.735	-221.735	7.844
3200	25.591	115.269	96.474	69.653	-221.699	-221.699	-221.699	7.404
3300	25.605	116.053	97.304	72.211	-221.673	-221.673	-221.673	7.012
3400	25.618	116.823	98.131	74.774	-221.639	-221.639	-221.639	6.645
3500	25.630	117.566	98.970	77.336	-221.618	-221.618	-221.618	6.058
3600	25.641	118.288	99.804	79.900	-221.594	-221.594	-221.594	5.674
3700	25.649	118.991	100.624	82.465	-221.575	-221.575	-221.575	5.345
3800	25.661	119.671	101.429	85.031	-221.559	-221.559	-221.559	5.061
3900	25.669	120.342	102.219	87.597	-221.537	-221.537	-221.537	4.819
4000	25.677	120.992	102.992	90.164	-221.574	-221.574	-221.574	4.326
4100	25.685	121.626	103.732	92.732	-221.564	-221.564	-221.564	4.033
4200	25.692	122.249	104.449	95.301	-221.597	-221.597	-221.597	3.752
4300	25.698	122.861	105.134	97.869	-221.630	-221.630	-221.630	3.482
4400	25.704	123.440	105.813	100.440	-221.639	-221.639	-221.639	3.228
4500	25.710	124.018	106.481	103.011	-221.667	-221.667	-221.667	2.993
4600	25.715	124.583	107.139	105.582	-221.701	-221.701	-221.701	2.749
4700	25.720	125.136	107.786	108.154	-221.741	-221.741	-221.741	2.525
4800	25.725	125.678	108.424	110.724	-221.781	-221.781	-221.781	2.316
4900	25.729	126.208	109.056	113.299	-221.837	-221.837	-221.837	2.104
5000	25.733	126.728	109.681	115.872	-221.894	-221.894	-221.894	1.906
5100	25.737	127.236	110.291	118.446	-221.957	-221.957	-221.957	1.716
5200	25.741	127.734	110.894	121.020	-222.025	-222.025	-222.025	1.533
5300	25.744	128.226	111.491	123.594	-222.094	-222.094	-222.094	1.357
5400	25.747	128.709	112.086	126.168	-222.161	-222.161	-222.161	1.187
5500	25.750	129.182	112.674	128.743	-222.226	-222.226	-222.226	1.024
5600	25.753	129.646	113.256	131.316	-222.290	-222.290	-222.290	0.866
5700	25.756	130.101	113.831	133.894	-222.359	-222.359	-222.359	0.714
5800	25.759	130.549	114.401	136.468	-222.428	-222.428	-222.428	0.566
5900	25.761	130.990	114.973	139.046	-222.473	-222.473	-222.473	0.424
6000	25.764	131.423	115.541	141.622	-222.520	-222.520	-222.520	0.287

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Sept. 30, 1964; June 30, 1969

CF 4

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
908.5 (1)	1283.0 (3)
435.0 (2)	631.5 (3)
Bond Distance: C-F = 1.320 Å	
Bond Angle: F-C-F = 109.47°	
Product of the Moments of Inertia: $I_A I_B I_C = 3.1489 \times 10^{-114} \text{ g cm}^6$	
$\sigma = 12$	

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of HF(g), HF(50 H₂O) and five closely related fluorides. Adjustment of 73 selected observations relating the 7 variables gives the following heats of formation in kcal/mol at 298.15°K: HF(g), -65.14 ± 0.2; HF(50 H₂O), -76.78 ± 0.1; NaF(c), -137.52 ± 0.2; BF₃(g), -271.42 ± 0.4; CF₄(g), -223.04 ± 0.3; NF₃(g), -31.43 ± 0.3; and C₂F₄(polymer), -198.2 ± 0.7. The ± values are estimates of the overall uncertainty including systematic error. Further details of the simultaneous adjustment are given in (1).

The selected value is essentially the same as that obtained by Greenberg and Hubbard (2) in their thorough calorimetric study of the combustion in fluorine of natural and synthetic graphite. Their result is confirmed by the data of Domalski and Armstrong (3) for combustion of graphite-Teflon mixtures. Reliable data (1) also link CF₄(g) with HF(n H₂O), NF₃(g) and C₂F₄(polymer). Armstrong (1, 3) critically reviewed the more uncertain data which were omitted from the adjustment.

Heat Capacity and Entropy

The fundamental vibrations are those observed in the gas-phase Raman spectra by Monostori and Weber (5) and the gas-phase infrared spectra by Maki et al. (6) and Chalmers and McKean (7). The frequencies are essentially the same as those selected by Shimanouchi (8) who also lists earlier spectral studies. Electron-diffraction studies of the gas were reported by Thornton (9) and Hoffman and Livingston (10). The adopted bond length is the average of these two results which differ by only 0.006 Å. The principal moments of inertia are $I_A = I_B = I_C = 14.657 \times 10^{-39} \text{ g cm}^2$.

The most significant uncertainty in the calculated thermodynamic functions is due to neglect of anharmonic contributions. Estimates for these contributions were given by Barho (11) and Albright et al. (12), and functions calculated with anharmonic terms were given by McBride et al. (13). Differences between McBride and this JANAF table vary from 0.1 to 0.75 gibbs/mol in Cp° and 0.05 to 0.49 gibbs/mol in S° over the range from 300 to 1000°K. Measurements (14) of Cp° (303-473°K) suggest that anharmonic contributions are significant, but the data are not sufficiently accurate to test the calculations of McBride (13). Heat capacity data (15) for the condensed phases were reviewed by Kelley and King (16) who derived S°_{298.15} = 62.8 ± 0.5 gibbs/mol for CF₄(g).

References

1. A. N. Syverud, Report AFRL-TR-69-70, Jan., 1969.
2. E. Greenberg and W. N. Hubbard, J. Phys. Chem., **72**, 222 (1968).
3. E. S. Domalski and G. T. Armstrong, J. Res. Nat. Bur. Stand., **71A**, 105 (1967).
4. G. T. Armstrong, U. S. Nat. Bur. Stand., Report 9803, 1-18 (1969).
5. B. Monostori and A. Weber, J. Chem. Phys., **33**, 1867 (1960).
6. A. Maki, E. K. Plyler and R. Thibault, J. Chem. Phys., **37**, 1899 (1962).
7. A. A. Chalmers and D. C. McKean, Spectrochim. Acta, **22**, 251 (1966).
8. T. Shimanouchi, U. S. Nat. Bur. Stand. NBS-NBS 6, 11 (1967).
9. C. G. Thornton, Dissertation Abstracts, **14**, 604 (1954); R. L. Livingston, Ann. Rev. Phys. Chem., **5**, 397 (1954).
10. C. W. W. Hoffman and R. L. Livingston, J. Chem. Phys., **21**, 565 (1953).
11. H. Barho, Kältetechnik, **17**, 219 (1965).
12. L. F. Albright, W. C. Categer and K. K. Innes, J. Am. Chem. Soc., **76**, 6017 (1954).
13. B. J. McBride, S. Helmel, J. G. Ehlers and S. Gordon, NASA SP-3001, 156 (1963).
14. Y. Huang and J. J. Martin, A. I. Ch. E. J., **10**, 89 (1964).
15. A. Eucken and E. Schröder, Z. Phys. Chem., **142**, 307 (1939).
16. K. K. Kelley and E. G. King, U. S. Bur. Mines Bull., **552**, 1961.

CF 4

Trifluoromethyl Hypofluorite (CF₃OF) (Ideal Gas) GFW = 104.004

Point Group C_{3v}

$$\Delta H_f^\circ = -181.9 \pm 3 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 77.06 \pm 0.7 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1



$$\Delta H_f^\circ = -182.9 \pm 3 \text{ kcal/mol}$$

T, °K	C _p	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	11.991	60.647	91.647	3.100	-182.182	3.86, 267
100	15.734	70.136	76.666	1.706	-182.516	3.86, 267
200	18.766	77.061	70.061	0.000	-182.516	124.510
300	19.029	77.179	77.061	-0.35	-182.803	123.184
400	21.755	83.042	77.842	2.366	-182.902	86.893
500	23.871	88.134	78.402	4.366	-182.911	69.893
600	25.685	92.632	81.259	6.835	-182.863	56.369
700	27.043	96.641	84.159	9.437	-182.777	47.096
800	27.744	100.242	85.073	12.135	-182.656	39.295
900	27.985	103.502	84.943	14.934	-182.546	34.382
1000	28.451	106.476	84.749	17.726	-182.413	29.951
1100	28.830	109.204	80.487	20.591	-182.274	26.326
1200	29.105	111.727	92.153	23.466	-182.132	23.311
1300	29.345	114.066	93.750	26.411	-181.992	20.760
1400	29.539	116.248	95.286	29.356	-181.850	18.675
1500	29.698	118.292	96.786	32.318	-181.709	16.963
1600	29.829	120.213	98.154	35.295	-181.571	15.530
1700	29.925	122.024	99.505	38.282	-181.434	13.571
1800	30.019	123.737	100.804	41.280	-181.304	12.276
1900	30.099	125.363	102.054	44.286	-181.176	11.118
2000	30.167	126.908	103.259	47.299	-181.052	10.076
2100	30.227	128.381	104.420	50.319	-180.931	9.136
2200	30.279	129.789	105.542	53.344	-180.819	8.279
2300	30.324	131.136	106.625	56.374	-180.709	7.598
2400	30.364	132.427	107.674	59.409	-180.604	6.983
2500	30.399	133.666	108.689	62.447	-180.510	6.415
2600	30.435	134.868	109.673	65.489	-180.420	5.897
2700	30.465	136.008	110.627	68.530	-180.337	5.425
2800	30.490	137.116	111.553	71.575	-180.259	4.997
2900	30.513	138.185	112.453	74.622	-180.189	4.613
3000	30.504	139.219	113.328	77.672	-180.127	4.268
3100	30.522	140.219	114.180	80.723	-180.069	3.975
3200	30.539	141.189	115.009	83.776	-180.019	3.728
3300	30.555	142.129	115.816	86.831	-179.975	3.515
3400	30.569	143.041	116.604	89.887	-179.937	3.328
3500	30.582	143.927	117.372	92.944	-179.908	3.165
3600	30.594	144.789	118.121	96.003	-179.882	3.017
3700	30.605	145.627	118.853	99.063	-179.865	2.883
3800	30.615	146.444	119.569	102.124	-179.853	2.761
3900	30.624	147.239	120.266	105.186	-179.850	2.649
4000	30.633	148.014	120.952	108.249	-179.859	2.546
4100	30.641	148.771	121.622	111.313	-179.861	2.451
4200	30.648	149.509	122.277	114.377	-179.877	2.365
4300	30.655	150.231	122.916	117.442	-179.898	2.287
4400	30.662	150.936	123.547	120.508	-179.929	2.215
4500	30.668	151.625	124.164	123.575	-179.964	2.148
4600	30.674	152.299	124.768	126.642	-180.005	2.086
4700	30.680	152.959	125.361	129.709	-180.055	2.028
4800	30.685	153.604	125.942	132.778	-180.109	1.974
4900	30.689	154.237	126.511	135.846	-180.171	1.924
5000	30.693	154.857	127.074	138.915	-180.239	1.876
5100	30.697	155.465	127.625	141.985	-180.315	1.830
5200	30.701	156.061	128.166	145.055	-180.396	1.786
5300	30.705	156.646	128.698	148.125	-180.483	1.743
5400	30.709	157.220	129.221	151.196	-180.579	1.701
5500	30.712	157.784	129.745	154.267	-180.680	1.660
5600	30.715	158.337	130.261	157.338	-180.788	1.620
5700	30.717	158.881	130.768	160.410	-180.904	1.581
5800	30.720	159.415	131.268	163.482	-181.023	1.543
5900	30.723	159.940	131.761	166.554	-181.151	1.505
6000	30.726	160.456	132.245	169.626	-181.284	1.467

Mar. 31, 1965, Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1294.4 (1)	679.0 (1)	1223.2 (1)
1262.5 (1)	584.1 (1)	807.5 (1)
947.3 (1)	433.7 (1)	250.0 (1)
882.1 (1)	227.5 (1)	Internal rotation

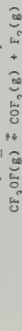
Bond Distances: C-F = [1.331] Å F-O = [1.42] Å C-O = [1.43] Å

Bond Angles: C-O-F = [103.2°] F-C-F = [109.5°]

Product of Moments of Inertia: I_AI_BI_C = 1.138 × 10⁻¹¹³ g³ cm⁶

Heat of Formation

Porter and Cady (1) measured equilibrium constants for the reaction



in the temperature range 630-750°K. Equilibrium constants were also determined with excess fluorine added to the system.

Second and third law analyses of these data yield the following heats of reaction:

Set 1	Set 2	Set 3	Set 4
27.65 ± 0.2	25.11 ± 0.3	30.09	7.2 ± 0.5
ΔH ₂₉₈ ^o 2nd law	ΔH ₂₉₈ ^o 3rd law	Drift	
kcal/mol	kcal/mol	gibbs/mol	

The third law analyses indicate significant trends within each set of equilibrium data. If the entire error is assigned to the free energy functions, then the drifts in the third law analysis imply that the free energy functions for CF₃OF should be increased by 3.6 or 7.2 gibbs/mol. However, the real error in these free energy functions is probably no larger than 1 gibbs/mol in the temperature range of the experimental data. Apparently, the equilibrium reaction investigated by Porter and Cady (1) was affected by side reactions possibly involving perfluorodimethyl peroxide. However, since the only other approach to the heat of formation of CF₃OF involves bond energies, we adopt the third law value, ΔH₂₉₈^o = 30.1 kcal/mol, and derive ΔH₂₉₈^o(CF₃OF, g) = -182.8 ± 3 kcal/mol with ΔH₂₉₈^o(COF₂, g) = -152.7 ± 0.4 kcal/mol (2).

Czarnowski et al. (3) recently determined the O-F bond energy in CF₃OF from kinetic studies on the thermal decomposition of CF₃OF in the presence of SO₃. They reported the value D(O-F) = 43.5 ± 0.5 kcal/mol. Combining this result with the following data,

ΔH ₂₉₈ ^o (C, g) = 170.89 ± 0.45 kcal/mol (4)
ΔH ₂₉₈ ^o (F, g) = 18.86 ± 0.40 kcal/mol (5)
ΔH ₂₉₈ ^o (O, g) = 59.559 ± 0.03 kcal/mol (6)
Do(C-F) = 117.4 kcal/mol (from ΔH ₂₉₈ ^o (CF ₄ , g) = -223.04 ± 0.3 kcal/mol (7))
Do(C-O) = 84 kcal/mol (8)

we derive ΔH₂₉₈^o(CF₃OF, g) = -173.8 kcal/mol.

The value determined from Porter and Cady's equilibrium data is adopted here. H₂O₂^o is determined to be -4.086 kcal/mol.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared and Raman studies of Wilt and Jones (9) and are in reasonable agreement with nine of the twelve expected fundamentals observed by Lagemann et al. (10). Bond lengths and angles are estimated quantities chosen by Wilt and Jones (9). Individual moments of inertia calculated from these estimated molecular constants are I_A = 14.723 × 10⁻³⁹ g cm², I_B = 27.796 × 10⁻³⁹ g cm², and I_C = 27.801 × 10⁻³⁹ g cm². The contributions of hindered internal rotation to the thermodynamic properties of CF₃OF are from the tables of Pitzer and Gwinn (11). The reduced moment of inertia, I_r, and the potential barrier, V₀, are from the work of Wilt and Jones (9) and are:

$$I_r = 2.939 \times 10^{-39} \text{ g cm}^2$$

$$V_0 = 1130 \text{ cal/mol (} V_{12} = 56 \text{ cm}^{-1} \text{)}$$

References

1. R. S. Porter and G. H. Cady, J. Amer. Chem. Soc., **79**, 5628 (1957).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Dec. 31, 1969.
3. J. Czarnowski, R. Castellano, and H. J. Schumacher, Chem. Commun., **20**, 1755 (1964).
4. R. S. Porter, J. Amer. Chem. Soc., **80**, 1862 (1958).
5. Ref. 2, Sept. 30, 1965.
6. Ref. 2, June 30, 1962.
7. Ref. 2, June 30, 1969.
8. E. S. Gould, "Inorganic Reactions and Structure," Revised Ed., Holt, Rinehart, and Winston, New York, 1962, p. 138.
9. R. M. Wilt and E. A. Jones, J. Inorg. Nucl. Chem., **30**, 2933 (1964).
10. R. M. Wilt and E. A. Jones, J. Mol. Spectry., **20**, 1768 (1952).
11. K. S. Pitzer and W. D. Gwinn, J. Chem. Phys., **10**, 428 (1942).



Methylidyne (CH)

(Ideal Gas)

GFW = 13.01912

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o ₂₉₈)/T	cal/mol ΔH ^o	ΔG ^o	Log K _p
0	∞.000	INFINITE	2.084	141.178	INFINITE
100	6.993	40.920	141.178	139.119	-306.046
200	6.972	41.258	141.178	138.615	-308.286
298	6.972	41.721	142.000	138.082	-309.821
300	6.972	41.764	142.002	138.073	-309.821
400	6.984	43.771	142.107	138.274	-309.599
500	7.027	46.512	142.139	138.566	-309.196
600	7.112	49.421	142.117	138.852	-308.602
700	7.240	52.477	142.059	139.136	-307.848
800	7.401	55.704	141.978	139.416	-306.955
900	7.586	59.166	141.885	139.693	-305.952
1000	7.783	62.831	141.789	139.968	-304.852
1100	7.985	66.686	141.690	140.242	-303.652
1200	8.196	70.724	141.596	140.517	-302.352
1300	8.380	74.941	141.503	140.787	-300.952
1400	8.564	79.341	141.418	141.057	-299.452
1500	8.735	83.929	141.336	141.326	-297.852
1600	8.893	88.696	141.258	141.596	-296.152
1700	9.036	93.641	141.187	141.866	-294.352
1800	9.165	98.764	141.120	142.136	-292.452
1900	9.280	104.064	141.057	142.406	-290.452
2000	9.382	109.541	140.998	142.676	-288.352
2100	9.472	115.196	140.942	142.946	-286.152
2200	9.552	120.929	140.886	143.216	-283.852
2300	9.619	126.741	140.833	143.486	-281.452
2400	9.678	132.624	140.780	143.756	-278.952
2500	9.730	138.579	140.727	144.026	-276.352
2600	9.774	144.604	140.673	144.296	-273.652
2700	9.811	150.699	140.619	144.566	-270.852
2800	9.844	156.864	140.564	144.836	-267.952
2900	9.871	163.099	140.507	145.106	-264.952
3000	9.895	169.404	140.448	145.376	-261.852
3100	9.916	175.779	140.389	145.646	-258.652
3200	9.933	182.224	140.326	145.916	-255.352
3300	9.949	188.739	140.261	146.186	-251.952
3400	9.962	195.324	140.194	146.456	-248.452
3500	9.975	201.979	140.123	146.726	-244.852
3600	9.985	208.694	140.051	146.996	-241.152
3700	9.995	215.469	139.978	147.266	-237.352
3800	10.005	222.304	139.896	147.536	-233.452
3900	10.014	229.199	139.814	147.806	-229.452
4000	10.023	236.144	139.730	148.076	-225.352
4100	10.032	243.139	139.643	148.346	-221.152
4200	10.040	250.184	139.552	148.616	-216.852
4300	10.050	257.279	139.456	148.886	-212.452
4400	10.059	264.424	139.362	149.156	-207.952
4500	10.069	271.619	139.262	149.426	-203.352
4600	10.079	278.864	139.160	149.696	-198.652
4700	10.089	286.159	139.055	149.966	-193.852
4800	10.100	293.504	138.947	150.236	-188.952
4900	10.112	300.899	138.838	150.506	-183.952
5000	10.124	308.344	138.725	150.776	-178.852
5100	10.137	315.839	138.608	151.046	-173.652
5200	10.150	323.384	138.491	151.316	-168.352
5300	10.164	330.979	138.370	151.586	-162.852
5400	10.178	338.624	138.247	151.856	-157.152
5500	10.193	346.319	138.121	152.126	-151.252
5600	10.208	354.064	137.994	152.396	-145.152
5700	10.224	361.859	137.864	152.666	-138.852
5800	10.240	369.704	137.731	152.936	-132.352
5900	10.257	377.599	137.596	153.206	-125.652
6000	10.274	385.544	137.460	153.476	-118.752

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1967

CH

(Ideal Gas)

METHYLIDYNE (CH)

Ground State Configuration ²ΠΔH_f^o = 141.2 ± 0.1 kcal/molS_{298.15}^o = 43.72 ± 0.01 gibbs/molΔH_f^o_{298.15} = 142.0 ± 0.1 kcal/mol

Electronic Levels and Multiplicities

e_i, cm⁻¹g_i

0	2
17.9	2
[4500]	4
23150	4
25949	2
31821	2

ω_ex_e^o = 64.29 cm⁻¹

σ = 1

B_e = 14.455 cm⁻¹r_e = 1.1198 Å

Heat of Formation

G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950, reanalyzed the rotational predissociation reported by T. Shidei, Japan J. Phys. 11, 23 (1936), and concluded that D₀^o = 80.0 kcal/mol (3.47 eV). This yields ΔH_f^o_{298.15}(CH, g) = 142.0 kcal/mol and is the adopted value.

R. G. Brewer and F. L. Kester, J. Chem. Phys. 40, 812 (1964), have confirmed the value as 142 ± 5 kcal/mol, from an equilibrium study of the temperature variation of the intensity of the ²Δ_g-²Π emission band.

M. Linevsky, J. Chem. Phys. 47, 3485 (1967), determined the concentration of CH radicals in equilibrium with 1 atm. of hydrogen gas, by application of a high resolution spectro-photographic technique to three electronic transitions in absorption.

A third law analysis, using the present functions, of 27 determinations in the temperature range 3065 - 3155°K yielded ΔH_f^o₂₉₈(CH, g) = 142.01 ± 1.28 kcal/mol with a negligible drift. This value is in excellent agreement with the spectroscopic predissociation value.

Heat Capacity and Entropy

The vibrational and rotational constants and electronic levels are from Herzberg, loc. cit., with the exception of the estimated ⁴Π level. All the constants have been adjusted to the normal isotopic abundances for both carbon and hydrogen. The ⁴Π level is estimated from the ab initio calculations of A. C. Hurley, Proc. Roy. Soc. (London), 249A, 402 (1959), which include electron correlation effects. Earlier LCAO calculations had predicted the ⁴Π level to be the ground state, but J. Higuchi, J. Chem. Phys. 22, 1339 (1954), used LCAO-SCF calculations and obtained the ⁴Π level at 800 cm⁻¹. M. Kraus and J. F. Wehrer, J. Chem. Phys. 29, 1287 (1958), using essentially the same technique as Hurley, obtained ⁴Π at 3000 cm⁻¹.

Monochloromethylene (CHCl)

GFW = 48.47212

(Ideal Gas)

Point Group C_s $\Delta H_f^\circ = [79.9 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = 56.12 \pm 0.05 \text{ gibbs/mol}$ $\Delta H_f^\circ = [80 \pm 10] \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	gibbs/mol		kcal/mol		Log Kp	
		S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	
100	7.000	47.000	INF INITE	2.427	79.939	79.939	INF INITE
200	8.170	52.750	56.900	1.830	80.007	77.509	84.697
298	8.780	56.118	56.118	.000	80.000	76.270	55.997
300	8.793	56.173	56.118	.016	79.998	76.247	55.546
400	9.494	58.799	56.472	.931	79.905	75.069	50.963
500	10.146	60.959	57.152	1.913	79.792	73.799	50.257
600	10.746	62.895	57.962	2.960	79.677	72.610	26.448
700	11.434	64.606	58.791	4.071	79.572	71.442	22.305
800	12.040	66.176	59.617	5.247	79.493	70.286	19.201
900	12.694	67.634	60.429	6.486	79.444	69.137	16.769
1000	13.247	69.001	61.217	7.784	79.430	68.093	14.060
1100	13.720	70.286	61.984	9.133	79.445	66.848	13.281
1200	14.104	71.497	62.727	10.525	79.484	65.702	11.966
1300	14.403	72.639	63.446	11.951	79.538	64.551	10.852
1400	14.654	73.715	64.141	13.402	79.604	63.337	9.897
1500	14.879	74.729	64.814	14.873	79.675	62.030	9.066
1600	14.881	75.666	65.464	16.357	79.746	61.071	8.342
1700	14.941	76.591	66.092	17.848	79.815	59.903	7.701
1800	14.970	77.466	66.699	19.344	79.878	58.729	7.131
1900	14.975	78.285	67.286	20.841	79.934	57.534	6.629
2000	14.964	79.053	67.854	22.330	79.981	56.374	6.160
2100	14.942	79.753	68.403	23.834	80.020	55.194	5.744
2200	14.912	80.487	68.935	25.326	80.047	54.009	5.365
2300	14.879	81.109	69.450	26.816	80.065	52.827	5.020
2400	14.845	81.714	69.944	28.304	80.076	51.637	4.704
2500	14.807	82.347	70.433	29.788	80.065	50.458	4.411
2600	14.771	82.927	70.903	31.263	80.057	49.273	4.142
2700	14.737	83.464	71.358	32.739	80.035	48.088	3.892
2800	14.704	84.019	71.801	34.211	80.004	46.906	3.661
2900	14.668	84.584	72.233	35.680	79.964	45.724	3.446
3000	14.645	85.031	72.650	37.145	79.913	44.544	3.245
3100	14.618	85.511	73.057	38.609	79.858	43.367	3.057
3200	14.593	85.975	73.453	40.069	79.799	42.191	2.882
3300	14.560	86.424	73.840	41.527	79.718	41.016	2.716
3400	14.521	86.858	74.214	42.984	79.624	39.846	2.566
3500	14.531	87.290	74.593	44.437	79.549	38.676	2.415
3600	14.513	87.689	74.942	45.890	79.455	37.508	2.277
3700	14.497	88.046	75.292	47.340	79.352	36.345	2.147
3800	14.482	88.419	75.633	48.789	79.244	35.186	2.024
3900	14.466	88.769	75.963	50.237	79.130	34.034	1.906
4000	14.456	89.215	76.294	51.683	79.006	32.878	1.796
4100	14.445	89.572	76.614	53.128	78.878	31.719	1.691
4200	14.434	89.920	76.926	54.572	78.744	30.573	1.591
4300	14.423	90.267	77.233	56.017	78.603	29.426	1.496
4400	14.415	90.591	77.532	57.457	78.459	28.285	1.405
4500	14.406	90.915	77.826	58.898	78.307	27.142	1.318
4600	14.398	91.231	78.114	60.338	78.151	26.010	1.236
4700	14.390	91.541	78.396	61.777	77.990	24.880	1.157
4800	14.381	91.847	78.673	63.216	77.823	23.752	1.081
4900	14.377	92.149	78.943	64.655	77.651	22.626	1.008
5000	14.370	92.430	79.212	66.091	77.477	21.505	.940
5100	14.364	92.715	79.474	67.524	77.296	20.385	.874
5200	14.358	92.994	79.731	68.964	77.111	19.272	.810
5300	14.351	93.267	80.000	70.400	76.921	18.165	.749
5400	14.347	93.535	80.233	71.833	76.727	17.064	.690
5500	14.342	93.799	80.477	73.269	76.529	15.954	.634
5600	14.337	94.057	80.717	74.703	76.324	14.852	.580
5700	14.332	94.311	80.953	76.136	76.115	13.753	.527
5800	14.327	94.561	81.185	77.569	75.902	12.653	.479
5900	14.323	94.805	81.416	78.999	75.687	11.554	.434
6000	14.318	95.046	81.640	80.433	75.468	10.448	.382

Dec. 31, 1969

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	1
[3000]	3
12288	1

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	
[2800] (1)	
1201 (1)	
815 (1)	

Bond Distance: C-H = 1.12 Å C-Cl = 1.689 Å

Bond Angle: H-C-Cl = 103.4°

 $\sigma = 1$ Product of the Moments of Inertia: $I_A I_B I_C = 3.9877 \times 10^{-117} \text{ g cm}^6$

Heat of Formation

The heat of formation can be estimated as the average of those of the CH₂ and CCl₂ radicals, which gives $\Delta H_f^\circ(\text{CHCl}, g) = 74.5 \pm 15 \text{ kcal/mol}$. A better value for the heat of formation can be obtained by considering the reactions $\text{CHCl} + \text{CH} + \text{Cl} \text{ and } \text{CHCl} + \text{CCl} + \text{H}$. When $\Delta H_f^\circ(\text{CCl}, g) = 74.5 \text{ kcal/mol}$ is substituted into the above equations it gives $D_{\text{C-Cl}} = 98 \text{ kcal}$ and $D_{\text{C-H}} = 98 \text{ kcal}$. Although these values are not unreasonable the $D_{\text{C-H}}$ value appears to be too high compared to that in CFH. Thus, we adopt $\Delta H_f^\circ(\text{CHCl}, g) = 80 \text{ kcal/mol}$ which gives $D_{\text{C-Cl}} = 91 \text{ kcal}$ and $D_{\text{C-H}} = 92 \text{ kcal}$.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis (1) from an analysis of the rotational structure of the visible absorption bands. The estimated triplet state is based on the electronic levels of CCl₂ and CH₂ as given in these tables. The vibrational levels are from Jacob and Milligan (2) who investigated the infrared spectrum of matrix-isolated CHCl, and also estimated the missing frequency. The individual moments of inertia are $I_A = 4.6455 \times 10^{-39} \text{ g cm}^2$, $I_B = 1.780 \times 10^{-40} \text{ g cm}^2$, and $I_C = 4.8235 \times 10^{-39} \text{ g cm}^2$.

References

1. A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 575 (1966).
2. M. E. Jacob and D. E. Milligan, J. Chem. Phys. **47**, 1626 (1967).

Chlorodifluoromethane (CHClF₂)

(Ideal Gas) GFW = 86.4689

CHLORODIFLUOROMETHANE (CHClF₂)

(IDEAL GAS)

GFW = 86.4689

Point Group C_{2v}

$\Delta H_f^\circ = -113.6 \pm 3$ kcal/mol

$S_{298.15}^\circ = 67.126 \pm 0.2$ gibbs/mol

$\Delta H_f^\circ = -115.1 \pm 3$ kcal/mol

Ground State Quantum Weight = 1

CHClF₂

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$

3024 (1) 812 (1) 1350 (1)

1312 (1) 598 (1) 1108 (1)

836 (1) 417 (1) 400 (1)

Bond Distance: C-H = 1.09 Å C-Cl = 1.74 Å C-F = 1.35 Å

Bond Angle: H-C-Cl = 107° Cl-C-F = 110.5° F-C-F = 107°

Product of the Moments of Inertia: $I_A I_B I_C = 3.43433 \times 10^{-114} \text{ g cm}^6$

Heat of Formation

Edwards and Small (1) determined a single equilibrium constant at 600°C for the reaction $2\text{CHClF}_2(\text{g}) + \text{C}_2\text{F}_4(\text{g}) + 2\text{HCl}(\text{g})$. The value was not obtained directly but was obtained by extrapolation to eliminate the effects of side reactions. The equilibrium constant was used with JANAF free energy functions (2) to obtain $\Delta H_f^\circ = 28.75$ kcal, which yields ΔH_f° (CHClF₂, g) = -115.1 kcal/mol. An uncertainty of ± 3 kcal/mol corresponds to an uncertainty of about $\pm 50\%$ in the equilibrium constant.

Heat Capacity and Entropy

The gas phase vibrational frequencies have been observed in the Raman by Holzer and Moser (3); they do not see anything in the 1350 cm⁻¹ region as reported in the liquid by Glockler and Edgell (4). Plyler and Benedict (5) in their assignment replaced an 831 cm⁻¹ frequency by 1178 cm⁻¹. We essentially adopt Glockler and Edgell's assignment with updated gas phase values for the observed frequencies. The microwave spectrum has been analysed by McLay and Mann (6) and Beeson et al. (7), who derive bond lengths and angles in excellent agreement with each other. The values given by Beeson et al. are adopted here.

Neelson and White (8) have measured the low temperature heat capacity and heat of vaporization and have reported an entropy in the gas phase at 232.5°K of 61.913 \pm 0.28 gibbs/mol. This compares with 63.959 gibbs/mol calculated from our adopted functions.

The individual moments of inertia are $I_A = 8.203 \times 10^{-39} \text{ g cm}^2$, $I_B = 17.402 \times 10^{-39} \text{ g cm}^2$ and $I_C = 24.060 \times 10^{-39} \text{ g cm}^2$.

References

1. J. W. Edwards and P. A. Small, Ind. Eng. Chem. Fundamentals **4**, 396 (1965).
2. JANAF Thermochemical Tables; C₂F₄ dated 6-30-69; HCl dated 9-30-64.
3. W. Holzer and H. Moser, J. Mol. Spectry, **20**, 185 (1966) and **25**, 123 (1968).
4. G. Glockler and W. F. Edgell, J. Chem. Phys. **9**, 224 (1941).
5. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **47**, 202 (1951).
6. D. B. McLay and C. R. Mann, Can. J. Phys. **40**, 61 (1962).
7. E. L. Beeson, T. L. Weatherly and Q. Williams, J. Chem. Phys. **37**, 2926 (1962).
8. E. F. Neelson and D. White, J. Amer. Chem. Soc. **79**, 5618 (1957).

gibbs/mol

$-(G^\circ - H^\circ_{298})/T$

$H^\circ - H^\circ_{298}$

ΔH_f°

ΔG_f°

Log Kp

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

ΔH_f°

ΔG_f°

Dec. 31, 1960; Sept. 30, 1961; Sept. 30, 1964; June 30, 1970

CHClF₂

Dichlorofluoromethane (CHCl₂F)

GFW = 102.9235

(Ideal Gas)

Point Group C_{2v}ΔH_f⁰ = [-66.36 ± 3] kcal/molS_{298.15}⁰ = 70.07 ± 0.2 gibbs/molΔH_f⁰_{298.15} = [-67.7 ± 3] kcal/mol

Ground State Quantum Weight = 1

T, °K	C _p ⁰	S ⁰	-(G ⁰ -H ⁰)/T	H ⁰ -H ²⁹⁸	ΔH ⁰	kcal/mol	Log K _p
0	-0.000	INFINITE	INFINITE	3.177	-	66.164	INFINITE
100	9.004	57.617	81.204	2.359	-66.983	64.954	141.937
200	11.993	64.786	71.322	1.307	-67.387	62.762	68.583
298	14.578	70.069	60.069	-0.000	-67.700	60.423	44.291
300	14.653	70.159	60.048	.027	-67.705	60.378	43.984
400	16.965	72.724	50.670	1.602	-67.939	57.636	24.201
500	18.447	78.607	41.873	3.367	-68.098	55.368	19.237
600	19.701	82.087	33.291	5.277	-68.201	52.812	15.866
700	20.661	84.159	24.774	7.296	-68.260	50.241	13.066
800	21.417	85.087	16.250	9.321	-68.285	47.666	10.946
900	22.017	85.705	7.725	11.375	-68.285	45.088	9.291
1000	22.510	86.113	0.200	13.402	-68.259	42.513	7.936
1100	22.918	86.359	-8.465	16.074	-68.216	39.941	6.906
1200	23.260	86.468	-17.768	19.384	-68.159	37.372	6.135
1300	23.559	86.459	-27.514	23.292	-68.093	34.803	5.535
1400	23.795	86.333	-37.221	26.768	-67.913	32.235	5.035
1500	24.005	86.113	-46.886	30.719	-67.648	29.668	4.623
1600	24.186	85.819	-56.519	34.119	-67.307	27.100	4.265
1700	24.343	85.468	-66.133	37.000	-66.893	24.531	3.950
1800	24.480	85.075	-75.738	39.415	-66.428	21.956	3.670
1900	24.599	84.659	-85.351	41.399	-65.928	19.379	3.420
2000	24.703	84.233	-95.000	43.000	-65.400	16.800	3.190
2100	24.796	83.819	-104.686	44.354	-64.854	14.225	2.980
2200	24.876	83.425	-114.425	45.468	-64.293	11.650	2.790
2300	24.943	83.059	-124.219	46.354	-63.719	9.075	2.620
2400	25.000	82.725	-134.068	47.028	-63.143	6.500	2.470
2500	25.047	82.425	-143.975	47.500	-62.567	3.925	2.330
2600	25.127	82.159	-153.938	47.875	-61.991	1.350	2.200
2700	25.217	81.925	-163.959	48.159	-61.415	-1.225	2.080
2800	25.317	81.725	-174.038	48.359	-60.839	-3.800	1.970
2900	25.426	81.559	-184.175	48.479	-60.263	-6.375	1.870
3000	25.542	81.425	-194.368	48.519	-59.687	-8.950	1.780
3100	25.664	81.325	-204.618	48.479	-59.111	-11.525	1.700
3200	25.791	81.259	-214.925	48.359	-58.535	-14.100	1.630
3300	25.923	81.225	-225.288	48.159	-57.959	-16.675	1.570
3400	26.060	81.225	-235.708	47.879	-57.383	-19.250	1.510
3500	26.201	81.259	-246.183	47.500	-56.807	-21.825	1.450
3600	26.345	81.325	-256.713	47.028	-56.231	-24.400	1.390
3700	26.493	81.425	-267.298	46.459	-55.655	-26.975	1.330
3800	26.644	81.559	-277.938	45.799	-55.079	-29.550	1.270
3900	26.798	81.725	-288.633	45.068	-54.503	-32.125	1.210
4000	26.955	81.925	-299.383	44.279	-53.927	-34.700	1.150
4100	27.115	82.159	-310.188	43.439	-53.351	-37.275	1.090
4200	27.278	82.425	-321.048	42.559	-52.775	-39.850	1.030
4300	27.443	82.725	-331.963	41.639	-52.199	-42.425	0.970
4400	27.610	83.059	-342.933	40.679	-51.623	-45.000	0.910
4500	27.779	83.425	-353.958	39.679	-51.047	-47.575	0.850
4600	27.950	83.819	-365.038	38.639	-50.471	-50.150	0.790
4700	28.123	84.233	-376.173	37.559	-49.895	-52.725	0.730
4800	28.298	84.659	-387.363	36.439	-49.319	-55.300	0.670
4900	28.475	85.075	-398.608	35.279	-48.743	-57.875	0.610
5000	28.653	85.468	-409.908	34.079	-48.167	-60.450	0.550
5100	28.832	85.819	-421.263	32.839	-47.591	-63.025	0.490
5200	29.012	86.113	-432.673	31.559	-47.015	-65.600	0.430
5300	29.193	86.359	-444.138	30.239	-46.439	-68.175	0.370
5400	29.375	86.559	-455.658	28.879	-45.863	-70.750	0.310
5500	29.558	86.725	-467.233	27.479	-45.287	-73.325	0.250
5600	29.742	86.859	-478.863	26.039	-44.711	-75.900	0.190
5700	29.927	86.959	-490.548	24.559	-44.135	-78.475	0.130
5800	30.112	87.025	-502.288	23.039	-43.559	-81.050	0.070
5900	30.297	87.068	-514.083	21.479	-42.983	-83.625	0.010
6000	30.482	87.088	-525.933	20.000	-42.407	-86.200	-0.050

Dec. 31, 1960; Sept. 30, 1964; June 30, 1970

Vibrational Frequencies and Degeneracies

ω ₁ , cm ⁻¹	ω ₂ , cm ⁻¹	ω ₃ , cm ⁻¹	ω ₄ , cm ⁻¹
3023 (1)	741 (1)	1242 (1)	
1313 (1)	455 (1)	806 (1)	
1079 (1)	270 (1)	368 (1)	
Bond Distance: C-H = 1.09 Å C-Cl = 1.75 Å C-F = 1.367 Å			
Bond Angle: Cl-C-Cl = 112°12' F-C-Cl = 109° H-C-Cl = 109°45'			
Product of the Moments of Inertia: I _A I _B I _C = 1.11593 × 10 ⁻¹¹³ g ³ cm ⁶			
σ = 1			

Heat of Formation

The change in heat of atomization by successive replacement of F by Cl in the CF₄ series follows a regular pattern (see CCl₂F₂ table). A similar pattern is to be expected in the CHCl₃ series. The first replacement of the series is, in fact, 4 kcal higher than the mean versus 3.8 kcal higher in the CF₃-CCl₃ series. Thus, we have selected the atomization energy of the second and third replacements to continue this pattern. In this manner we have selected the atomization energy of CHCl₂F as 367.4 kcal which corresponds to ΔH_f⁰ (CHCl₂F, g) = -67.7 kcal/mol. With this adopted value, the successive replacement of F by Cl changes the heat of atomization by 41.4, 37.3 and 33.0 kcal.

Heat Capacity and Entropy

Holzer (1) has reported the gas phase Raman spectrum which is in excellent agreement with the assignments of Plyler and Benedict (2). The only discrepancy is in ν₇, which Plyler and Benedict assign at 1242 cm⁻¹, and Holzer (1) does not report a band in this region. Holzer does, however, report a band at 728 cm⁻¹ which has not been reported in the earlier liquid studies. There is strong evidence from correlations with CHCl₃ and CHF₃ that two frequencies should occur between 1220 and 1376 cm⁻¹. On this basis we adopt the assignment of Plyler and Benedict for ν₇, while accepting the gas phase values of Holzer for the other frequencies. The extra band at 728 cm⁻¹ is not used. It is probable that the bands at 741 and 728 cm⁻¹ are due to Fermi resonance of ν₄ with 2ν₉; the unperturbed level would lie at 735 cm⁻¹. The symmetry classes of ν₄ and 2ν₉ are identical and thus Fermi resonance is allowed.

Holzer (3) has reported the molecular structure from his microwave investigations. The individual principal moments of inertia are I_A = 12.053 × 10⁻³⁹ g cm², I_B = 25.684 × 10⁻³⁹ g cm² and I_C = 36.047 × 10⁻³⁹ g cm².

References

1. W. Holzer, J. Mol. Spectry, **25**, 123 (1968).
2. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **42**, 202 (1951).
3. D. B. McLay, Can. J. Phys. **42**, 720 (1964).

Chloroform (CHCl₃)

(Ideal Gas) GFW = 119.3781

Point Group C_{3v}S°_{298.15} = 70.628 ± 0.01 gibbs/mol
Ground State Quantum Weight = 1ΔH°_f = -23.49 ± 0.3 kcal/molΔH°_f = -24.66 ± 0.3 kcal/mol

Bond Distances: C-H = 1.100 Å C-Cl = 1.758 Å

Bond Angles: Cl-C-Cl = 111°18', H-C-Cl = 107°34', σ = 3

Product of the Moments of Inertia: I_AI_BI_C = 3.2811 × 10⁻¹¹³ g³cm⁶

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	g, cm ⁻¹
3034 (1)	1220 (2)
680 (1)	774 (2)
363 (1)	261 (2)

Heat of Formation

Hu and Sinke (1) have measured the heat of combustion of CHCl₃(l) in the rotating bomb calorimeter, using As₂O₃ solution as the reducing agent. The reported ΔH°_c = -113.10 kcal/mol for CHCl₃(l) + 0.5O₂ + H₂O(l) + CO₂(g) + 3HCl(600H₂O, aq) which leads to ΔH°_f(CHCl₃, l) = -32.10 kcal/mol, using ΔH°_f = -84.051, -39.823, -68.315 kcal/mol for CO₂(g), HCl(600H₂O, aq) and H₂O(l), respectively (2). The standard deviation of six combustion runs was 0.09 kcal/mol. Employing the heat of vaporization of chloroform at 298°K as 7.44 kcal/mol (3), we obtain ΔH°_f298 (CHCl₃, g) = -24.66 kcal/mol which is adopted in the tabulation.

L. Smith et al. (4), based on the combustion data of E. Efring (5), re-evaluated the heat of combustion of chloroform at 18.7°C as ΔH°_c/M = -847.7 cal/g for CHCl₃(l) + 0.5O₂(g) + H₂O(l) + CO₂(g) + 3HCl(600H₂O, aq). This value needs to be further corrected for a change in the heat of oxidation of As₂O₃(g) and calculated to 25°C to give ΔH°_f298 = -113.44 kcal/mol, ΔH°_f298 (CHCl₃, l) = -31.76 kcal/mol and ΔH°_f298 (CHCl₃, g) = -24.32 kcal/mol.

Heat Capacity and Entropy

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (7), based on infrared and Raman spectra measured by Nielsen and Ward (8), Madigan and Cleveland (9), Gibian and McKinney (10) and Stanevich and Yaroslavskii (11).

The bond distances and angles were obtained from the microwave spectra by Jen and Lide (12). The three principal moments of inertia are I_A = 7.719 × 10⁻³⁹ and I_C = 49.603 × 10⁻³⁹ g cm².

References

- (1) A. T. Hu and G. C. Sinke, presented at the 23rd Calorimetry Conference, Midland, Mich., 1968.
- (2) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
- (3) J. H. Mathews, J. Am. Chem. Soc. 88, 562 (1926).
- (4) L. Smith, L. Bjallerup, S. Krook and H. Westermarck, Acta Chem. Scand. 7, 65 (1953).
- (5) E. Efring, Ph. D. Thesis, University of Lund, Lund, Sweden, 1938.
- (6) S. Sunner and S. Thoren, Acta Chem. Scand. 18, 1528 (1964).
- (7) T. Shimanouchi, U. S. Natl. Bur. Std. NBS-RS-56, 1967.
- (8) J. R. Nielsen and N. E. Ward, J. Chem. Phys. 10, 81 (1941).
- (9) J. R. Madigan and F. F. Cleveland, J. Chem. Phys. 12, 119 (1951).
- (10) T. G. Gibian and D. S. McKinney, J. Am. Chem. Soc. 73, 1431 (1951).
- (11) A. E. Stanevich and N. G. Yaroslavskii, Opt. Spectry, 3, 31 (1961).
- (12) M. Jen and D. R. Lide, Jr., J. Chem. Phys. 36, 2525 (1962).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	9.000	0.000	INFINITE	23.488	23.488	INFINITE
100	9.637	57.180	62.642	24.089	21.794	47.430
200	12.978	64.933	71.975	24.419	19.363	21.459
298	15.627	70.628	76.628	24.660	16.868	12.335
300	15.671	70.724	76.628	24.664	16.780	12.324
400	17.477	75.532	71.269	24.826	14.125	7.717
500	19.266	79.664	72.545	24.919	11.437	4.999
600	20.378	83.280	74.039	24.966	8.736	3.182
800	21.672	89.365	79.337	24.977	5.479	1.662
900	22.198	91.072	78.643	24.983	5.324	1.551
1000	22.831	94.355	80.097	24.978	2.075	0.454
1100	23.191	96.849	81.494	24.800	4.766	0.947
1200	23.465	98.571	82.839	24.716	10.426	1.475
1300	23.751	100.471	85.351	24.632	10.260	1.998
1400	24.047	102.539	88.165	24.532	15.463	2.253
1500	24.160	103.900	86.533	24.432	18.117	2.475
1600	24.323	105.464	87.667	24.328	20.770	2.670
1700	24.465	106.943	88.758	24.220	24.111	2.847
1800	24.597	108.371	90.819	24.111	26.051	2.997
1900	24.697	109.677	91.794	24.000	28.682	3.134
2000	24.793	110.947	91.794	23.890	31.307	3.258
2100	24.877	112.159	92.735	23.778	33.926	3.370
2200	24.952	113.318	93.644	23.670	36.545	3.476
2300	25.019	114.436	94.521	23.566	39.154	3.566
2400	25.079	115.494	95.376	23.456	41.740	3.651
2500	25.133	116.519	96.201	23.355	44.365	3.729
2600	25.181	117.506	97.002	23.256	46.982	3.801
2700	25.224	118.457	97.779	23.161	49.591	3.868
2800	25.262	119.372	98.532	23.068	52.195	3.930
2900	25.300	120.262	99.268	22.985	54.798	3.986
3000	25.332	121.121	99.982	22.905	57.326	4.041
3100	25.362	121.952	100.677	22.828	59.912	4.092
3200	25.389	122.759	101.355	22.759	62.486	4.140
3300	25.414	123.539	102.019	22.696	65.075	4.183
3400	25.437	124.298	102.659	22.636	67.649	4.224
3500	25.458	125.036	103.280	22.585	70.299	4.263
3600	25.478	125.753	103.902	22.538	72.907	4.301
3700	25.497	126.448	104.502	22.499	75.467	4.336
3800	25.513	127.132	105.085	22.464	77.989	4.369
3900	25.528	127.795	105.663	22.436	80.524	4.400
4000	25.543	128.441	106.224	22.415	83.102	4.430
4100	25.556	129.072	106.774	22.397	85.677	4.458
4200	25.569	129.688	107.312	22.387	88.246	4.485
4300	25.581	130.287	107.835	22.382	90.804	4.511
4400	25.592	130.878	108.346	22.381	93.330	4.536
4500	25.602	131.453	108.843	22.387	95.967	4.559
4600	25.611	132.016	109.361	22.395	98.543	4.582
4700	25.619	132.567	109.857	22.408	101.064	4.605
4800	25.626	133.107	110.335	22.426	103.641	4.625
4900	25.637	133.635	110.798	22.451	106.264	4.645
5000	25.645	134.153	111.260	22.477	108.839	4.664
5100	25.652	134.661	111.713	22.507	111.417	4.683
5200	25.658	135.158	112.157	22.541	114.000	4.701
5300	25.665	135.646	112.597	22.579	116.589	4.718
5400	25.671	136.128	113.029	22.621	119.150	4.735
5500	25.677	136.599	113.454	22.666	121.724	4.751
5600	25.682	137.061	113.871	22.714	124.298	4.766
5700	25.687	137.516	114.282	22.766	126.868	4.780
5800	25.692	137.964	114.683	22.823	129.434	4.794
5900	25.697	138.402	115.085	22.883	132.004	4.808
6000	25.701	138.834	115.477	22.947	134.574	4.821

Monofluoromethylene (CHF)

(Ideal Gas) GFW = 32.01752

Point Group C_s $\Delta H_f^\circ = [29.9 \pm 7] \text{ kcal/mol}$

$S^\circ_{298.15} = 53.35 \pm 0.05 \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = [30 \pm 7] \text{ kcal/mol}$

Ground State Quantum Weight = 1

CHF

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^b	ΔG ^c	Log K ^d
0	.000	.000	INFINITE	-2.366	29.933	29.933	INFINITE
100	7.989	44.609	60.518	-1.591	28.801	28.801	62.945
200	7.926	40.123	34.410	-1.000	28.545	28.545	34.137
298	8.271	53.355	53.355	.000	28.372	28.372	19.331
300	8.279	53.406	53.355	.015	28.349	28.349	19.195
400	8.810	55.857	53.665	.869	25.151	25.151	13.742
500	9.387	57.685	54.328	1.779	23.988	23.988	10.485
600	9.919	59.645	55.071	2.744	22.860	22.860	8.327
700	10.387	61.210	55.838	3.760	21.763	21.763	6.795
800	10.795	62.624	56.599	4.820	20.692	20.692	5.653
900	11.149	63.916	57.341	5.918	19.644	19.644	4.770
1000	11.458	65.107	58.059	7.048	18.616	18.616	4.068
1100	11.727	66.212	58.751	8.208	17.605	17.605	3.498
1200	11.962	67.243	59.416	9.392	16.612	16.612	3.025
1300	12.171	68.209	60.056	10.599	15.630	15.630	2.628
1400	12.357	69.118	60.671	11.826	14.664	14.664	2.289
1500	12.526	69.976	61.263	13.070	13.707	13.707	1.997
1600	12.682	70.790	61.833	14.331	12.758	12.758	1.743
1700	12.830	71.563	62.383	15.606	11.823	11.823	1.520
1800	12.971	72.300	62.913	16.896	10.893	10.893	1.323
1900	13.110	73.005	63.426	18.200	9.975	9.975	1.147
2000	13.246	73.681	63.922	19.518	9.063	9.063	.990
2100	13.382	74.331	64.402	20.849	8.157	8.157	.849
2200	13.517	74.956	64.868	22.194	7.256	7.256	.721
2300	13.653	75.560	65.320	23.553	6.365	6.365	.605
2400	13.789	76.144	65.759	24.925	5.476	5.476	.499
2500	13.925	76.710	66.186	26.311	4.590	4.590	.401
2600	14.061	77.259	66.601	27.710	3.711	3.711	.312
2700	14.195	77.792	67.006	29.123	2.834	2.834	.229
2800	14.328	78.311	67.400	30.549	1.961	1.961	.153
2900	14.458	78.816	67.781	31.989	1.094	1.094	.087
3000	14.586	79.308	68.161	33.444	.223	.223	.016
3100	14.709	79.788	68.528	34.906	.261	.261	.045
3200	14.829	80.257	68.888	36.382	.260	.260	.103
3300	14.943	80.715	69.239	37.871	.237	.237	.157
3400	15.053	81.163	69.583	39.371	.206	.206	.207
3500	15.157	81.601	69.920	40.881	.166	.166	.255
3600	15.255	82.029	70.251	42.402	.115	.115	.300
3700	15.347	82.448	70.575	43.932	.054	.054	.343
3800	15.434	82.859	70.893	45.471	.000	.000	.383
3900	15.513	83.261	71.205	47.019	.000	.000	.421
4000	15.587	83.655	71.511	48.574	.000	.000	.457
4100	15.655	84.040	71.812	50.136	.000	.000	.492
4200	15.716	84.418	72.108	51.705	.000	.000	.524
4300	15.771	84.789	72.398	53.279	.000	.000	.555
4400	15.821	85.152	72.684	54.859	.000	.000	.585
4500	15.865	85.508	72.965	56.443	.000	.000	.614
4600	15.904	85.857	73.241	58.032	.000	.000	.641
4700	15.937	86.199	73.514	59.624	.000	.000	.667
4800	15.965	86.535	73.781	61.219	.000	.000	.692
4900	15.989	86.865	74.045	62.816	.000	.000	.716
5000	16.008	87.188	74.305	64.416	.000	.000	.739
5100	16.023	87.505	74.560	66.018	.000	.000	.761
5200	16.034	87.816	74.812	67.621	.000	.000	.782
5300	16.042	88.122	75.061	69.225	.000	.000	.802
5400	16.046	88.422	75.305	70.829	.000	.000	.821
5500	16.047	88.716	75.546	72.434	.000	.000	.840
5600	16.045	89.005	75.784	74.038	.000	.000	.858
5700	16.041	89.289	76.019	75.643	.000	.000	.876
5800	16.034	89.568	76.250	77.246	.000	.000	.893
5900	16.024	89.842	76.478	78.842	.000	.000	.909
6000	16.013	90.111	76.703	80.451	.000	.000	.924

Dec. 31, 1969

CHF

$\sigma = 1$

Bond Distance: C-H = 1.121 Å C-F = 1.314 Å

Bond Angle: H-C-F = 101.6°

Product of the Moments of Inertia: $I_A I_B I_C = 1.0217 \times 10^{-117} \text{ g cm}^6$

Heat of Formation

The heat of formation can be estimated as the average of those of the CH₂ and CF₂ radicals, which gives $\Delta H_f^\circ(\text{CHF}, g) = 25 \pm 20 \text{ kcal/mol}$. A better value for the heat of formation can be obtained by considering the bond energies CHF → CH + F and CHF → CF + H. When $\Delta H_f^\circ(\text{CHF}, g) = 25 \text{ kcal/mol}$ is substituted into the above equations it gives D_{C-F} = 136 kcal and D_{C-H} = 86 kcal. These are not unreasonable values but are probably close to the upper and lower limits respectively. A value of $\Delta H_f^\circ(\text{CHF}, g) = 30 \text{ kcal/mol}$ gives D_{C-F} = 131 kcal and D_{C-H} = 81 kcal which are more probable since both fall within the bounds of normal bond strengths. The strongest established C-F bond is 135 kcal in CF₃ and the weakest established C-H bond is 80 kcal in CH. We adopt $\Delta H_f^\circ(\text{CHF}, g) = 30 \pm 7 \text{ kcal/mol}$.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis (1) from an analysis of the rotational structure of the visible absorption bands. The estimated triplet state is based on the electronic levels of CF₂ and CH₂ as given in these tables. The vibrational levels are from Merer and Travis (1) and Jacox and Milligan (2), the latter investigated the infrared spectrum of matrix-isolated HCF and also estimated the missing frequency.

The individual moments of inertia are $I_A = 2.2379 \times 10^{-39} \text{ g cm}^2$, $I_B = 1.795 \times 10^{-40} \text{ g cm}^2$, and $I_C = 2.4774 \times 10^{-39} \text{ g cm}^2$.

References

1. A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 1541 (1966).
2. M. E. Jacox and D. E. Milligan, J. Chem. Phys. **50**, 3252 (1969).

Formyl Fluoride (CHFO)

(Ideal Gas) Mol. Wt. = 48.019

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	ΔH _f ^o	ΔF ^o	Log K _p
0	7.040	INFINITE	2.494	89.139	89.139	INFINITE
100	7.949	46.744	1.701	89.142	89.142	154.642
200	8.478	55.371	1.866	89.197	89.197	66.810
298	8.659	58.961	2.000	90.000	87.994	64.498
300	8.685	59.020	2.018	90.006	87.982	64.092
400	9.1078	61.968	2.357	90.301	87.261	67.675
500	12.352	64.610	2.229	90.566	86.471	37.794
600	13.432	66.961	3.520	90.796	85.930	31.189
700	14.307	69.151	4.800	90.977	84.751	26.895
800	14.971	71.098	6.061	91.170	83.825	23.625
900	15.701	72.878	7.291	91.318	82.924	20.136
1000	16.223	74.560	8.518	91.442	81.984	17.917
1100	16.662	76.127	9.579	91.549	81.034	16.099
1200	17.034	77.593	10.486	91.639	80.072	14.582
1300	17.351	78.974	11.274	91.700	79.136	13.179
1400	17.621	80.266	11.951	91.760	78.207	11.849
1500	17.853	81.489	12.529	91.854	77.153	11.241
1600	18.053	82.648	13.019	91.913	76.173	10.404
1700	18.226	83.748	13.426	91.967	75.187	9.665
1800	18.379	84.791	13.751	92.009	74.197	8.995
1900	18.509	85.791	14.000	92.049	73.207	8.380
2000	18.625	86.744	14.128	92.118	72.213	7.801
2100	18.728	87.655	14.198	92.167	71.215	7.411
2200	18.819	88.529	14.206	92.219	70.219	6.975
2300	18.901	89.369	14.157	92.265	69.221	6.500
2400	18.971	90.173	14.057	92.325	68.211	6.211
2500	19.036	90.948	13.915	92.383	67.209	5.875
2600	19.094	91.696	13.744	92.443	66.199	5.564
2700	19.146	92.416	13.546	92.506	65.189	5.276
2800	19.193	93.107	13.324	92.572	64.180	4.997
2900	19.237	93.774	13.081	92.642	63.158	4.759
3000	19.276	94.442	12.819	92.716	62.143	4.527
3100	19.312	95.075	12.536	92.792	61.121	4.309
3200	19.344	95.688	12.231	92.874	60.099	4.104
3300	19.373	96.276	11.907	92.959	59.074	3.912
3400	19.402	96.843	11.567	93.049	58.046	3.712
3500	19.427	97.428	11.219	93.144	57.016	3.560
3600	19.450	97.973	10.864	93.243	55.981	3.398
3700	19.472	98.506	10.497	93.347	54.944	3.245
3800	19.493	99.024	10.119	93.454	53.902	3.100
3900	19.510	99.532	9.734	93.568	52.861	2.962
4000	19.528	100.027	9.342	93.685	51.815	2.831
4100	19.548	100.509	8.948	93.807	50.770	2.706
4200	19.559	100.980	8.551	93.935	49.716	2.587
4300	19.571	101.441	8.151	94.068	48.666	2.473
4400	19.583	101.891	7.748	94.203	47.606	2.365
4500	19.598	102.331	7.341	94.345	46.549	2.261
4600	19.609	102.762	6.935	94.491	45.480	2.161
4700	19.620	103.184	6.526	94.643	44.413	2.065
4800	19.633	103.598	6.114	94.799	43.349	1.973
4900	19.648	104.002	5.700	94.959	42.289	1.884
5000	19.664	104.398	5.284	95.125	41.193	1.800
5100	19.657	104.786	4.866	95.297	40.116	1.719
5200	19.665	105.170	4.448	95.471	39.031	1.640
5300	19.668	105.548	4.029	95.651	37.946	1.564
5400	19.671	105.921	3.609	95.831	36.861	1.491
5500	19.687	106.273	3.188	96.026	35.756	1.421
5600	19.693	106.628	2.768	96.221	34.660	1.353
5700	19.700	106.977	2.348	96.421	33.562	1.287
5800	19.707	107.321	1.928	96.625	32.456	1.223
5900	19.713	107.656	1.508	96.831	31.351	1.161
6000	19.718	107.988	1.088	97.048	30.238	1.101

June 30, 1961

FORMYL FLUORIDE (CHFO)

(IDEAL GAS)

MOL. WT. = 48.019

CHFO

$\Delta H_{f, 298}^{\circ} = [-92] \text{ kcal. mole}^{-1}$
 $\Delta H_{f, 298.15}^{\circ} = [-90] \text{ kcal. mole}^{-1}$
 $S_{298.15}^{\circ} = 58.96 \pm 0.2 \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Point Group C₁

Vibrational Levels and Multiplicities	$\Delta \text{ cm}^{-1}$	$\Delta \text{ cm}^{-1}$
2981 (1)	1064.8 (1)	
1836.9 (1)	862.5 (1)	
1542.5 (1)	[1030] (1)	

Bond Lengths and Angles C-F = 1.31 ± 0.02 Å C-O = 1.185 ± 0.003 Å C-H = 1.10 ± 0.02 Å
 $\angle \text{FCO} = 122.7 \pm 0.05^{\circ}$ $\angle \text{HCF} = 109 \pm 3^{\circ}$ $\angle \text{HCO} = 129 \pm 3^{\circ}$

Moments of Inertia $I_A = 0.92052 \times 10^{-39} \text{ g. cm}^2$ $I_B = 7.13510 \times 10^{-39} \text{ g. cm}^2$ $I_C = 8.07084 \times 10^{-39} \text{ g. cm}^2$ $r = 1$

Heat of Formation

ΔH_f for III was estimated to be the average of the ΔH_f 's of I and II.

(I) $\text{CH}_2\text{O(g)} = \text{CO(g)} + 2\text{H(g)}$ 106 kcal.

(II) $\text{CF}_2\text{O(g)} = \text{CO(g)} + 2\text{F(g)}$ 162 kcal.

(III) $\text{CHFO(g)} = \text{CO(g)} + \text{F(g)} + \text{H(g)}$ [134] kcal.

The auxiliary ΔH_f 288.15 of $\text{CH}_2\text{O} = -28$, H = 52, F = 19, CO = -26, $\text{CF}_2\text{O} = -150 \text{ kcal. mole}^{-1}$ was used. See the respective sheets for details. The estimated heat of formation is consistent with the instability of CHFO(g) at room temperature.

Heat Capacities and Entropies

The molecular structural parameters were obtained by O. H. LeBlanc, V. W. Laurie and W. D. Gwinn, J. Chem. Phys. **35**, 598 (1960), from combining the results of microwave measurements with those of electron diffraction determined by M. E. Jones, K. Hedberg, and V. Schomaker, J. Am. Chem. Soc. **77**, 5278 (1955). Agreement within the assigned uncertainties was obtained by R. P. Stratton and A. H. Nielsen, J. Mol. Spect. **4**, 373 (1960), on the basis of infrared measurements.

Five of the fundamentals were observed by Stratton and Nielsen, loc. cit. in agreement with those obtained by H. W. Morgan, P. A. Staats and J. H. Goldstein, J. Chem. Phys. **25**, 337 (1956). The estimated frequency was based upon the observed value of 857.4 cm^{-1} for the fundamental in the infrared spectrum of the deuterated compound and the application of the Teller-Redlich isotope rule.

CHFO

T, °K	C _p ^a	gibbs/mol S ^b - (G° - H° ₂₉₈)/T	h ^c - H° ₂₉₈	ΔH ^c	Log K _p
100	8.000	INF	2.764	-164.925	INF
150	9.553	37.667	1.081	-166.600	175.923
200	9.853	43.071	0.000	-166.600	116.089
250	12.199	62.032	0.023	-166.609	115.336
300	12.244	82.033	1.366	-167.014	84.937
400	14.579	105.956	2.926	-167.332	60.690
500	16.357	119.377	4.664	-167.571	54.492
600	18.128	127.593	6.541	-167.746	45.218
700	19.359	134.884	8.527	-167.871	36.122
800	20.331	140.514	10.600	-167.955	30.043
900	21.109	144.966	12.744	-168.004	26.704
1000	21.742	148.931	14.945	-168.027	23.922
1100	22.262	152.560	17.193	-168.027	21.568
1200	22.691	155.957	19.481	-168.014	19.402
1300	23.057	159.149	21.811	-167.990	17.400
1400	23.373	162.173	24.152	-167.950	15.536
1500	23.624	165.056	26.526	-167.896	13.784
1600	23.847	167.813	28.921	-167.828	12.139
1700	24.040	170.454	31.333	-167.746	10.590
1800	24.207	172.993	33.763	-167.650	9.125
1900	24.352	175.435	36.220	-167.542	7.744
2000	24.480	177.787	38.704	-167.420	6.429
2100	24.592	180.055	41.211	-167.282	5.167
2200	24.691	182.241	43.746	-167.130	3.951
2300	24.776	184.353	46.304	-166.963	2.787
2400	24.849	186.397	48.884	-166.782	1.686
2500	24.909	188.373	51.487	-166.586	0.640
2600	24.958	190.283	54.115	-166.376	0.590
2700	25.006	192.129	56.768	-166.152	5.197
2800	25.053	193.913	59.446	-165.915	4.829
2900	25.098	195.637	62.146	-165.663	4.483
3000	25.141	197.301	64.869	-165.400	4.157
3100	25.182	198.913	67.615	-165.125	3.851
3200	25.222	200.475	70.388	-164.838	3.561
3300	25.260	202.000	73.187	-164.539	3.287
3400	25.296	203.487	76.015	-164.228	3.028
3500	25.330	204.945	78.874	-163.904	2.787
3600	25.362	206.373	81.759	-163.567	2.567
3700	25.393	207.779	84.685	-163.217	2.367
3800	25.422	209.163	87.651	-162.854	2.187
3900	25.449	210.534	90.659	-162.478	2.027
4000	25.474	211.891	93.709	-162.089	1.887
4100	25.497	213.234	96.804	-161.687	1.767
4200	25.519	214.564	99.946	-161.272	1.667
4300	25.539	215.881	103.126	-160.844	1.587
4400	25.557	217.185	106.344	-160.402	1.527
4500	25.573	218.476	109.599	-160.047	1.487
4600	25.588	219.754	112.891	-159.678	1.457
4700	25.601	221.019	116.220	-159.294	1.437
4800	25.613	222.271	119.591	-158.896	1.427
4900	25.624	223.510	122.999	-158.483	1.427
5000	25.633	224.736	126.444	-158.056	1.437
5100	25.640	225.950	129.926	-157.615	1.457
5200	25.645	227.152	133.444	-157.159	1.487
5300	25.649	228.342	136.999	-156.688	1.527
5400	25.652	229.519	140.591	-156.202	1.577
5500	25.655	230.683	144.219	-155.701	1.637
5600	25.656	231.834	147.884	-155.185	1.707
5700	25.656	232.971	151.586	-154.654	1.787
5800	25.655	234.094	155.324	-154.108	1.877
5900	25.653	235.203	159.099	-153.547	1.977
6000	25.649	236.297	162.911	-152.971	2.087

Dec. 31, 1950; Dec. 31, 1963; June 30, 1969

The molecular structure has been derived from electron-diffraction data by Thornton (8) and from microwave data by Ghosh (6). The results are in close agreement and average values are adopted. Vibrational frequencies are from the assignment of Long (7) who reviewed the spectral data and gave force-constant calculations. Preference has been given to the gas-phase spectra, particularly the Raman data of Claassen (9). Shimanouchi (9) assigned $\nu_2 = 1117$ rather than 1137 cm^{-1} , but he apparently did not consider the gas-phase data of (8, 10). Principal moments of inertia are $I_A = 14.786 \times 10^{-38}$ and $I_B = I_C = 8.108 \times 10^{-39} \text{ g cm}^2$.

Valentine (11) used low-temperature calorimetric data to derive the ideal gas entropy at the normal boiling point of 130.97°K . The experimental value of 57.18 gibbs/mol is in good agreement with 57.216 gibbs/mol obtained from this table. Schwing (12) measured C_p for CHF_3 vapor ($25\text{--}100^\circ\text{C}$) and confirmed that the vibrational assignment is adequate. Uncertainty in C_p and S° increases at higher temperatures due to neglect of anharmonicity in the calculations. Discussions of anharmonic contributions are given on the tables for $\text{CF}_4(\text{g})$ and $\text{CClF}_3(\text{g})$. The error probably does not exceed 0.3 gibbs/mol in S° at 1000°K . C_p° is consistent with C_p° measured at 300°K by the wire-ribbon method (13).

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. C. A. Neugebauer and J. L. Margrave, J. Phys. Chem. **62**, 1043 (1958).
3. C. A. Goy, A. Lord and H. O. Pritchard, J. Phys. Chem. **71**, 1086 (1967).
4. J. W. Coomber and E. Whittle, Trans. Faraday Soc. **63**, 608 (1967).
5. C. G. Thornton, Dissertation Abstracts **24**, 604 (1954); R. L. Livingston, Ann. Rev. Phys. Chem. **5**, 397 (1954).
6. S. N. Ghosh, R. Tambarulo and W. Gordy, J. Chem. Phys. **20**, 605 (1952); C. A. Burrus and W. Gordy, ibid. **26**, 391 (1957); M. Jen and D. R. Lide, ibid. **36**, 2525 (1962).
7. D. A. Long, R. B. Grevner and D. T. L. Jones, Trans. Faraday Soc. **60**, 1508 (1964).
8. H. H. Claassen and J. R. Nielsen, J. Opt. Soc. Amer. **43**, 352 (1953).
9. T. Shimanouchi, U. S. Nat. Bur. Stand. NBS-RS 17, 17 (1967).
10. W. F. Edgell and C. May, J. Chem. Phys. **23**, 1901 (1955); **22**, 1308 (1954).
11. R. H. Valentine, G. E. Brodale and W. F. Glauque, J. Phys. Chem. **66**, 392 (1962).
12. R. C. Schwing, Dissertation Abstracts **25**, 2404 (1964).
13. W. N. Vanderkooi and T. DeVries, J. Phys. Chem. **60**, 636 (1956).

HYDROGEN CYANIDE (HCN)

(IDEAL GAS)

GFW = 27.02582

Point Group $C_{\infty v}$ $\Delta H_f^\circ = 32.39 \pm 2.0$ kcal/mol $S_{298.15}^\circ = 48.21 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = 32.3 \pm 2.0$ kcal/mol

Ground State Quantum Weight = 1

Hydrogen Cyanide (HCN)

(Ideal Gas)

GFW = 27.02582

T, K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	2.207	32.393	32.393	INFINITE
100	6.871	40.093	35.143	1.713	32.387	32.387	21.877
200	11.674	58.002	51.642	6.237	32.380	32.380	21.877
298	6.570	48.212	48.212	0.000	32.300	29.806	21.849
300	6.567	48.265	48.212	0.016	32.299	29.791	21.702
400	9.376	50.649	48.559	1.916	32.286	28.961	15.423
500	9.974	53.006	49.239	1.865	32.206	28.142	12.301
600	10.470	54.871	50.026	2.907	32.145	27.335	9.957
700	10.909	56.519	50.838	3.576	32.074	26.539	8.286
800	11.309	58.002	51.642	5.088	32.002	25.754	7.036
900	11.674	59.355	52.425	6.237	31.929	24.974	6.045
1000	12.005	60.603	53.181	7.421	31.861	24.207	5.290
1100	12.305	61.761	53.909	8.637	31.797	23.444	4.658
1200	12.574	62.843	54.609	9.881	31.737	22.689	4.132
1300	12.815	63.860	55.282	11.151	31.680	21.936	3.688
1400	13.031	64.817	55.929	12.443	31.629	21.190	3.308
1500	13.224	65.723	56.552	13.756	31.581	20.446	2.979
1600	13.396	66.582	57.152	15.087	31.535	19.704	2.691
1700	13.551	67.399	57.731	16.435	31.493	18.968	2.438
1800	13.689	68.177	58.290	17.797	31.454	18.230	2.213
1900	13.813	68.921	58.830	19.172	31.417	17.498	2.013
2000	13.925	69.632	59.353	20.559	31.383	16.766	1.832
2100	14.027	70.314	59.859	21.957	31.350	16.037	1.669
2200	14.118	70.969	60.349	23.364	31.318	15.306	1.521
2300	14.202	71.598	60.824	24.780	31.288	14.581	1.385
2400	14.278	72.204	61.286	26.204	31.258	13.856	1.262
2500	14.347	72.789	61.734	27.636	31.228	13.131	1.148
2600	14.411	73.353	62.171	29.077	31.199	12.407	1.043
2700	14.470	73.898	62.595	30.518	31.170	11.683	0.946
2800	14.523	74.425	63.008	31.967	31.141	10.962	0.856
2900	14.573	74.936	63.411	33.422	31.112	10.244	0.772
3000	14.620	75.430	63.803	34.882	31.082	9.524	0.694
3100	14.662	75.910	64.186	36.346	31.054	8.805	0.621
3200	14.702	76.377	64.560	37.814	31.023	8.088	0.552
3300	14.739	76.830	64.925	39.286	30.990	7.371	0.488
3400	14.774	77.270	65.281	40.762	30.959	6.657	0.428
3500	14.806	77.699	65.630	42.241	30.924	5.940	0.371
3600	14.836	78.116	65.971	43.723	30.889	5.227	0.317
3700	14.864	78.523	66.305	45.208	30.851	4.516	0.267
3800	14.890	78.920	66.631	46.696	30.813	3.807	0.219
3900	14.914	79.307	66.952	48.186	30.772	3.098	0.174
4000	14.937	79.685	67.265	49.679	30.730	2.388	0.130
4100	14.959	80.054	67.573	51.173	30.685	1.678	0.089
4200	14.979	80.415	67.874	52.670	30.637	0.974	0.051
4300	14.998	80.767	68.170	54.169	30.588	0.267	0.014
4400	15.015	81.112	68.466	55.670	30.536	0.439	0.022
4500	15.031	81.450	68.745	57.172	30.481	1.145	0.056
4600	15.046	81.781	69.025	58.676	30.424	1.843	0.086
4700	15.060	82.104	69.300	60.181	30.364	2.544	0.118
4800	15.073	82.421	69.570	61.688	30.300	3.242	0.148
4900	15.085	82.732	69.835	63.196	30.234	3.942	0.176
5000	15.096	83.037	70.096	64.705	30.165	4.636	0.203
5100	15.107	83.336	70.353	66.215	30.092	5.339	0.229
5200	15.116	83.630	70.605	67.726	30.017	6.030	0.253
5300	15.124	83.918	70.854	69.238	29.938	6.720	0.277
5400	15.131	84.200	71.098	70.751	29.856	7.412	0.300
5500	15.137	84.478	71.339	72.264	29.769	8.109	0.322
5600	15.143	84.751	71.576	73.778	29.679	8.790	0.343
5700	15.148	85.019	71.810	75.293	29.585	9.477	0.363
5800	15.152	85.283	72.040	76.808	29.487	10.161	0.383
5900	15.155	85.542	72.266	78.323	29.386	10.841	0.402
6000	15.157	85.796	72.490	79.839	29.280	11.527	0.420

Dec. 31, 1960; Mar. 31, 1961; June 30, 1969; Dec. 31, 1969

HYDROGEN CYANIDE (HCN)

(IDEAL GAS)

GFW = 27.02582

Point Group $C_{\infty v}$ $\Delta H_f^\circ = 32.39 \pm 2.0$ kcal/mol $S_{298.15}^\circ = 48.21 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = 32.3 \pm 2.0$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 ω_e, cm^{-1}

2096.3 (1)

713.5 (2)

3311.5 (1)

 $\sigma = 1$

C-H = 1.066 Å

C-N = 1.153 Å

Bond Angle: H-C-N = 180°

Rotational Constant: $B_0 = 1.4782 \text{ cm}^{-1}$ Spectroscopic constants used in calculating corrections to the rigid-rotator harmonic oscillator approximation (cm^{-1}): $a_1 = 10.10 \times 10^{-3}$ $a_2 = -3.61 \times 10^{-3}$ $a_3 = 10.42 \times 10^{-3}$ $-x_{11} = 7.07$ $-x_{12} = 2.53$ $-x_{22} = 2.65$ $-x_{23} = 19.01$ $-x_{33} = 52.49$ $-x_{13} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$ $\delta_{33} = 10.44$ $\delta_{22} = 5.18$ $\delta_{23} = 10.44$

Isocyanic Acid (HNCO)

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 43.027

ISOCYANIC ACID (HNCO) (Ideal Gas)

T, °K.	C_p^0	$S^0 - (F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _P
0	8.000	INFINITE	2.615	27.179	27.179	INFINITE
100	9.000	42.953	27.700	27.700	27.700	26.936
200	10.000	47.339	28.975	28.975	28.975	26.806
298	10.724	56.909	.000	27.900	28.481	16.053
300	10.732	56.975	.020	27.904	28.667	16.668
400	12.085	60.299	1.165	28.055	28.897	13.602
500	13.114	63.071	2.827	28.179	28.993	10.531
600	13.934	65.537	5.236	28.287	23.266	6.474
700	14.613	67.738	8.029	28.387	22.421	7.000
800	15.191	69.728	11.353	28.479	21.561	5.890
900	15.690	71.546	16.291	28.563	20.691	5.034
1000	16.125	73.222	23.387	28.639	19.814	4.330
1100	16.507	74.778	34.352	28.705	18.927	3.740
1200	16.842	76.259	49.282	28.764	18.036	3.285
1300	17.136	77.589	68.177	28.818	17.140	2.881
1400	17.394	78.688	91.061	28.867	16.339	2.535
1500	17.622	80.076	118.068	28.915	15.536	2.234
1600	17.823	81.220	148.667	28.964	14.730	1.971
1700	18.001	82.306	197.437	28.993	13.920	1.736
1800	18.159	83.339	260.181	29.039	12.608	1.531
1900	18.299	84.325	340.900	29.075	11.594	1.355
2000	18.424	85.267	444.595	29.109	10.778	1.176
2100	18.535	86.168	572.268	29.192	9.961	1.026
2200	18.635	87.033	729.919	29.310	9.042	.886
2300	18.725	87.863	912.511	29.421	8.021	.762
2400	18.805	88.662	1116.064	29.526	7.096	.646
2500	18.878	89.431	1347.600	29.629	6.174	.540
2600	18.944	90.173	1603.138	29.730	5.249	.441
2700	19.004	90.889	1888.791	29.833	4.321	.350
2800	19.059	91.581	2200.549	29.937	3.390	.265
2900	19.108	92.251	2544.281	30.042	2.458	.185
3000	19.154	92.899	2916.093	30.149	1.526	.111
3100	19.195	93.528	3312.000	30.260	.592	.042
3200	19.234	94.138	3738.032	30.372	.000	.000
3300	19.269	94.731	4199.300	30.486	.000	.000
3400	19.301	95.306	4691.811	30.600	.000	.000
3500	19.331	95.866	5211.566	30.715	.000	.000
3600	19.359	96.411	5764.569	30.831	.000	.000
3700	19.384	96.942	6357.822	30.949	.000	.000
3800	19.408	97.459	6988.333	31.068	.000	.000
3900	19.430	97.964	7653.100	31.188	.000	.000
4000	19.451	98.456	8350.133	31.314	.000	.000
4100	19.470	98.936	9087.433	31.446	.000	.000
4200	19.488	99.406	9863.000	31.582	.000	.000
4300	19.505	99.865	10675.833	31.722	.000	.000
4400	19.521	100.313	11524.033	31.867	.000	.000
4500	19.536	100.752	12406.600	32.016	.000	.000
4600	19.550	101.182	13323.533	32.169	.000	.000
4700	19.563	101.602	14274.833	32.326	.000	.000
4800	19.575	102.014	15259.500	32.488	.000	.000
4900	19.586	102.418	16277.633	32.655	.000	.000
5000	19.597	102.814	17328.233	32.827	.000	.000
5100	19.608	103.202	18411.300	33.003	.000	.000
5200	19.617	103.583	19526.833	33.184	.000	.000
5300	19.627	103.956	20674.833	33.370	.000	.000
5400	19.635	104.323	21855.300	33.561	.000	.000
5500	19.644	104.684	23068.333	33.757	.000	.000
5600	19.652	105.038	24313.833	33.958	.000	.000
5700	19.659	105.386	25591.833	34.164	.000	.000
5800	19.666	105.728	26902.300	34.375	.000	.000
5900	19.673	106.064	28245.333	34.591	.000	.000
6000	19.679	106.395	29620.833	34.812	.000	.000

December 31, 1960.

Mol. Wt. = 43.027

 ΔH_f^0 298.15 = -27.9 kcal. mole⁻¹ S^0 298.15 = 56.909 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω cm. ⁻¹	
572 (1)	
670 (1)	
797 (1)	
1327 (1)	
2274 (1)	
3531 (1)	

Moments of Inertia: $I_A = 7.7276 \times 10^{-39}$ g. cm.², $I_B = 7.6356 \times 10^{-39}$ g. cm.², $I_C = 0.09157 \times 10^{-39}$ g. cm.²
 $\sigma = 1$.

Data from J. S. Gordon, Thiokol Chemical Corp., Reaction Motors Division, Denver, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Formyl (HCO)

(Ideal Gas) Mol. Wt. = 29.019

CHO

MOL. WT. = 29.019

(IDEAL GAS)

FORMYL (HCO)

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.949	46.930	2.387	2.986	2.986	INFINITE
200	7.949	46.930	2.941	2.941	2.941	INFINITE
298	6.264	33.683	1.000	2.980	2.980	4.786
300	6.271	33.734	.015	2.902	6.566	4.783
400	6.703	36.171	.863	3.002	7.773	4.247
500	6.984	38.164	1.758	3.142	8.950	3.912
600	7.160	39.881	2.700	3.305	10.097	3.678
700	7.280	41.404	3.689	3.481	11.214	3.501
800	7.359	42.781	4.720	3.661	12.307	3.362
900	7.408	44.042	5.791	3.840	13.378	3.248
1000	7.436	45.206	6.896	4.013	14.428	3.153
1100	7.450	46.289	8.033	4.182	15.462	3.072
1200	7.458	47.301	9.196	4.346	16.479	3.001
1300	7.462	48.264	10.383	4.506	17.484	2.939
1400	7.464	49.186	11.591	4.665	18.475	2.884
1500	7.465	50.067	12.817	4.822	19.456	2.835
1600	7.466	50.909	14.059	4.978	20.429	2.790
1700	7.467	51.711	15.314	5.131	21.388	2.750
1800	7.468	52.476	16.582	5.285	22.341	2.712
1900	7.469	53.207	17.860	5.440	23.283	2.678
2000	7.470	53.907	19.148	5.594	24.219	2.646
2100	7.471	54.576	20.444	5.750	25.145	2.617
2200	7.472	55.214	21.747	5.909	26.067	2.589
2300	7.473	55.822	23.058	6.068	26.978	2.563
2400	7.474	56.407	24.374	6.232	27.883	2.539
2500	7.475	56.967	25.695	6.398	28.784	2.516
2600	7.476	57.504	27.022	6.566	29.675	2.494
2700	7.477	58.019	28.353	6.736	30.562	2.474
2800	7.478	58.512	29.687	6.912	31.440	2.454
2900	7.479	58.985	31.025	7.091	32.311	2.435
3000	7.480	59.438	32.367	7.273	33.179	2.417
3100	7.481	59.872	33.711	7.457	34.039	2.400
3200	7.482	60.288	35.058	7.646	34.894	2.383
3300	7.483	60.687	36.408	7.839	35.744	2.367
3400	7.484	61.069	37.760	8.035	36.586	2.352
3500	7.485	61.434	39.114	8.235	37.425	2.337
3600	7.486	61.783	40.470	8.439	38.255	2.322
3700	7.487	62.117	41.828	8.648	39.080	2.308
3800	7.488	62.438	43.187	8.859	39.897	2.294
3900	7.489	62.746	44.548	9.075	40.711	2.281
4000	7.490	63.042	45.911	9.294	41.520	2.268
4100	7.491	63.327	47.275	9.518	42.325	2.256
4200	7.492	63.601	48.640	9.746	43.119	2.244
4300	7.493	63.864	50.006	9.978	43.912	2.232
4400	7.494	64.117	51.373	10.214	44.700	2.220
4500	7.495	64.367	52.741	10.454	45.484	2.209
4600	7.496	64.615	54.111	10.698	46.265	2.198
4700	7.497	64.861	55.481	10.946	47.045	2.187
4800	7.498	65.105	56.852	11.198	47.819	2.176
4900	7.499	65.347	58.224	11.453	48.581	2.165
5000	7.500	65.587	59.596	11.712	49.336	2.155
5100	7.501	65.824	60.969	11.977	50.087	2.145
5200	7.502	66.058	62.343	12.244	50.802	2.135
5300	7.503	66.290	63.718	12.515	51.535	2.125
5400	7.504	66.519	65.093	12.791	52.272	2.115
5500	7.505	66.746	66.469	13.070	53.009	2.106
5600	7.506	66.971	67.845	13.353	53.725	2.097
5700	7.507	67.194	69.222	13.640	54.446	2.087
5800	7.508	67.415	70.599	13.932	55.158	2.078
5900	7.509	67.634	71.977	14.226	55.862	2.069
6000	7.510	67.851	73.355	14.525	56.570	2.060

March 31, 1961

$\Delta H_f^0 = -3.0 \pm 3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 \text{ 298.15} = -2.9 \pm 3 \text{ kcal. mole}^{-1}$
 $S_f^0 \text{ 298.15} = [53.683] \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Point Group C_s

Ground State Multiplicity = [2]

Vibrational Levels and Multiplicities

(<i>v</i>), cm. ⁻¹	[3000] (1)
1860 (1)	
1083 (1)	

HC bond length = [1.08] Å CO bond length = 1.198 ± 0.005 Å HCO angle = 119°30' ± 1°

Product of Moments of Inertia = $I_A I_B I_C = 4.73 \times 10^{-118} \text{ g.}^3 \text{ cm.}^6$ $\sigma^* = 1$

Heat of Formation

Calculated from $\Delta H_f^0 = 75.1 \pm 2.3 \text{ kcal. for the reaction H}_2\text{CO(g)} \rightarrow \text{HCO(g)} + \text{H(g)}$, reported by J. C. D. Brand and R. T. Reed, J. Chem. Soc. 2386 (1957).

Heat Capacity and Entropy

The vibrational levels and multiplicities are from G. E. Ewing, W. E. Thompson, and G. C. Pimentel, J. Chem. Phys. 32, 927 (1960), while the ground state multiplicity and structural data are from G. Herzberg and D. A. Ramsay, Proc. Roy. Soc. A233, 34 (1955).

CHO

Point Group [C_{∞v}]
 $S_{298.15}^{\circ} = [48.3]$ gibbs/mol
 Ground State Quantum Weight = [1]

$$\Delta H_{\text{f}}^{\circ} = 203.0 \pm 10 \text{ kcal/mol}$$

$$\Delta H_{\text{f}}^{\circ}{}_{298.15} = 204.4 \pm 10 \text{ kcal/mol}$$

Vibrational Frequencies and Degeneracies

ω_e , cm⁻¹
 [2310](1)
 [700](2)
 [3540](1)

Bond Distance: C-H = [1.029] Å C-O = [1.090] Å

Bond Angle: H-C-O = [180°]

Rotational Constant: B₀ = [1.56015] cm⁻¹

Heat of Formation.

The selected heat of formation, $\Delta H_{\text{f}}^{\circ}$ (HCO⁺, g) = 203 kcal/mol, was obtained from electron impact studies on cis-and trans-HCOOH by P. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957. A higher value, $\Delta H_{\text{f}}^{\circ} = 220$ kcal/mol, has also been reported from appearance potential measurements on CH₃CHO by J. R. Mejer, C. R. Patrick and J. C. Robb, Trans-Faraday Soc. 57, 14 (1961). Generally, errors in the heat of formation derived from electron impact studies are such as to cause the quantities to be high because of unaccounted excitations or residual kinetic energy in the fragments; therefore, the value of 203 kcal/mol is preferable, assuming the same reliability of the experiments.

Heat Capacity and Entropy.

Since the molecule HCO⁺(g) has the same number of valence electrons as HCN(g), a linear molecular configuration is assumed for HCO⁺(g) in the tabulation. The bond distances H-C and C-O were estimated by comparison with those in similar molecules by D. G. Clifton, J. Chem. Phys. 41, 3656 (1964). The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton. The principal moment of inertia is 1.7941×10^{-39} g cm².

June 30, 1966

CHO⁺

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o) ₂₉₈ /T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0						
100						
200						
298	8.617	48.344	4000	204.400	200.862	-147.236
300						
400	8.634	48.397	48.444	204.408	200.839	-146.311
500	8.692	48.474	1.888	205.291	198.212	-146.638
600	10.385	50.002	2.905	205.700	196.757	-146.669
700	10.777	50.633	3.963	206.089	195.235	-146.955
800	11.172	51.268	4.995	206.459	193.653	-147.235
900	11.572	51.928	6.100	206.849	192.034	-147.505
1000	11.971	60.653	7.353	207.230	190.367	-147.765
1100	12.064	61.789	8.545	207.614	188.663	-147.984
1200	12.220	62.850	9.713	208.003	186.924	-148.164
1300	12.446	64.783	12.274	208.792	183.349	-148.627
1400	12.660	66.670	13.560	209.192	181.518	-148.947
1500	12.866	68.511	14.863	209.594	179.657	-149.240
1600	13.113	69.311	16.182	210.006	177.667	-149.510
1700	13.395	69.970	17.525	210.426	175.555	-149.755
1800	13.615	70.800	18.860	210.819	173.939	-149.984
1900	13.822	72.589	20.217	211.230	171.986	-150.194
2000	14.017	74.289	21.584	211.653	170.014	-150.384
2100	14.163	75.911	22.963	212.084	168.012	-150.554
2200	14.282	77.468	24.349	212.464	166.012	-150.704
2300	14.382	78.961	25.737	212.874	163.984	-150.834
2400	14.453	80.401	27.126	213.281	161.915	-150.944
2500	14.506	81.789	28.560	213.688	159.874	-151.034
2600	14.546	83.134	29.946	214.094	157.767	-151.114
2700	14.575	84.439	31.335	214.496	155.600	-151.174
2800	14.600	85.704	32.729	214.894	153.479	-151.224
2900	14.620	86.934	34.209	215.292	151.479	-151.264
3000	14.636	88.129	35.637	215.688	149.343	-151.294
3100	14.646	89.289	37.024	216.084	147.184	-151.314
3200	14.652	90.414	38.253	216.470	145.041	-151.324
3300	14.656	91.504	39.540	216.855	142.870	-151.334
3400	14.659	92.559	40.781	217.238	140.688	-151.344
3500	14.662	93.582	42.824	217.619	138.494	-151.354
3600	14.664	94.574	44.766	217.994	136.284	-151.364
3700	14.666	95.534	46.716	218.378	134.081	-151.374
3800	14.668	96.464	48.618	218.738	131.860	-151.384
3900	14.669	97.364	48.618	219.104	129.624	-151.394
4000	14.670	98.234	50.071	219.466	127.378	-151.404
4100	14.671	99.074	51.924	219.824	125.124	-151.414
4200	14.672	99.884	53.784	220.184	122.874	-151.424
4300	14.673	100.654	55.594	220.534	120.608	-151.434
4400	14.674	101.394	57.354	220.879	118.329	-151.444
4500	14.675	102.104	59.064	221.224	116.052	-151.454
4600	14.676	102.784	60.724	221.564	113.764	-151.464
4700	14.677	103.434	62.334	221.904	111.464	-151.474
4800	14.678	104.054	63.904	222.236	109.161	-151.484
4900	14.679	104.644	65.424	222.565	106.850	-151.494
5000	14.680	105.204	66.894	222.890	104.524	-151.504
5100	14.681	105.734	68.314	223.214	102.184	-151.514
5200	14.682	106.234	69.684	223.532	99.874	-151.524
5300	14.683	106.704	71.004	223.847	97.536	-151.534
5400	14.684	107.144	72.274	224.158	95.200	-151.544
5500	14.685	107.554	73.504	224.465	92.845	-151.554
5600	14.686	107.934	74.684	224.765	90.474	-151.564
5700	14.687	108.284	75.814	225.059	88.084	-151.574
5800	14.688	108.604	76.894	225.346	85.674	-151.584
5900	14.689	108.894	77.924	225.628	83.244	-151.594
6000	14.690	109.154	78.904	225.904	80.794	-151.604

$$\Delta H_f^\circ = [39.9 \pm 15] \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = [40 \pm 15] \text{ kcal/mol}$$

$$S^\circ_{298.15} = 51.37 \pm 0.01 \text{ gibbs/mol}$$

$$C_{p,m}$$



Methinophosphide (HCP)

$$QFW = 43.99292$$

(Ideal Gas)

T, K	C _p ^o	S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	ΔH ^o	Log K _p
0	6.000	0.000	INFINITE	2.235	39.891	INFINITE
100	6.978	48.067	56.470	1.540	37.184	-61.266
200	7.978	48.070	52.152	0.814	40.130	-37.411
300	8.863	51.375	51.375	0.000	40.000	-31.365
400	9.694	51.430	51.375	0.016	39.997	-22.610
500	10.458	54.134	51.737	0.959	39.813	-15.541
600	11.236	58.024	53.284	3.084	39.370	-8.323
700	12.024	63.179	55.004	5.420	38.106	-4.281
800	12.815	68.913	58.838	6.646	36.309	-2.751
900	13.607	74.545	64.545	7.902	34.746	-1.751
1000	14.397	80.000	70.000	9.166	33.527	-1.002
1100	15.189	85.300	75.300	10.425	32.524	-0.514
1200	15.982	90.460	80.460	11.675	31.684	-0.226
1300	16.776	95.490	85.490	12.915	30.976	-0.099
1400	17.570	100.400	90.400	14.145	30.370	-0.054
1500	18.364	105.190	95.190	15.365	29.836	-0.035
1600	19.158	109.860	99.860	16.575	29.356	-0.026
1700	19.952	114.410	104.410	17.775	28.916	-0.022
1800	20.746	118.840	108.840	18.965	28.506	-0.020
1900	21.540	123.150	113.150	20.145	28.116	-0.019
2000	22.334	127.350	117.350	21.315	27.746	-0.018
2100	23.128	131.440	121.440	22.475	27.396	-0.017
2200	23.922	135.430	125.430	23.625	27.066	-0.016
2300	24.716	139.320	129.320	24.765	26.756	-0.015
2400	25.510	143.110	133.110	25.895	26.466	-0.014
2500	26.304	146.800	136.800	27.015	26.186	-0.013
2600	27.098	150.490	140.490	28.125	25.916	-0.012
2700	27.892	154.080	144.080	29.225	25.656	-0.011
2800	28.686	157.570	147.570	30.315	25.406	-0.010
2900	29.480	160.960	150.960	31.395	25.166	-0.009
3000	30.274	164.250	154.250	32.465	24.936	-0.008
3100	31.068	167.440	157.440	33.525	24.716	-0.007
3200	31.862	170.530	160.530	34.575	24.506	-0.006
3300	32.656	173.520	163.520	35.615	24.306	-0.005
3400	33.450	176.410	166.410	36.645	24.116	-0.004
3500	34.244	179.200	169.200	37.665	23.936	-0.003
3600	35.038	181.890	171.890	38.675	23.766	-0.002
3700	35.832	184.480	174.480	39.675	23.606	-0.001
3800	36.626	186.970	176.970	40.665	23.456	0.000
3900	37.420	189.360	178.360	41.645	23.316	0.001
4000	38.214	191.650	180.650	42.615	23.186	0.002
4100	39.008	193.840	182.840	43.575	23.066	0.003
4200	39.802	195.930	184.930	44.525	22.956	0.004
4300	40.596	197.920	186.920	45.465	22.856	0.005
4400	41.390	199.810	188.810	46.395	22.766	0.006
4500	42.184	201.600	190.600	47.315	22.686	0.007
4600	42.978	203.290	192.290	48.225	22.616	0.008
4700	43.772	204.880	193.880	49.125	22.556	0.009
4800	44.566	206.370	195.370	50.015	22.506	0.010
4900	45.360	207.760	196.760	50.895	22.466	0.011
5000	46.154	209.050	198.050	51.765	22.436	0.012
5100	46.948	210.240	199.240	52.625	22.416	0.013
5200	47.742	211.330	200.330	53.475	22.406	0.014
5300	48.536	212.320	201.320	54.315	22.406	0.015
5400	49.330	213.210	202.210	55.145	22.416	0.016
5500	50.124	214.000	203.000	55.965	22.436	0.017
5600	50.918	214.790	203.790	56.775	22.466	0.018
5700	51.712	215.580	204.580	57.575	22.506	0.019
5800	52.506	216.270	205.270	58.365	22.556	0.020
5900	53.299	216.960	205.960	59.145	22.616	0.021
6000	54.093	217.650	206.650	59.915	22.686	0.022

Chlorofluoromethane (CH₂ClF)

(Ideal Gas)

GFw = 68.4785

CH₂ClF

CHLOROFUOROMETHANE (CH₂ClF)

(IDEAL GAS)

GFw = 68.4785

Point Group C_s

ΔHf° = [-60.9 ± 3] kcal/mol

S°_{298.15} = 63.17 ± 0.1 gibbs/mol

ΔHf°_{298.15} = [-62.6 ± 3] kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
2993 (1)	1068 (1)	3048 (1)
1470 (1)	760 (1)	1236 (1)
1351 (1)	385 (1)	1004 (1)

Bond Distance: C-H = 1.078 Å C-Cl = 1.759 Å C-F = 1.378 Å

Bond Angle: H-C-H = 111°54' F-C-Cl = 110° H-C-Cl = 109°06'

Product of the Moments of Inertia: I_AI_BI_C = 4.8154 × 10⁻¹¹⁵ g³ cm⁶

σ = 1

Heat of Formation

The change in heat of atomization by successive replacement of F by Cl, in the CF₄ to CCl₄ series and CHF₃ to CHCl₃ series, follows a regular pattern (see CCl₂F₂ and CHCl₂F tables). We make the assumption that this same regular variation occurs also in the CH₂F₂ to CH₂Cl₂ series. Thus, the difference between the atomization energies of CH₂F₂ and CH₂Cl₂ is divided into two unequal parts which fall into the pattern established in the CF₄ and CHF₃ sequences. We adopt a heat of atomization of 385.5 kcal which corresponds to a ΔHf°₂₉₈(CH₂ClF, g) = -62.6 kcal/mol. The changes, in kcal, in the heat of atomization by successive replacement of F by Cl are tabulated, below for all three series.

CF₄

CF₃Cl

CHF₃

CH₂F₂

CH₂Cl₂

CFCl₃

CHFCF₂

CH₂FCF₂

CCl₄

CHCl₃

CH₂Cl₂

Heat Capacity and Entropy

Plyler and Benedict (1) assigned the vibrational frequencies from the infrared and Raman data for the liquid. The molecular structure was obtained from the microwave measurements of Muller (2). The individual moments of inertia are I_A = 2.008 × 10⁻³⁹ g cm², I_B = 16.241 × 10⁻³⁹ g cm², and I_C = 14.766 × 10⁻³⁹ g cm².

References

1. E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std. **57**, 202 (1951).
2. N. Muller, J. Amer. Chem. Soc. **75**, 800 (1953).

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	INFINITE		2.689	60.861	60.861	INFINITE
100	8.195	53.443	71.942	1.850	61.530	60.083	134.311
200	9.458	59.077	64.138	1.012	62.047	58.444	63.865
298	11.242	63.171	63.171	0.000	62.600	56.558	41.858
300	11.279	63.240	63.171	0.021	62.611	56.521	41.176
400	13.281	66.761	63.637	1.249	63.122	54.411	29.729
500	15.072	69.423	64.584	2.670	63.550	52.183	22.409
600	16.561	72.407	65.717	4.254	63.894	49.876	18.167
700	17.866	75.092	67.042	6.002	64.166	47.535	14.535
800	18.960	77.493	68.462	7.864	64.388	45.158	11.371
900	19.860	79.664	69.854	9.728	64.534	42.767	8.503
1000	20.386	82.274	70.542	11.732	64.644	40.277	6.003
1100	21.005	84.246	71.699	13.802	64.717	37.837	4.445
1200	21.595	85.840	72.913	15.930	64.777	35.452	3.382
1300	22.159	87.140	74.188	18.116	64.822	33.123	2.649
1400	22.387	88.484	74.966	20.326	64.853	30.841	2.170
1500	22.729	91.441	75.986	22.562	64.755	28.604	1.866
1600	23.026	92.517	76.874	24.870	64.727	25.599	1.608
1700	23.152	93.254	77.655	27.156	64.688	22.716	1.357
1800	23.172	94.536	78.752	31.688	64.582	18.272	1.052
1900	23.712	96.536	80.622	34.268	64.523	15.836	0.810
2000	23.888	97.756	81.466	36.655	64.400	13.403	0.610
2100	24.045	98.428	82.576	38.734	64.330	10.955	0.445
2200	24.180	99.123	83.680	40.577	64.285	8.503	0.312
2300	24.304	100.123	84.607	42.364	64.262	6.131	0.203
2400	24.419	102.162	85.955	46.364	64.205	3.763	0.124
2500	24.519	103.161	86.886	48.841	64.138	1.282	0.08
2600	24.609	104.125	87.340	51.706	64.077	0.92	0.06
2700	24.680	105.053	87.923	54.258	63.991	5.942	0.49
2800	24.740	105.824	88.424	56.428	63.886	8.368	0.610
2900	24.891	107.667	88.886	58.744	63.908	10.777	0.760
3000	24.947	108.464	89.731	61.236	63.857	13.184	0.900
3100	24.986	109.267	90.390	63.734	63.811	15.594	1.032
3200	25.018	110.075	90.577	66.243	63.731	17.994	1.152
3300	25.088	110.795	91.169	71.253	63.700	20.396	1.274
3400	25.128	111.523	91.169	73.768	63.671	22.799	1.384
3500	25.165	112.432	91.749	76.269	63.650	25.202	1.489
3600	25.196	113.562	92.255	78.769	63.621	27.606	1.586
3700	25.220	114.250	93.395	81.332	63.621	30.006	1.681
3800	25.259	114.250	93.395	83.859	63.615	32.407	1.771
3900	25.286	114.690	93.925	86.389	63.614	34.804	1.855
4000	25.312	115.514	94.444	88.922	63.620	37.209	1.936
4100	25.337	116.124	95.053	91.453	63.620	39.615	2.017
4200	25.353	117.004	95.942	93.983	63.627	42.027	2.098
4300	25.378	117.304	96.423	96.532	63.671	44.403	2.157
4400	25.397	117.875	96.423	99.072	63.698	46.810	2.224
4500	25.415	118.433	96.699	101.615	63.732	49.215	2.286
4600	25.422	118.500	97.360	104.160	63.772	51.616	2.347
4700	25.428	118.500	98.000	106.705	63.816	54.025	2.410
4800	25.464	120.440	98.264	109.252	63.867	56.427	2.466
4900	25.478	120.555	98.704	111.800	63.924	58.831	2.521
5000	25.491	121.060	99.138	114.350	63.959	61.241	2.574
5100	25.516	121.245	99.584	116.900	64.000	63.646	2.625
5200	25.524	121.245	100.397	119.453	64.126	66.059	2.673
5300	25.527	122.518	100.397	122.006	64.206	68.473	2.721
5400	25.536	122.518	100.803	124.561	64.290	70.883	2.766
5500	25.546	123.446	101.203	127.116	64.382	73.296	2.810
5600	25.529	124.943	101.386	132.229	64.480	75.713	2.853
5700	25.576	124.780	101.369	134.767	64.580	78.133	2.893
5800	25.576	124.780	101.369	137.311	64.688	80.547	2.933
5900	25.584	125.210	102.746				
6000	25.584	125.210					

Dec. 31, 1960; Sept. 30, 1984; June 30, 1970

CH₂ClF

Dichloromethane (CH₂Cl₂)

(Ideal Gas)

GFW = 84.9331

Point Group C_{2v}

ΔH_f^o = -21.19 ± 0.3 kcal/mol

S_{298.15}^o = 84.574 ± 0.01 gibbs/mol

ΔH_f^o_{298.15} = -22.83 ± 0.3 kcal/mol

Ground State Quantum Weight = 1

T, °K	Cp ^o	gibbs/mol S ^o - (C ^o - H ^o ₂₉₈)/T	ΔH ^o _f ^o	ΔG ^o	Log Kp
0	6.847	∞	21.190	21.190	INFINITE
100	53.781	71.991	20.253	18.464	20.253
200	10.126	60.160	22.328	16.481	20.195
298	12.164	64.574	22.830	16.485	12.064
300	12.204	64.650	22.839	16.464	11.941
400	16.237	68.446	23.285	14.245	7.783
500	15.633	71.811	23.645	11.941	5.220
600	17.296	74.841	23.928	9.573	3.487
700	18.403	77.593	24.146	7.162	2.036
800	19.256	80.133	24.327	5.111	1.031
900	20.095	82.566	24.472	3.487	0.433
1000	20.755	84.933	24.591	2.220	0.195
1100	21.322	86.592	24.687	1.267	0.087
1200	21.809	88.469	24.755	0.613	0.037
1300	22.216	90.511	24.800	0.280	0.017
1400	22.556	92.792	24.828	0.122	0.008
1500	22.843	95.362	24.840	0.053	0.004
1600	23.190	98.250	24.839	0.028	0.002
1700	23.431	101.393	24.830	0.014	0.001
1800	23.674	104.744	24.816	0.007	0.000
1900	23.931	108.342	24.798	0.003	0.000
2000	24.196	112.219	24.766	0.001	0.000
2100	24.443	116.393	24.721	0.000	0.000
2200	24.674	120.874	24.666	0.000	0.000
2300	24.895	125.682	24.603	0.000	0.000
2400	25.107	130.842	24.528	0.000	0.000
2500	25.309	136.375	24.443	0.000	0.000
2600	25.500	142.319	24.350	0.000	0.000
2700	25.681	148.704	24.249	0.000	0.000
2800	25.852	155.562	24.141	0.000	0.000
2900	26.013	162.924	24.018	0.000	0.000
3000	26.164	170.722	23.882	0.000	0.000
3100	26.304	178.992	23.733	0.000	0.000
3200	26.434	187.762	23.570	0.000	0.000
3300	26.554	197.062	23.395	0.000	0.000
3400	26.664	206.922	23.208	0.000	0.000
3500	26.764	217.282	23.010	0.000	0.000
3600	26.854	228.182	22.800	0.000	0.000
3700	26.934	239.662	22.579	0.000	0.000
3800	27.004	251.762	22.348	0.000	0.000
3900	27.064	264.522	22.108	0.000	0.000
4000	27.114	277.982	21.859	0.000	0.000
4100	27.154	292.182	21.600	0.000	0.000
4200	27.184	307.062	21.331	0.000	0.000
4300	27.204	322.662	21.052	0.000	0.000
4400	27.214	338.922	20.764	0.000	0.000
4500	27.214	355.782	20.467	0.000	0.000
4600	27.204	373.182	20.162	0.000	0.000
4700	27.184	391.162	19.849	0.000	0.000
4800	27.154	409.682	19.528	0.000	0.000
4900	27.114	428.702	19.200	0.000	0.000
5000	27.064	448.182	18.865	0.000	0.000
5100	26.994	468.062	18.524	0.000	0.000
5200	26.904	488.282	18.177	0.000	0.000
5300	26.794	508.782	17.824	0.000	0.000
5400	26.664	529.502	17.465	0.000	0.000
5500	26.504	550.382	17.100	0.000	0.000
5600	26.314	571.462	16.729	0.000	0.000
5700	26.094	592.682	16.352	0.000	0.000
5800	25.844	614.082	15.969	0.000	0.000
5900	25.564	635.682	15.582	0.000	0.000
6000	25.254	657.422	15.191	0.000	0.000

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1968

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
2999 (1)	282 (1)	898 (1)
1467 (1)	1153 (1)	1288 (1)
717 (1)	3040 (1)	758 (1)

Bond Distances: C-H = 1.068 Å C-Cl = 1.772 Å

Bond Angles: H-C-H = 112° Cl-C-Cl = 111.8°

Product of the Moments of Inertia: I_AI_BI_C = 1.8686 × 10⁻¹¹⁴ g cm⁶

Heat of Formation

Hu and Sinke (1) have measured the heat of combustion of CH₂Cl₂(l) in the rotating bomb calorimeter, using As₂O₃ solution as the reducing agent. They reported ΔH_c^o₂₉₈ = -144.00 kcal/mole for CH₂Cl₂(l) + O₂(g) → CO₂(g) + 2HCl(600H₂O, aq) which leads to ΔH_f^o₂₉₈(CH₂Cl₂, l) = -29.70 kcal/mol, using ΔH_f^o₂₉₈ = -94.051 and -39.823 kcal/mol for CO₂(g) and HCl(600H₂O, aq), respectively (2). The standard deviation of five combustion runs was 0.12 kcal/mol. Employing the heat of vaporization of CH₂Cl₂(l) at 298°K as 6.87 kcal/mol (3), we obtain ΔH_f^o₂₉₈(CH₂Cl₂, g) = -22.83 kcal/mol which is adopted in the tabulation.

L. Smith et al. (4), based on the combustion data of E. Efring (5), re-evaluated the heat of combustion of dichloromethane at 18.7°C as ΔH_c^o₂₉₈ = -170.14 cal/g for CH₂Cl₂(l) + O₂(g) → CO₂(g) + 2HCl(600H₂O, aq). This value needs to be further corrected for a change in the heat of oxidation of As₂O₃(s) (6) and calculated to 25°C to give ΔH_c^o₂₉₈ = ΔH_c^o₂₉₈ - 144.89 kcal/mol, ΔH_f^o₂₉₈(CH₂Cl₂, l) = -28.80 kcal/mol and ΔH_f^o₂₉₈(CH₂Cl₂, g) = -21.93 kcal/mol. J. Lacher et al. (7) have measured the heat of hydrogenation of dichloromethane to methane and hydrogen chloride at 250°C as -40.07 kcal/mol. Correction to 298°K gives ΔH_f^o₂₉₈(CH₂Cl₂, g) = -23.05 kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy

The bond distances and angles have been determined from the microwave spectra by R. J. Myers and W. D. Gwinn (8). The three principal moments of inertia are I_A = 2.630 × 10⁻³⁹, I_B = 2.5623 × 10⁻³⁸ and I_C = 2.7727 × 10⁻³⁸ g cm².

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection (9), based on infrared and Raman spectra by Shimanouchi and Syzaki (10), Palma et al. (11), and Welsh et al. (12).

References

- (1) A. T. Hu and G. C. Sinke, presented at the 23rd Calorimetry Conference, Midland, Mich., 1968.
- (2) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
- (3) J. H. Mathews, J. Am. Chem. Soc. **48**, 562 (1926).
- (4) L. Smith, L. Bjellerv, S. Krook and H. Westermark, Acta Chem. Scand. **7**, 65 (1953).
- (5) E. Efring, Ph. D. Dissertation, University of Lund, Lund, Sweden, 1938.
- (6) S. Sunner and S. Thoren, Acta Chem. Scand. **18**, 1528 (1964).
- (7) J. R. Lacher, A. Amador and J. D. Park, Trans. Faraday Soc. **53**, 1608 (1957).
- (8) R. J. Myers and W. D. Gwinn, J. Chem. Phys. **20**, 1420 (1952).
- (9) T. Shimanouchi, U. S. Natl. Bur. Std. NBS-RS-NBS6, 1967.
- (10) T. Shimanouchi and I. Suzuki, J. Mol. Spectry. **18**, 222 (1962).
- (11) F. E. Palma, E. A. Piotrowski, S. Sundram and F. F. Claveland, J. Mol. Spectry. **13**, 119 (1964).
- (12) H. L. Welsh, M. F. Crawford, T. R. Thomas and C. R. Love, Can. J. Phys. **30**, 577 (1952).

Difluoromethane (CH₂F₂)

(Ideal Gas)

GFW = 52.0239

DIFLUOROMETHANE (CH₂F₂)

(IDEAL GAS)

GFW = 52.0239

Point Group C_{2v}

$\Delta H_f^\circ = -105.9 \pm 0.4$ kcal/mol

$S_{298.15}^\circ = 58.93 \pm 0.01$ gibbs/mol

$\Delta H_f^\circ_{298.15} = -107.7 \pm 0.4$ kcal/mol

Ground State Quantum Weight = 1



T, °K	C _p ^a	gibbs/mol S ^b	-(C _p ^a - H ₂₉₈)/T	H ^c - H ₂₉₈	kcal/mol ΔH ^f	ΔG ^f	Log K ^p
0	0.000	INFINITE	INFINITE	2.555	-105.879	-105.879	INFINITE
100	8.005	49.445	67.038	-1.759	-104.967	-104.967	229.404
200	18.786	55.812	57.016	-0.752	-104.160	-104.160	172.110
298	10.243	58.935	58.935	0.000	-103.710	-101.127	77.120
300	10.277	58.998	58.935	.019	-107.722	-101.087	73.442
400	12.216	62.217	59.361	1.142	-108.309	-96.784	53.973
500	14.095	65.149	60.229	2.460	-108.816	-86.343	42.111
600	15.719	67.864	61.278	3.953	-109.233	-81.808	34.169
700	17.079	70.394	62.402	5.595	-109.569	-81.208	28.476
800	18.215	72.751	63.550	7.361	-109.834	-80.567	24.195
900	19.169	74.953	64.696	9.232	-110.038	-80.886	20.858
1000	19.975	77.016	65.826	11.190	-110.189	-81.206	18.185
1100	20.659	78.953	66.932	13.223	-110.297	-80.503	15.994
1200	21.241	80.776	68.011	15.318	-110.369	-77.789	14.167
1300	21.740	82.494	69.059	17.468	-110.415	-75.072	12.621
1400	22.169	84.124	70.078	19.664	-110.436	-72.351	11.295
1500	22.538	85.666	71.066	21.900	-110.441	-69.629	10.145
1600	22.858	87.131	72.025	24.170	-110.434	-66.912	9.100
1700	23.137	88.525	72.955	26.470	-110.413	-64.190	8.252
1800	23.381	89.855	73.857	28.796	-110.385	-61.475	7.464
1900	23.594	91.125	74.733	31.145	-110.348	-58.757	6.759
2000	23.782	92.340	75.583	33.514	-110.306	-56.042	6.124
2100	23.949	93.504	76.409	35.901	-110.260	-53.330	5.550
2200	24.097	94.622	77.211	38.303	-110.214	-50.622	5.029
2300	24.228	95.696	77.992	40.720	-110.163	-47.912	4.553
2400	24.346	96.730	78.751	43.149	-110.111	-45.206	4.117
2500	24.452	97.726	79.490	45.589	-110.066	-42.506	3.716
2600	24.547	98.687	80.210	48.039	-110.018	-39.802	3.346
2700	24.633	99.615	80.912	50.498	-109.971	-37.103	3.003
2800	24.711	100.512	81.596	52.965	-109.925	-34.406	2.686
2900	24.781	101.380	82.263	55.439	-109.883	-31.705	2.389
3000	24.846	102.222	82.915	57.921	-109.843	-29.016	2.114
3100	24.906	103.037	83.551	60.408	-109.804	-26.321	1.854
3200	24.958	103.829	84.172	62.902	-109.769	-23.628	1.616
3300	25.007	104.598	84.779	65.400	-109.739	-20.938	1.387
3400	25.053	105.345	85.373	67.903	-109.711	-18.247	1.173
3500	25.094	106.072	85.954	70.410	-109.690	-15.556	.971
3600	25.133	106.770	86.523	72.922	-109.670	-12.867	.781
3700	25.169	107.448	87.069	75.437	-109.658	-10.177	.601
3800	25.202	108.100	87.625	77.955	-109.649	-7.485	.430
3900	25.232	108.795	88.160	80.477	-109.647	-4.799	.269
4000	25.261	109.434	88.684	83.002	-109.648	-2.108	.115
4100	25.287	110.058	89.197	85.529	-109.654	-.574	.031
4200	25.312	110.668	89.701	88.059	-109.670	3.269	-.170
4300	25.335	111.264	90.196	90.592	-109.688	5.957	-.303
4400	25.357	111.846	90.681	93.126	-109.714	8.644	-.429
4500	25.377	112.417	91.158	95.663	-109.744	11.330	-.550
4600	25.394	112.974	91.626	98.202	-109.781	14.026	-.666
4700	25.416	113.521	92.086	100.742	-109.825	16.719	-.777
4800	25.431	114.056	92.538	103.284	-109.874	19.414	-.884
4900	25.447	114.581	92.983	105.828	-109.929	22.109	-.986
5000	25.462	115.095	93.420	108.374	-109.990	24.801	-1.084
5100	25.476	115.590	93.850	110.921	-110.059	27.492	-1.178
5200	25.489	116.094	94.273	113.469	-110.133	30.184	-1.269
5300	25.502	116.580	94.689	116.018	-110.214	32.879	-1.357
5400	25.513	117.056	95.099	118.569	-110.302	35.573	-1.441
5500	25.525	117.525	95.503	121.121	-110.396	38.268	-1.522
5600	25.536	117.985	95.900	123.674	-110.497	40.962	-1.600
5700	25.546	118.437	96.291	126.228	-110.605	43.707	-1.676
5800	25.555	118.881	96.677	128.783	-110.719	46.414	-1.749
5900	25.564	119.318	97.057	131.339	-110.840	49.127	-1.820
6000	25.573	119.748	97.432	133.896	-110.967	51.832	-1.888

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
2949 (1)	529 (1)	1176 (1)
1508 (1)	1282 (1)	1435 (1)
1116 (1)	3013 (1)	1090 (1)

Bond Distances: C-F = 1.358 ± 0.001 Å C-H = 1.092 ± 0.003 Å

Bond Angles: F-C-F = 108° 17' ± 6' H-C-H = 111° 52' ± 25'

Product of the Moments of Inertia: I_AI_BI_C = 1.2272 × 10⁻¹¹⁵ g³ cm⁶

Heat of Formation

Neugebauer and Margrave (1) measured the enthalpy of combustion of CH₂F₂. Their result for the combustion reaction



was $\Delta H_{298}^\circ = -139.84 \pm 0.22$ kcal/mole. Using ΔH_{298}° (HF(21.5 H₂O)) = -76.75 ± 0.1 kcal/mol (2), obtained with dilution data compiled by Parker (3), we derive,

ΔH_{298}° (CH₂F₂, g) = -107.7 ± 0.4 kcal/mol.

from Margrave's data.

Heat Capacity and Entropy

The vibrational frequencies are average values from the infrared studies of Stewart and Nielsen (4) and Plyler and Benedict (5). Individual moments of inertia are calculated from the rotational constants reported by Lide (6) with the result I_A = 1.702 × 10⁻³⁹ g cm², I_B = 7.916 × 10⁻³⁹ g cm², and I_C = 9.0734 × 10⁻³⁹ g cm². The molecular structure data are from the microwave studies of Lide (6) and are in excellent agreement with electron-diffraction studies of Brockway, Thornton, and Bartall whose results are reported in the Annual Review of Physical Chemistry (7).

References

1. C. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **62**, 1043 (1958).
2. JANAF Table for HF(g), 12-31-68.
3. V. B. Parker, *U. S. Natl. Bur. Std. NBS-RS-NBS 2*, 1965.
4. H. B. Stewart and H. H. Nielsen, *Phys. Rev.*, **75**, 840 (1949).
5. E. K. Plyler and W. S. Benedict, *J. Research Nat. Bur. Standards*, **57**, 202 (1951).
6. D. R. Lide, Jr., *J. Amer. Chem. Soc.*, **74**, 3548 (1952).
7. R. L. Livingston, *Annual Review of Phys. Chem.*, **5**, 397 (1954).



Formaldehyde (CH₂O)

(Ideal Gas) Mol. Wt. = 30.027

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	7.000	48.000	INFINITE	2.395	26.782	INFINITE	
100	8.000	48.996	53.016	1.604	27.381	26.782	
200	8.997	49.991	53.016	1.000	27.700	26.782	
300	9.994	50.986	53.016	0.616	27.700	26.782	
400	10.990	51.981	53.016	0.416	27.700	26.782	
500	11.986	52.976	53.016	0.300	27.700	26.782	
600	12.982	53.971	53.016	0.246	27.700	26.782	
700	13.978	54.966	53.016	0.214	27.700	26.782	
800	14.974	55.961	53.016	0.194	27.700	26.782	
900	15.970	56.956	53.016	0.180	27.700	26.782	
1000	16.966	57.951	53.016	0.170	27.700	26.782	
1100	17.962	58.946	53.016	0.163	27.700	26.782	
1200	18.958	59.941	53.016	0.158	27.700	26.782	
1300	19.954	60.936	53.016	0.154	27.700	26.782	
1400	20.950	61.931	53.016	0.150	27.700	26.782	
1500	21.946	62.926	53.016	0.146	27.700	26.782	
1600	22.942	63.921	53.016	0.142	27.700	26.782	
1700	23.938	64.916	53.016	0.138	27.700	26.782	
1800	24.934	65.911	53.016	0.134	27.700	26.782	
1900	25.930	66.906	53.016	0.130	27.700	26.782	
2000	26.926	67.901	53.016	0.126	27.700	26.782	
2100	27.922	68.896	53.016	0.122	27.700	26.782	
2200	28.918	69.891	53.016	0.118	27.700	26.782	
2300	29.914	70.886	53.016	0.114	27.700	26.782	
2400	30.910	71.881	53.016	0.110	27.700	26.782	
2500	31.906	72.876	53.016	0.106	27.700	26.782	
2600	32.902	73.871	53.016	0.102	27.700	26.782	
2700	33.898	74.866	53.016	0.098	27.700	26.782	
2800	34.894	75.861	53.016	0.094	27.700	26.782	
2900	35.890	76.856	53.016	0.090	27.700	26.782	
3000	36.886	77.851	53.016	0.086	27.700	26.782	
3100	37.882	78.846	53.016	0.082	27.700	26.782	
3200	38.878	79.841	53.016	0.078	27.700	26.782	
3300	39.874	80.836	53.016	0.074	27.700	26.782	
3400	40.870	81.831	53.016	0.070	27.700	26.782	
3500	41.866	82.826	53.016	0.066	27.700	26.782	
3600	42.862	83.821	53.016	0.062	27.700	26.782	
3700	43.858	84.816	53.016	0.058	27.700	26.782	
3800	44.854	85.811	53.016	0.054	27.700	26.782	
3900	45.850	86.806	53.016	0.050	27.700	26.782	
4000	46.846	87.801	53.016	0.046	27.700	26.782	
4100	47.842	88.796	53.016	0.042	27.700	26.782	
4200	48.838	89.791	53.016	0.038	27.700	26.782	
4300	49.834	90.786	53.016	0.034	27.700	26.782	
4400	50.830	91.781	53.016	0.030	27.700	26.782	
4500	51.826	92.776	53.016	0.026	27.700	26.782	
4600	52.822	93.771	53.016	0.022	27.700	26.782	
4700	53.818	94.766	53.016	0.018	27.700	26.782	
4800	54.814	95.761	53.016	0.014	27.700	26.782	
4900	55.810	96.756	53.016	0.010	27.700	26.782	
5000	56.806	97.751	53.016	0.006	27.700	26.782	
5100	57.802	98.746	53.016	0.002	27.700	26.782	
5200	58.798	99.741	53.016	0.000	27.700	26.782	
5300	59.794	100.736	53.016	0.000	27.700	26.782	
5400	60.790	101.731	53.016	0.000	27.700	26.782	
5500	61.786	102.726	53.016	0.000	27.700	26.782	
5600	62.782	103.721	53.016	0.000	27.700	26.782	
5700	63.778	104.716	53.016	0.000	27.700	26.782	
5800	64.774	105.711	53.016	0.000	27.700	26.782	
5900	65.770	106.706	53.016	0.000	27.700	26.782	
6000	66.766	107.701	53.016	0.000	27.700	26.782	

March 31, 1961

FORMALDEHYDE (CH₂O)

(IDEAL GAS)

MOL. WT. = 30.027

$$\Delta H_f^\circ = -26.8 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -27.7 \pm 1.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 52.26 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Point Group C_{2v}

Vibrational Levels and Multiplicities

ω , cm. ⁻¹	ω , cm. ⁻¹
2766.4 (1)	2843.4 (1)
1746.07 (1)	1247.4 (1)
1500.6 (1)	1163.5 (1)

$$\text{Bond Lengths and Angles} \quad \text{C-H} = 1.12 \pm 0.01 \text{ \AA} \quad \text{C-O} = 1.21 \pm 0.01 \text{ \AA} \quad \text{H-C-H} = 118 \pm 2^\circ$$

$$\text{Moments of Inertia} \quad I_A = 2.975 \times 10^{-40} \text{ g. cm.}^2 \quad I_B = 2.161 \times 10^{-39} \text{ g. cm.}^2 \quad I_C = 2.468 \times 10^{-39} \text{ g. cm.}^2$$

$$\sigma = 2$$

Heats of Formation

M. Delepine and M. Badoche, Compt. rend. 231, 777 (1942), measured the heat of combustion of a formaldehyde polymer. Their value is revised to $\Delta H_f^\circ = -25.0 \text{ kcal. mole}^{-1}$ based on the following thermochemical cycle:

$$\text{I} \quad \text{C(c)} + 1/2\text{O}_2(\text{g}) + \text{H}_2(\text{g}) = \frac{1}{n} (\text{CH}_2\text{O})_n(\text{c}) \quad -42.3 \text{ kcal.}$$

$$\text{II} \quad \frac{1}{n} (\text{CH}_2\text{O})_n(\text{c}) + \text{H}_2\text{O} = \text{CH}_2\text{O}(\text{aq}) \quad 2.4$$

$$\text{III} \quad \text{CH}_2\text{O}(\text{g}) = \text{CH}_2\text{O}(\text{aq}) \quad 14.9$$

Equation I and II are based upon data listed by Delepine and Badoche. For reaction III Delepine and Badoche obtained 15 kcal. mole⁻¹. Whereas, P. Walker, J. Am. Chem. Soc. 55, 2821 (1933) obtained 14.8 kcal. mole⁻¹. A value of -27.7 kcal. mole⁻¹ is obtained from the combustion experiments of H. von Wartenberg and B. Lerner-Steinberg, Z. angew. Chem. 38, 591 (1925). Corrections of -0.6 and 0.1 kcal. mole⁻¹ were applied to obtain a heat of reaction at constant pressure and at 298.15°K.

Equilibrium constant determinations of reaction (IV) by R. H. Newton and B. P. Dodge, J. Am. Chem. Soc. 55, 4747 (1933), lead to a $\Delta H_f^\circ = -29.0 \text{ kcal. mole}^{-1}$.

$$\text{IV} \quad \text{H}_2(\text{g}) + \text{CO}(\text{g}) = \text{H}_2\text{CO}(\text{g})$$

The value obtained from the measurements of Wartenberg and Lerner-Steinberg is believed to be the most reliable.

Heat Capacities and Entropies

Frequencies were measured by H. H. Blau and H. H. Nielsen, J. Molec. Spect. 1, 124 (1957) in the I. R. Microwave determinations of R. B. Lawrence and M. P. W. Strandberg, Phys. Rev. 83, 365 (1951), and those of G. Erlanson, J. Chem. Phys. 25, 579 (1956) are in essential agreement.



Methyl Chloride (CH₃Cl)

(Ideal Gas) Mol. Wt. = 50.492

METHYL CHLORIDE (CH₃Cl) (IDEAL GAS)

MOL. WT. = 50.492

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.955	46.811	18.764	18.764	18.764	INFINITE
200	8.399	52.409	18.472	18.472	18.472	39.806
298	8.726	55.987	18.213	18.213	18.213	18.326
300	8.756	56.047	18.213	18.213	18.213	11.029
400	11.496	59.090	21.313	21.313	21.313	10.935
500	13.167	61.838	23.315	23.315	23.315	7.117
600	14.639	64.372	24.937	24.937	24.937	10.888
700	15.917	66.727	26.243	26.243	26.243	4.759
800	17.031	68.927	27.273	27.273	27.273	3.149
900	18.005	70.990	28.043	28.043	28.043	1.976
1000	18.857	72.951	28.637	28.637	28.637	1.083
1100	19.603	74.765	29.085	29.085	29.085	0.380
1200	20.253	76.500	29.405	29.405	29.405	0.187
1300	20.822	78.144	29.599	29.599	29.599	0.155
1400	21.318	79.705	29.688	29.688	29.688	0.137
1500	21.752	81.191	29.671	29.671	29.671	0.124
1600	22.133	82.607	29.549	29.549	29.549	0.113
1700	22.467	83.959	29.326	29.326	29.326	0.103
1800	22.761	85.252	28.999	28.999	28.999	0.093
1900	23.021	86.490	28.571	28.571	28.571	0.083
2000	23.251	87.677	28.045	28.045	28.045	0.073
2100	23.456	88.816	27.424	27.424	27.424	0.063
2200	23.638	89.912	26.709	26.709	26.709	0.053
2300	23.802	90.966	25.906	25.906	25.906	0.043
2400	23.948	91.982	25.019	25.019	25.019	0.033
2500	24.080	92.962	24.056	24.056	24.056	0.023
2600	24.199	93.909	23.020	23.020	23.020	0.013
2700	24.307	94.825	21.913	21.913	21.913	0.003
2800	24.404	95.710	20.740	20.740	20.740	0.003
2900	24.493	96.568	19.506	19.506	19.506	0.003
3000	24.574	97.400	18.213	18.213	18.213	0.003
3100	24.648	98.207	16.864	16.864	16.864	0.003
3200	24.716	98.991	15.464	15.464	15.464	0.003
3300	24.779	99.752	14.019	14.019	14.019	0.003
3400	24.836	100.493	12.534	12.534	12.534	0.003
3500	24.889	101.214	11.006	11.006	11.006	0.003
3600	24.938	101.915	9.434	9.434	9.434	0.003
3700	24.983	102.599	7.819	7.819	7.819	0.003
3800	25.025	103.266	6.164	6.164	6.164	0.003
3900	25.064	103.917	4.464	4.464	4.464	0.003
4000	25.101	104.552	2.719	2.719	2.719	0.003
4100	25.134	105.172	0.934	0.934	0.934	0.003
4200	25.166	105.778	-0.887	-0.887	-0.887	0.003
4300	25.196	106.371	-2.692	-2.692	-2.692	0.003
4400	25.223	106.950	-4.447	-4.447	-4.447	0.003
4500	25.249	107.517	-6.154	-6.154	-6.154	0.003
4600	25.273	108.072	-7.819	-7.819	-7.819	0.003
4700	25.296	108.616	-9.434	-9.434	-9.434	0.003
4800	25.318	109.149	-11.006	-11.006	-11.006	0.003
4900	25.338	109.671	-12.534	-12.534	-12.534	0.003
5000	25.357	110.183	-14.019	-14.019	-14.019	0.003
5100	25.375	110.686	-15.464	-15.464	-15.464	0.003
5200	25.392	111.179	-16.864	-16.864	-16.864	0.003
5300	25.408	111.662	-18.213	-18.213	-18.213	0.003
5400	25.423	112.137	-19.506	-19.506	-19.506	0.003
5500	25.436	112.604	-20.740	-20.740	-20.740	0.003
5600	25.445	113.063	-21.913	-21.913	-21.913	0.003
5700	25.455	113.513	-23.020	-23.020	-23.020	0.003
5800	25.467	113.956	-24.056	-24.056	-24.056	0.003
5900	25.479	114.392	-25.019	-25.019	-25.019	0.003
6000	25.500	114.820	-25.906	-25.906	-25.906	0.003

Dec. 31, 1960; Sept. 30, 1964

Point Group C_{3v}S_{298.15} = 55.99 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f^o 0 = -18.76 ± 0.17 kcal. mole⁻¹ΔH_f^o 298.15 = -20.68 ± 0.17 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
2928 (1)	3047 (2)
1355 (1)	1460 (2)
732 (1)	1020 (2)

Bond Distances: C-H = 1.0959 Å C-Cl = 1.7812 Å

Bond Angle: H-C-H = 108° H-C-Cl = 110°54'

Product of the Moments of Inertia: I_AI_BI_C = 21.460 X 10⁻¹¹⁷ g.³ cm.⁶

σ = 3

Heat of Formation.

The heat of formation was measured using hydrogenation to give methane and hydrogen chloride, by J. R. Lacher, E. Emery, E. Bohmalk and J. D. Park, J. Phys. Chem. 60, 492 (1956). The value adopted was recalculated using JANAF auxiliary data for methane and HCl.

Heat Capacity and Entropy.

The vibrational frequencies were tabulated by E. K. Plyler and W. S. Benedict, J. Research Natl. Bur. Standards 47, 202 (1951). C. C. Costain, J. Chem. Phys. 29, 864 (1958) has calculated the bond distances and angles based on an isotopic substitution method. From these the individual moments of inertia were calculated to be I_A = 0.5262 X 10⁻³⁹ g.² cm.² and I_B = I_C = 6.3863 X 10⁻³⁹ g.² cm.²



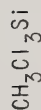
Trichloromethylsilane (Si(CH₃)Cl₃)

(Ideal Gas) Mol. Wt. = 149.496

INTERIM TABLE

T, °K.	C _p	S° -(F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0							
100							
200							
300	24.470	83.900	83.900	.000	-126.400	-111.098	82.020
400	27.120	86.082	83.900	.045	-126.410	-111.098	81.908
500	29.610	87.683	86.075	5.504	-127.168	-101.838	81.511
600	31.340	103.442	89.183	6.555	-127.441	-96.744	81.237
700	32.750	108.382	91.579	11.762	-127.621	-91.613	80.601
800	33.930	112.684	93.962	15.096	-127.733	-86.459	80.168
900	34.920	116.481	96.321	17.566	-127.780	-81.176	79.740
1000	35.620	120.620	98.537	22.083	-127.802	-76.128	79.637
1100	36.580	124.070	100.703	25.704	-127.771	-70.963	79.098
1200	37.230	127.282	102.766	29.395	-127.705	-65.799	78.983
1300	37.600	130.285	104.767	33.147	-127.612	-60.644	78.195
1400	37.820	133.104	106.710	36.952	-127.499	-55.499	77.663
1500	38.120	135.761	108.539	40.803	-127.374	-50.360	77.337

December 31, 1960.



Trichloromethylsilane (Si(CH₃)Cl₃) (Ideal gas)

Mol. Wt. = 149.496

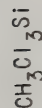
ΔH_f[°] 298.15 = [-126.4] kcal. mole⁻¹

S_{298.15}[°] = 83.9 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Heat of Formation. ΔH_f[°] 298.15 was estimated.

Heat Capacity and Entropy. C_p and S_{298.15} were taken from G. J. Janz, Y. Mikawa, and P. Bennke, private communication, March 16, 1960.





Trifluoromethylsilane ($\text{Si}(\text{CH}_3)_3\text{F}_3$)
(Ideal Gas) Mol. Wt. = 100.125

INTERIM TABLE

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$\text{cal. mole}^{-1}\text{deg}^{-1}$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0							
100							
200							
298	21.720	75.070	75.070	.000	-294.425	-279.456	204.984
300	21.780	75.205	75.070	.040	-294.438	-279.564	203.652
400	25.140	81.054	75.948	2.145	-295.235	-274.485	149.942
500	27.840	87.867	77.768	5.049	-295.767	-269.191	117.658
600	29.950	93.136	76.698	7.944	-296.062	-263.853	96.104
700	31.640	97.885	75.135	11.025	-296.325	-258.462	80.692
800	33.040	102.205	84.378	14.262	-296.507	-253.041	69.124
900	34.210	106.166	93.171	17.626	-296.625	-247.598	60.122
1000	35.200	109.823	88.725	21.098	-296.690	-242.149	52.919
1100	36.060	113.219	90.799	24.662	-296.706	-236.694	47.024
1200	36.780	116.389	92.801	28.305	-296.684	-231.237	42.112
1300	37.410	119.356	94.731	32.015	-296.633	-225.765	37.956
1400	37.950	122.151	96.581	35.785	-296.557	-220.338	34.395
1500	38.430	124.727	98.393	39.606	-296.465	-214.895	31.309

Trifluoromethylsilane ($\text{Si}(\text{CH}_3)_3\text{F}_3$) (Ideal Gas)

Mol. Wt. = 100.125

$\Delta H_f^\circ 298.15 = [-294.625] \text{ kcal. mole}^{-1}$

$S_{298.15}^\circ = 75.07 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Heat of Formation. $\Delta H_f^\circ 298.15$ was estimated.

Heat Capacity and Entropy. C_p and $S_{298.15}^\circ$ were taken from G. Janz, Y. Mikawa, and P. Behnke, private communication, March 16, 1960.



(Ideal Gas) Mol. Wt. = 16.043

(IDEAL GAS)

METHANE (CH₄)

MOL. WT. = 16.043

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	7.090	0.000	INFINITE	2.394	15.991	15.991	INFINITE	
100	7.949	35.706	17.716	1.401	13.400	13.400	13.400	
200	8.601	31.222	15.247	0.805	12.216	12.216	12.216	
298	8.518	44.490	14.490	0.000	17.995	17.995	17.995	
300	8.535	44.503	14.490	0.016	17.909	17.909	17.909	
400	9.640	47.144	14.637	0.233	16.436	16.436	16.436	
500	11.076	49.453	14.533	1.260	19.316	19.316	19.316	
600	12.483	51.597	14.367	3.138	19.916	19.916	19.916	
700	13.613	53.622	14.260	4.454	20.429	20.429	20.429	
800	14.587	55.565	14.185	5.285	20.807	20.807	20.807	
900	15.417	57.385	14.131	5.958	21.097	21.097	21.097	
1000	17.160	59.141	14.016	9.125	21.482	21.482	21.482	
1100	18.052	60.619	13.922	10.887	21.696	21.696	21.696	
1200	19.542	62.560	13.842	12.574	21.974	21.974	21.974	
1300	20.654	64.541	13.772	14.185	22.250	22.250	22.250	
1400	20.130	65.431	13.719	15.637	22.050	22.050	22.050	
1500	20.688	66.840	13.687	16.679	22.104	22.104	22.104	
1600	21.161	68.191	13.672	20.772	22.137	22.137	22.137	
1700	21.974	69.794	13.674	22.046	22.144	22.144	22.144	
1800	21.907	70.790	13.694	22.298	22.127	22.127	22.127	
1900	22.273	71.926	13.729	27.550	22.222	22.222	22.222	
2000	22.562	73.076	13.766	56.306	22.099	22.099	22.099	
2100	22.620	74.183	13.783	59.036	22.065	22.065	22.065	
2200	23.050	75.259	13.783	38.109	22.026	22.026	22.026	
2300	23.450	76.294	13.774	38.753	21.991	21.991	21.991	
2400	23.811	77.293	13.753	41.106	21.935	21.935	21.935	
2500	23.608	78.253	13.723	61.781	21.868	21.868	21.868	
2600	23.786	79.162	13.682	62.441	21.839	21.839	21.839	
2700	24.074	80.032	13.637	63.707	21.740	21.740	21.740	
2800	24.348	80.878	13.588	64.909	21.694	21.694	21.694	
2900	24.545	81.778	13.535	66.300	21.694	21.694	21.694	
3000	24.233	82.597	13.495	53.079	21.649	21.649	21.649	
3100	24.327	83.394	13.486	55.507	21.602	21.602	21.602	
3200	24.433	84.150	13.466	57.946	21.561	21.561	21.561	
3300	24.550	84.862	13.435	60.400	21.526	21.526	21.526	
3400	24.565	85.532	13.399	62.842	21.488	21.488	21.488	
3500	24.633	86.365	13.365	67.707	21.459	21.459	21.459	
3600	24.695	87.060	13.325	67.768	21.433	21.433	21.433	
3700	24.826	87.726	13.282	69.752	21.397	21.397	21.397	
3800	24.866	88.358	13.236	70.719	21.369	21.369	21.369	
3900	24.855	89.043	13.192	75.202	21.389	21.389	21.389	
4000	24.901	89.673	13.144	77.690	21.366	21.366	21.366	
4100	24.944	90.288	13.094	70.732	21.367	21.367	21.367	
4200	24.984	90.878	13.042	82.076	21.397	21.397	21.397	
4300	25.022	91.440	12.989	87.583	21.432	21.432	21.432	
4400	25.057	92.054	12.934	87.583	21.432	21.432	21.432	
4500	25.090	92.617	12.875	90.190	21.463	21.463	21.463	
4600	25.121	93.169	12.817	92.701	21.498	21.498	21.498	
4700	25.157	93.740	12.756	97.218	21.580	21.580	21.580	
4800	25.197	94.340	12.692	100.249	21.644	21.644	21.644	
4900	25.203	94.739	12.626	102.771	21.706	21.706	21.706	
5000	25.227	95.268	12.568	105.295	21.777	21.777	21.777	
5100	25.250	95.766	12.512	107.820	21.851	21.851	21.851	
5200	25.282	96.240	12.456	110.348	21.927	21.927	21.927	
5300	25.311	96.684	12.401	112.879	22.029	22.029	22.029	
5400	25.330	97.213	12.346	115.411	22.128	22.128	22.128	
5500	25.347	97.676	12.293	117.945	22.234	22.234	22.234	
5600	25.387	98.134	12.241	120.478	22.344	22.344	22.344	
5700	25.400	98.568	12.190	122.557	22.459	22.459	22.459	
5800	25.394	99.024	12.141	124.018	22.598	22.598	22.598	
5900	25.394	99.456	12.094	125.557	22.732	22.732	22.732	
6000	25.409	99.685	12.050	126.067	22.732	22.732	22.732	

March 31, 1961

$\Delta H_{fO}^0 = -15.99 \pm 0.08$ kcal. mole⁻¹
 $\Delta H_f^0 = -17.895 \pm 0.08$ kcal. mole⁻¹
Point Group T_d
 $S_{298.15} = 44.48 \pm 0.01$ cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω , cm. ⁻¹	
2916.5 (1)	
1534.0 (2)	
3018.7 (3)	
1306 (3)	

Bond Lengths and Angles \angle H-C-H = 109° 28' C-H = 1.091 ± 0.002 ÅMoments of Inertia $I_A = I_B = I_C = 5.313 \times 10^{-40}$ g. cm.²

Heat of Formation

P. D. Rossini, J. Research Nat. Bur. Standards 57, 37 (1951) measured the heat of combustion of methane gas. His value at 298.15°K was corrected to the presently accepted molecular weight of water. The heat of formation was calculated using -68.3174 and -84.0540 kcal. mole⁻¹ for the heat of formation of H₂O(l) and CO₂(g) respectively.

Heat Capacities and Entropies

D. P. Stevenson and J. A. Ibers, J. Chem. Phys. 33, 762 (1960), calculated the bond distance from an analysis of available spectroscopic data. Vibrational frequencies listed by L. H. Jones and R. S. McDowell, J. Mol. Spect. 3, 632 (1959), are consistent with their results of a force constant calculation.

Cyanogen Iodide (ICN)

(Ideal Gas)

GFW = 152.9225

CIN

CYANOGEN IODIDE (ICN)

(IDEAL GAS)

GFW = 152.9225

Point Group $C_{\infty v}$ $\Delta H_f^\circ = 54.1 \pm 1.5$ kcal/mol $S_{298.15}^\circ = 61.48 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = 54.0 \pm 1.5$ kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

 $\frac{\omega_e}{\text{cm}^{-1}}$

485.8 (1)

304.5 (2)

2188 (1)

 $\sigma = 1$

Bond Distance: C-I = 1.994 Å C-N = 1.159 Å

Bond Angle: I-C-N = 180°

Rotational Constant: $B_0 = 0.1076$ cm⁻¹

Heat of Formation

The heat of formation is calculated from $\Delta H_f^\circ(\text{ICN}, c) = 39.71$ kcal/mol (1) and $\Delta H_f^\circ = 14.29 \pm 0.15$ kcal/mol. This latter value is obtained from a 2nd and 3rd law analysis of the vapor pressure data of Yost and Stone (2) and Ketelaar and Krueyer (3), which are in good agreement after dropping the lowest point in the first set and the lowest 3 points in the second set.

The heat of formation of the crystal is calculated from $\Delta H_{f,298}^\circ = -46.3 \pm 0.08$ kcal obtained by Lord and Woolf (4) for the reaction $\text{ICN}(c) + 2 \text{NaOH}(56 \text{ H}_2\text{O}) = \text{NaCNO}(2800 \text{ H}_2\text{O}) + \text{H}_2\text{O}(l)$. The auxiliary data used were $\Delta H_{f,298}^\circ \text{NaOH} \cdot 56 \text{ H}_2\text{O} = -112.28$ kcal/mol (1, 5); $\Delta H_{f,298}^\circ \text{NaCNO} \cdot 2800 \text{ H}_2\text{O} = -92.25$ kcal/mol (1, 5) and $\Delta H_{f,298}^\circ \text{H}_2\text{O} = -70.54$ kcal/mol (1, 5). The uncertainty in the final value reflects the uncertainty in $\Delta H_{f,298}^\circ \text{NaCNO} \cdot 2800 \text{ H}_2\text{O}$ which was determined by Lord and Woolf to be -93.6 kcal/mol in excess $\text{NaOH} \cdot 56 \text{ H}_2\text{O}$.

Heat Capacity and Entropy

The molecular structure, bond distances and angle were determined using microwave spectroscopy by Tyler and Sheridan (5). The infrared spectrum of the gas has been reported by Hemple and Nixon (1) using a 10m folded path cell. The fundamentals have been confirmed by the Raman data of West and Farnsworth (6) on a solution in methanol; and by the infrared data of Freitag and Nixon (3) on solid ICN.

References

1. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
2. D. M. Yost and W. E. Stone, J. Amer. Chem. Soc. 55, 1889 (1933).
3. J. A. A. Ketelaar and S. Krueyer, Rec. Trav. Chim. 52, 550 (1943).
4. G. Lord and A. A. Woolf, J. Chem. Soc. (London), 2546 (1954).
5. V. B. Parker, U. S. Natl. Bur. Std. NBS-2, 1965.
6. J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 53, 2661 (1957).
7. S. Hemple and E. R. Nixon, J. Chem. Phys. 47, 4273 and 48, 5288 (1968).
8. W. West and M. Farnsworth, J. Chem. Phys. 3, 402 (1933).
9. W. O. Freitag and E. R. Nixon, J. Chem. Phys. 24, 109 (1956).

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	2.741	54.124	54.124	INFINITE
100	8.023	50.687	70.913	2.023	54.117	51.707	-113.006
200	10.483	57.089	62.507	1.084	54.037	49.336	-53.912
298	11.573	61.479	61.479	0.000	54.000	47.037	-34.479
300	11.587	61.550	61.479	0.021	53.999	46.993	-34.235
400	12.152	64.969	61.941	1.211	52.008	44.735	-24.442
500	12.523	67.722	62.631	2.446	46.811	43.407	-16.973
600	12.895	70.033	63.884	3.713	44.494	42.718	-15.560
700	13.050	72.030	64.824	5.009	44.953	42.017	-13.119
800	13.323	73.794	65.681	6.330	46.993	41.309	-11.285
900	13.524	75.375	66.649	7.673	47.017	40.596	-9.656
1000	13.698	76.809	67.775	9.034	47.033	39.861	-8.716
1100	13.845	78.122	68.854	10.412	47.040	39.145	-7.781
1200	13.971	79.132	69.496	11.803	47.040	38.450	-7.003
1300	14.078	80.434	70.296	13.205	47.034	37.734	-6.344
1400	14.169	81.501	71.060	14.618	47.024	37.021	-5.779
1500	14.247	82.481	71.789	16.039	47.010	36.306	-5.290
1600	14.314	83.403	72.486	17.467	46.993	35.593	-4.842
1700	14.372	84.273	73.158	18.901	46.974	34.881	-4.446
1800	14.422	85.096	73.795	20.341	46.951	34.170	-4.149
1900	14.466	85.877	74.411	21.785	46.924	33.462	-3.849
2000	14.504	86.619	75.003	23.234	46.902	32.752	-3.579
2100	14.537	87.328	75.573	24.686	46.874	32.047	-3.335
2200	14.567	88.005	76.123	26.144	46.846	31.339	-3.111
2300	14.593	88.653	76.653	27.599	46.815	30.637	-2.911
2400	14.617	89.275	77.166	29.060	46.783	29.934	-2.726
2500	14.638	89.872	77.663	30.522	46.748	29.232	-2.555
2600	14.654	90.444	78.143	31.987	46.712	28.532	-2.398
2700	14.673	91.000	78.609	33.452	46.675	27.837	-2.253
2800	14.689	91.534	79.062	34.922	46.635	27.137	-2.118
2900	14.702	92.049	79.501	36.391	46.593	26.442	-1.993
3000	14.715	92.548	79.927	37.862	46.550	25.746	-1.876
3100	14.726	93.031	80.342	39.334	46.505	25.055	-1.766
3200	14.735	93.494	80.742	40.800	46.458	24.372	-1.660
3300	14.746	93.932	81.139	42.262	46.409	23.672	-1.560
3400	14.755	94.352	81.523	43.757	46.358	22.946	-1.478
3500	14.763	94.820	81.897	45.233	46.305	22.294	-1.392
3600	14.771	95.236	82.261	46.709	46.250	21.611	-1.312
3700	14.778	95.605	82.613	48.183	46.193	20.948	-1.235
3800	14.784	95.935	82.945	49.655	46.133	20.288	-1.165
3900	14.790	96.419	83.305	51.146	46.073	19.569	-1.097
4000	14.795	96.794	83.638	52.623	46.009	18.868	-1.032
4100	14.800	97.159	83.963	54.103	45.944	18.211	-0.971
4200	14.805	97.503	84.283	55.583	45.875	17.562	-0.912
4300	14.810	97.844	84.596	57.065	45.805	16.942	-0.857
4400	14.814	98.205	84.899	58.545	45.731	16.346	-0.804
4500	14.818	98.538	85.199	60.026	45.655	15.717	-0.754
4600	14.821	98.863	85.492	61.508	45.577	15.051	-0.706
4700	14.825	99.174	85.783	62.987	45.498	14.372	-0.660
4800	14.828	99.494	86.062	64.473	45.413	13.670	-0.617
4900	14.831	99.800	86.340	65.956	45.327	12.954	-0.573
5000	14.834	100.100	86.612	67.439	45.236	12.194	-0.533
5100	14.836	100.384	86.879	68.923	45.144	11.527	-0.494
5200	14.839	100.662	87.140	70.405	45.051	10.817	-0.459
5300	14.841	100.944	87.400	71.891	44.955	10.117	-0.421
5400	14.843	101.242	87.654	73.375	44.855	9.565	-0.387
5500	14.846	101.514	87.903	74.859	44.751	8.912	-0.354
5600	14.848	101.782	88.149	76.344	44.645	8.250	-0.322
5700	14.850	102.045	88.390	77.828	44.535	7.583	-0.292
5800	14.851	102.303	88.628	79.314	44.423	6.913	-0.263
5900	14.853	102.557	88.862	80.799	44.308	6.320	-0.234
6000	14.855	102.806	89.092	82.284	44.189	5.674	-0.207

Sept. 30, 1962; Dec. 31, 1966; June 30, 1969

CIN

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+0.00	∞	∞	-28.284	-28.284	INFINITE
100	13.261	11.762	45.884	-3.412	-26.720	58.397
200	15.972	24.186	31.094	-1.562	-25.358	27.710
298	15.868	30.340	+0.00	-27.120	-24.309	17.677
300	15.866	30.638	+0.29	-27.114	-24.372	17.755
400	15.850	35.198	31.162	-1.614	-23.390	12.780
500	15.859	38.736	32.336	-1.620	-22.400	9.791
600	15.868	41.628	33.451	-1.626	-21.439	7.809
700	15.878	44.075	34.570	-1.637	-20.496	6.399
800	15.887	46.196	35.644	-1.652	-19.562	5.344
900	15.897	48.068	36.652	-1.665	-18.633	4.525
1000	15.906	49.743	38.602	-1.681	-17.703	3.869
1100	15.915	51.250	39.485	-1.697	-16.764	3.128
1200	15.925	52.645	40.708	-1.712	-15.825	2.368
1300	15.934	53.920	41.676	-1.727	-14.887	1.727
1400	15.944	55.101	42.493	-1.751	-13.951	1.179
1500	15.953	56.201	43.064	-1.768	-13.018	0.705
1600	15.962	57.231	44.203	-1.782	-12.088	0.292
1700	15.972	58.199	45.082	-1.796	-11.161	-0.072
1800	15.981	59.112	45.637	-1.810	-10.238	-0.394
1900	15.991	59.977	46.058	-1.824	-9.314	-0.682
2000	16.000	60.797	47.250	-1.838	-8.391	-0.941

June 30, 1962; Mar. 31, 1966

POTASSIUM CYANIDE (KCN)

(CRYSTAL)

CKN

MOL. WT. = 65.11985

$S_{298.15}^0 = 30.54 \pm 0.25$ cal. deg. ⁻¹ mole ⁻¹	$\Delta H_f^0 = -28.28 \pm 0.2$ kcal. mole ⁻¹
$T_f = 188.3 \pm 0.1$ °K.	$\Delta H_f^0 = -27.12 \pm 0.2$ kcal. mole ⁻¹
$T_m = 895 \pm 2$ °K.	$\Delta H_f^0 = 0.279$ kcal. mole ⁻¹
	$\Delta H_m^0 = 3.5$ kcal. mole ⁻¹
	$\Delta H_g^0 = 298.15$ (to dimer) = 52 ± 10 kcal. mole ⁻¹
	$\Delta H_g^0 = 298.15$ (to monomer) = 46 ± 5 kcal. mole ⁻¹

Heat of Formation.

The enthalpy change, ΔH_f^0 298.15 = 2.80 ± 0.10 kcal. mole⁻¹, for the reaction $\text{KCN}(c) \rightarrow \text{KCN}(g, \text{H}_2\text{O})$ was reported by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heat of formation for $\text{K}^+(\text{aq}, \text{H}_2\text{O})$ and $\text{CN}^-(\text{aq}, \text{H}_2\text{O})$, reported by D. D. Wagman, M. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of ΔH_f^0 298.15 for $\text{KCN}(c)$ was evaluated to be -27.12 ± 0.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The heat capacity for $\text{KCN}(c)$ has been measured with a heat conduction method by C. E. Messer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2703 (1941), 101.6-345.8°K., and adiabatically by H. Suga, T. Matsuo and S. Seki, Bull. Chem. Soc. Japan, 38, 1115 (1965), 14.23-308.5°K. The data of Suga, Matsuo and Seki were adopted after correction for curvature. The anomalous region between 50-105°K. has been treated as second order by inclusion of the enthalpy in the heat capacity. The C_p values above 310°K. were estimated by graphical extrapolation. The value of $S_{298.15}^0$ was evaluated based on $S_{15}^0 = 0.193$ cal. deg.⁻¹ mole⁻¹. This extrapolated value appears more reasonable than the value, $S_{15}^0 = 0.307$ cal. deg.⁻¹ mole⁻¹ reported by Suga, Matsuo and Seki.

Transition Data.

T_f was taken from Suga, Matsuo and Seki, loc. cit. ΔH_f^0 was calculated as the difference between the total enthalpy change, $H_{298.15}^0 - H_{15}^0 = 0.533$ kcal. mole⁻¹ obtained from C_p values measured by Messer and Ziegler, loc. cit., and the enthalpy change, 0.254 kcal. mole⁻¹, calculated from the arbitrarily smoothed C_p curve. Suga, et al. reported $\Delta H_f^0 = 0.339$ kcal. mole⁻¹; however, their C_p data do not adequately define the total enthalpy change through the transition region. The values of T_f and ΔH_f^0 reported by Messer and Ziegler, loc. cit., were 188.3 ± 0.4 °K. and 0.30 kcal. mole⁻¹, respectively. The lower transition, $T = 82.9 \pm 0.2$ °K. and $\Delta H^0 = 0.095 \pm 0.001$ kcal. mole⁻¹ reported by Suga, et al., was treated as second order by inclusion of the enthalpy in the heat capacity.

Melting Data.

See KCN(1) table.

Heat of Sublimation.

The difference between ΔH_f^0 298.15 for $(\text{KCN})_2(g)$ and $2\text{KCN}(c)$ is ΔH_g^0 298.15 (to dimer) and for $\text{KCN}(g)$ and $\text{KCN}(c)$ is ΔH_g^0 298.15 (to monomer).

CKN

Potassium Cyanide (KCN)

(Liquid) Mol. Wt. = 65.11985

CKN

MOL. WT. = 65.11985

(LIQUID)

POTASSIUM CYANIDE (KCN)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
cal. mole ⁻¹ deg. ⁻¹ kcal. mole ⁻¹							
100							
200	18.000	32.104	32.104	+0.00	-24.891	-22.626	16.352
298	18.000	32.215	32.215	-0.33	-24.891	-22.612	16.479
300	18.000	32.216	32.216	-0.33	-24.891	-22.612	16.479
400	18.000	32.596	32.596	1.833	-24.990	-21.821	11.822
500	18.000	41.410	34.144	3.633	-24.603	-21.075	9.212
600	18.000	44.692	35.636	5.433	-24.263	-20.401	7.431
700	18.000	47.407	37.133	7.233	-23.968	-19.781	6.176
800	18.000	50.500	38.532	9.033	-23.713	-19.202	5.255
900	18.000	53.500	39.832	10.833	-23.483	-18.657	4.561
1000	18.000	53.887	41.254	12.633	-23.303	-18.126	3.961
1100	18.000	55.602	42.481	14.433	-23.037	-16.591	3.296
1200	18.000	57.169	43.641	16.233	-22.691	-14.282	2.603
1300	18.000	58.509	44.736	18.033	-22.283	-12.073	2.021
1400	18.000	59.683	45.768	19.833	-21.832	-10.073	1.549
1500	18.000	61.185	46.763	21.633	-21.342	-8.273	1.101
1600	18.000	62.347	47.701	23.433	-20.811	-6.673	0.733
1700	18.000	63.438	48.595	25.233	-20.240	-5.173	0.410
1800	18.000	64.467	49.449	27.033	-19.629	-3.773	0.124
1900	18.000	65.436	50.260	28.833	-18.978	-2.473	0.000
2000	18.000	66.364	51.027	30.633	-18.287	-1.273	0.000
2100	18.000	67.242	51.797	32.433	-17.556	-0.173	0.000
2200	18.000	68.079	52.518	34.233	-16.785	0.923	0.000
2300	18.000	68.879	53.213	36.033	-15.974	2.023	0.000
2400	18.000	69.639	53.887	37.833	-15.123	3.123	0.000
2500	18.000	70.380	54.527	39.633	-14.232	4.223	0.000
2600	18.000	71.086	55.150	41.433	-13.301	5.323	0.000
2700	18.000	71.765	55.753	43.233	-12.330	6.423	0.000
2800	18.000	72.420	56.337	45.033	-11.319	7.523	0.000
2900	18.000	73.054	56.900	46.833	-10.268	8.623	0.000
3000	18.000	73.662	57.451	48.633	-9.177	9.723	0.000

$$\Delta H_f^{\circ} 298.15 = -24.891 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 3.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = [37.55] \text{ kcal. mole}^{-1}$$

$$S^{\circ} 298.15 = 32.104 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 895 \pm 2^{\circ} \text{ K.}$$

$$T_b = [1698]^{\circ} \text{ K.}$$

Heat of Formation.

$\Delta H_f^{\circ} 298.15(1)$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between $H_{298}^{\circ} - H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity was estimated and assumed constant in the temperature range 298.15-3000°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by M. Truthe, Z. anorg. Chem. 76, 129 (1912). The value of ΔH_m° was taken from K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936, based on phase diagrams of the systems KCN-AgCN, KCN-Cu₂(CN)₂, KCN-KCl, KCN-NaCN, and KCN-Zn(CN)₂ reported by M. Truthe, loc. cit.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction $\text{KCN}(1) = \text{KCN}(g)$ becomes zero. The difference between ΔH_f° for KCN(g) and KCN(l) at T_b is ΔH_v° .

CKN

Potassium Cyanide (KCN)

Mol. Wt. = 65.11985

(Ideal Gas)

CKN

POTASSIUM CYANIDE (KCN) (IDEAL GAS) MOL. WT. = 65.11985

T, °K	C _p	S° - (F° - H° ₃₀₀)/T	H° - H° ₃₀₀	ΔH° _f	ΔF° _f	Log K _p
0	0.000	INFINITE	-2.977	19.004	INFINITE	INFINITE
100	6.223	48.562	70.601	18.988	16.919	-36.976
200	11.406	58.760	61.569	18.999	16.224	-16.224
298	12.135	60.477	60.477	19.000	15.806	-9.367
300	12.164	60.552	60.477	18.999	12.767	9.301
400	12.520	64.104	60.959	18.326	10.811	5.907
500	12.778	66.826	61.880	18.178	8.948	3.911
600	13.015	69.277	62.922	18.008	7.119	2.493
700	13.238	71.401	65.978	17.816	5.318	1.440
800	13.443	73.082	68.007	17.607	3.547	0.969
900	13.625	74.676	70.164	17.382	1.802	0.436
1000	13.782	76.120	72.484	17.139	0.083	0.018
1100	13.918	77.440	74.961	16.880	-0.586	-0.116
1200	14.034	78.650	77.583	16.603	-1.261	-0.402
1300	14.133	79.783	80.346	16.309	-1.916	-0.653
1400	14.218	80.834	83.243	16.000	-2.547	-0.875
1500	14.290	81.817	86.279	15.679	-3.151	-1.075
1600	14.352	82.742	89.461	15.348	-3.729	-1.250
1700	14.406	83.613	92.785	15.000	-4.281	-1.400
1800	14.453	84.438	96.253	14.639	-4.808	-1.528
1900	14.494	85.217	99.869	14.268	-5.311	-1.638
2000	14.529	85.965	103.629	13.889	-5.790	-1.733
2100	14.561	86.675	107.539	13.503	-6.245	-1.815
2200	14.589	87.353	111.597	13.113	-6.678	-1.885
2300	14.613	88.002	115.803	12.719	-7.090	-1.945
2400	14.635	88.624	120.157	12.323	-7.481	-1.995
2500	14.655	89.222	124.669	11.925	-7.853	-2.037
2600	14.672	89.797	129.339	11.517	-8.207	-2.072
2700	14.688	90.351	134.166	11.100	-8.543	-2.101
2800	14.702	90.886	139.153	10.675	-8.861	-2.125
2900	14.715	91.402	144.300	10.243	-9.162	-2.145
3000	14.727	91.901	149.609	9.805	-9.447	-2.161
3100	14.738	92.384	155.082	9.363	-9.717	-2.174
3200	14.747	92.852	160.720	8.917	-9.973	-2.185
3300	14.756	93.306	166.523	8.467	-10.215	-2.194
3400	14.765	93.747	172.492	8.013	-10.443	-2.201
3500	14.772	94.175	178.629	7.555	-10.658	-2.207
3600	14.779	94.591	184.935	7.093	-10.860	-2.211
3700	14.786	94.996	191.409	6.627	-11.049	-2.214
3800	14.791	95.390	198.052	6.157	-11.226	-2.216
3900	14.797	95.775	204.864	5.683	-11.391	-2.218
4000	14.802	96.149	211.844	5.205	-11.544	-2.219
4100	14.807	96.515	218.992	4.723	-11.686	-2.220
4200	14.811	96.872	226.309	4.237	-11.818	-2.221
4300	14.815	97.220	233.786	3.747	-11.941	-2.222
4400	14.819	97.561	241.424	3.253	-12.055	-2.223
4500	14.823	97.894	249.223	2.755	-12.160	-2.224
4600	14.826	98.220	257.183	2.253	-12.257	-2.225
4700	14.830	98.539	265.304	1.747	-12.345	-2.226
4800	14.833	98.851	273.586	1.237	-12.425	-2.227
4900	14.835	99.157	282.029	0.723	-12.497	-2.228
5000	14.838	99.457	290.634	0.205	-12.561	-2.229
5100	14.841	99.751	299.400	-0.317	-12.617	-2.230
5200	14.843	100.039	308.327	-0.833	-12.665	-2.231
5300	14.845	100.321	317.414	-1.345	-12.706	-2.232
5400	14.847	100.599	326.661	-1.853	-12.740	-2.233
5500	14.849	100.871	336.068	-2.357	-12.767	-2.234
5600	14.851	101.139	345.635	-2.857	-12.787	-2.235
5700	14.853	101.402	355.362	-3.353	-12.800	-2.236
5800	14.855	101.660	365.250	-3.845	-12.806	-2.237
5900	14.856	101.914	375.298	-4.333	-12.806	-2.238
6000	14.858	102.164	385.506	-4.817	-12.800	-2.239

June 30, 1962; Mar. 31, 1966

 $\Delta H_f^\circ 0 = [19 \pm 5] \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ 298.15 = [19 \pm 5] \text{ kcal. mole}^{-1}$ Point Group C_{∞v} $S^\circ_{298.15} = [60.48] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

(J), cm.⁻¹

[370] (1)

207 (2)

2158 (1)

K-C = [2.284] Å

G° = 1

Bond Distance: C-N = 1.16 ± 0.01 Å

Bond Angle: K-C-N = 180°

Rotational Constant: B = 0.11891 cm.⁻¹

Heat of Formation.

The vapor pressure of KCN(g) at 870°C. was estimated to be 1-10 mm. Hg by D. S. Villars, J. Am. Chem. Soc. 53, 405 (1931). Assuming the vapor pressure at this temperature to be 1 mm. Hg, the heat of vaporization ($\Delta H^\circ_{298.15}$) for KCN(l) was evaluated as 44 kcal. mole⁻¹. Based on $\Delta H^\circ_{298.15} = -24.89 \text{ kcal. mole}^{-1}$ for KCN(l), the value of $\Delta H^\circ_{298.15}$ for KCN(g) was calculated to be $19 \pm 5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The molecular structure of KCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was determined by N. Elliott and J. Hastings, Acta Cryst. 1, 1018 (1961) by use of neutron diffraction measurements. The K-C bond distance was taken from G. E. Leroy, Ph. D. Thesis, Harvard University, 1961, which was estimated. The vibrational frequencies, $2/2$ and $2/3$, were obtained from G. E. Leroy and W. Klemperer, J. Chem. Phys. 35, 774 (1961). The value of $2/1$ was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is $2.3540 \times 10^{-38} \text{ g. cm.}^2$.

CKN

Potassium Carbonate (K_2CO_3)

Mol. Wt. = 138. 21335

(Crystal)

T, °K.	C_p^*	S^*	$-(F^* - H_{298}^*)/T$	$H^* - H_{298}^*$	ΔH_f^*	ΔF_f^*	Log K_p
0	0.000	0.000	INFINITE	- 5.419	- 273.569	- 273.569	INFINITE
100	17.300	12.690	58.810	- 4.612	- 274.673	- 267.991	585.693
200	23.695	27.012	39.557	- 2.509	- 274.908	- 261.183	285.407
298	27.351	37.170	0.000	0.000	- 274.900	- 254.444	185.313
300	27.414	37.239	37.171	0.051	- 274.899	- 254.317	185.270
400	30.625	45.675	38.285	2.956	- 275.934	- 247.254	135.093
500	33.473	52.821	40.494	6.164	- 275.628	- 240.115	104.954
600	36.010	59.152	43.086	9.660	- 275.114	- 233.056	84.891
700	38.356	64.881	45.706	13.359	- 274.419	- 226.009	70.591
800	40.641	70.152	48.315	17.309	- 273.549	- 219.255	59.898
900	42.905	75.070	51.196	21.487	- 272.503	- 212.530	51.609
1000	45.160	79.707	53.817	25.860	- 271.288	- 205.929	45.008
1100	47.400	84.117	56.272	30.518	- 307.716	- 107.613	39.222
1200	49.640	88.437	58.662	35.370	- 307.666	- 107.714	34.743
1300	51.880	92.399	61.286	40.446	- 303.418	- 177.714	29.876
1400	54.120	96.325	63.649	45.746	- 300.964	- 168.132	26.247
1500	56.360	100.136	65.955	51.270	- 298.305	- 158.736	23.128
1600	58.600	103.845	68.208	57.018	- 295.436	- 149.524	20.424
1700	60.840	107.476	70.400	62.986	- 292.472	- 140.500	18.127
1800	63.080	111.005	72.563	69.186	- 289.470	- 131.659	15.986
1900	65.320	114.476	74.683	75.606	- 286.574	- 123.009	14.149
2000	67.560	117.883	76.758	82.250	- 283.665	- 114.547	12.517

POTASSIUM CARBONATE (K_2CO_3)

(CRYSTAL)

MOL. WT. = 138.21335

$$\Delta H_f^* 0 = -273.57 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^* 298.15 = -274.9 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^* = 6.6 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$S^*_{298.15} = 37.17 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1174 \pm 1^\circ K.$$

Heat of Formation.

The heat of formation was obtained from the heat of solution $\Delta H_{sol}^* = -7.6 \pm 0.5 \text{ kcal. mole}^{-1}$ and the heats of formation for $K^+(aq)$ and $CO_3^{2-}(aq)$, -60.32 and -161.84 kcal. mole $^{-1}$, respectively. The standard heat of solution, ΔH_{sol}^* , was calculated by extrapolation to infinite dilution of the calorimetric data of L. Benjamin, J. Chem. Eng. Data **7**, 238-40 (1962), using the methods suggested by J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, J. Phys. Chem. **69**, 3059-62 (1965). The equilibrium constant for the hydrolysis $CO_3^{2-}(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + OH^-(aq)$ was taken as $K = 2.1 \times 10^{-4}$ based on the selected values of D. D. Wagman, V. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965. The resulting extrapolations were not so consistent as those of Rupert et al. (loc. cit.) for Na_2CO_3 . The ionic heats of formation were taken from Wagman et al. (loc. cit.). This procedure was adopted even though it may involve an inconsistency between the extrapolations for ΔH_{sol}^* and $CO_3^{2-}(aq)$. The alternative evaluation of ΔH_f^* 298.15 for K_2CO_3 (~1900 H $_2$ O) from the heats of mixing given by J. A. Muller, Ann. chim. phys. (6), **15**, 517 (1889) and M. Berthelot, Ann. chim. phys. (4) **29**, 433 (1873) may be subject to significant error if dissolved CO_2 was not excluded from the solutions. Presumably, this path was used by D. D. Wagman, NBS Report 8628, January 1965, in the selection of ΔH_f^* 298.15 = -274.3 kcal. mole $^{-1}$. This value is 0.6 kcal. mole $^{-1}$ less negative than the value adopted here.

Heat Capacity and Entropy.

The low temperature heat capacity, 14.0-315°K. was measured by P. L. Oetting, unpublished data, Thermal Research Laboratory, Dow Chemical Company, Midland, Michigan, 1963. G. I. Janz, E. Neuenschwander and P. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963) measured the heat content by drop calorimetry in the temperature range 650-1250°K., and gave enthalpy and heat capacity equations based on their measurements. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity above 298°K. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point. The entropy at 14.0°K. was calculated from the extrapolated low temperature C_p data, using the cubic law. The value of $S^*_{14.0} = 0.109 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m was obtained from A. Reisman, J. Am. Chem. Soc. **80**, 3558 (1958) and ΔH_m^* was taken from Janz et al. (loc. cit.).

Potassium Carbonate (K₂CO₃)

Mol. St. = 138. 21335

(Liquid)

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₃₉₈)/T	H°-H° ₃₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100	27.351	40.719	40.719	0.000	-270.220	-250.822	-250.822	183.858
200	27.414	40.888	40.720	0.051	-270.210	-250.702	-250.702	182.636
300	30.625	49.224	41.634	2.956	-271.254	-243.994	-243.994	133.312
400	33.473	56.370	44.043	6.164	-270.948	-237.209	-237.209	103.684
500	36.016	62.701	46.638	9.440	-270.434	-230.506	-230.506	83.062
600	38.456	68.440	49.430	12.738	-269.730	-223.806	-223.806	68.456
700	40.800	73.690	52.082	17.309	-268.869	-217.413	-217.413	59.394
800	50.000	79.588	54.800	22.309	-267.001	-211.094	-211.094	51.260
900	50.000	84.856	57.546	27.309	-265.189	-204.879	-204.879	44.708
1000	50.000	89.621	60.249	32.309	-263.245	-198.695	-198.695	39.139
1100	50.000	93.972	62.901	37.309	-261.047	-192.510	-192.510	34.459
1200	50.000	97.974	65.428	42.309	-258.875	-186.319	-186.319	29.995
1300	50.000	101.670	67.887	47.309	-256.721	-180.364	-180.364	26.442
1400	50.000	105.129	70.256	52.309	-254.586	-174.506	-174.506	23.586
1500	50.000	108.385	72.588	57.309	-252.465	-168.741	-168.741	20.781
1600	50.000	111.537	74.795	62.309	-250.355	-163.069	-163.069	18.119
1700	50.000	114.594	76.891	67.309	-248.267	-157.488	-157.488	15.633
1800	50.000	117.569	78.891	72.309	-246.191	-151.991	-151.991	13.300
1900	50.000	120.463	80.888	77.309	-244.126	-146.568	-146.568	11.119
2000	50.000	123.283	82.788	82.309	-242.078	-141.214	-141.214	9.022
2100	50.000	126.031	84.593	87.309	-240.044	-135.922	-135.922	7.833
2200	50.000	128.629	86.307	92.309	-238.022	-130.690	-130.690	6.636
2300	50.000	131.070	87.947	97.309	-236.010	-125.518	-125.518	5.433
2400	50.000	133.363	89.547	102.309	-234.008	-120.406	-120.406	4.233
2500	50.000	135.513	91.113	107.309	-232.016	-115.354	-115.354	3.033

Dec. 31, 1961; Mar. 31, 1966

POTASSIUM CARBONATE (K₂CO₃)

(LIQUID)

MOL. WT. = 138.21355

$$S_{298.15}^{\circ} = 40.719 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -270.22 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^{\circ} = 6.60 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$T_m = 1174 \pm 1^{\circ}\text{K.}$$

Heat of Formation.

The $\Delta H_f^{\circ} 298.15$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between $H_m^{\circ} - H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 800°K. The heat capacity below 800°K. was obtained from the heat capacity of the crystal. Above 800°K. the heat capacity was adopted as 50.0 cal. deg.⁻¹ mole⁻¹, based on the enthalpy measurements in the range 1169-1250°K. reported by O. J. Jens, E. Neuenchwander and F. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See K₂CO₃(c) table.

Lithium Carbonate (Li_2CO_3)

(Crystal) Mol. Wt. = 73.88735

 Cl_2O_3

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	∞.000	∞.000	INFINITE	- 3.627	- 288.692	- 288.692	INFINITE
100	8.320	4.792	37.648	- 3.306	- 289.693	- 289.571	619.744
200	17.310	13.507	23.487	- 3.066	- 290.361	- 277.152	302.857
298	23.000	21.551	15.591	∞.000	- 290.640	- 270.598	196.353
300	23.080	21.694	15.522	∞.043	- 290.643	- 270.474	197.040
400	26.810	28.860	22.504	2.543	- 290.697	- 263.738	144.098
500	30.820	35.259	24.424	5.418	- 292.074	- 256.855	112.271
600	35.700	41.295	26.736	8.735	- 291.692	- 249.839	91.004
700	39.670	46.633	28.779	12.127	- 290.293	- 242.954	75.874
800	38.000	52.611	31.023	16.711	- 289.749	- 236.225	64.534
900	42.310	57.535	34.507	20.726	- 288.824	- 229.586	55.751
1000	46.540	62.225	37.044	25.181	- 287.495	- 223.070	48.752
1100	49.230	66.795	39.542	29.978	- 285.856	- 216.706	43.056
1200	50.850	71.192	41.987	34.986	- 283.932	- 210.490	38.937
1300	51.760	75.259	44.399	40.118	- 282.107	- 204.451	34.371
1400	52.420	79.120	46.743	45.329	- 280.118	- 198.549	30.995
1500	52.840	82.752	49.023	50.592	- 278.091	- 192.795	28.090
1600	53.200	86.174	51.239	55.896	- 276.035	- 187.174	25.567
1700	53.500	89.446	53.326	61.227	- 273.848	- 181.682	23.306
1800	53.600	92.463	55.477	66.576	- 271.612	- 176.387	20.566
1900	53.800	95.367	57.501	71.946	- 339.161	- 159.885	18.391
2000	54.000	98.131	59.464	77.336	- 336.702	- 150.516	16.448

LITHIUM CARBONATE (Li_2CO_3)

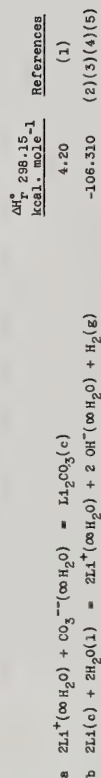
(CRYSTAL)

MOL. WT. = 73.88735

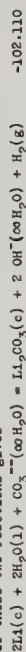
$S_{298.15}^\circ = 21.551 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $S_{298.15}^\circ = -288.69 \pm 0.04 \text{ kcal. mole}^{-1}$
 $\Delta H_{298.15}^\circ = -290.64 \pm 0.04 \text{ kcal. mole}^{-1}$
 $\Delta H_{298.15}^\circ = [0.134] \text{ kcal. mole}^{-1}$
 $\Delta H_{298.15}^\circ = [0.535] \text{ kcal. mole}^{-1}$
 $\Delta H_{298.15}^\circ = 10.70 \pm 0.1 \text{ kcal. mole}^{-1}$
 $T_m = 985 \pm 1^\circ\text{K.}$
 $T_{\text{Li}_2\text{O}} = 623^\circ\text{K.}$
 $T_{\text{Li}_2\text{O}} = 683 \pm 3^\circ\text{K.}$

Heat of Formation

The heat of formation was derived from the enthalpy change of the following reactions:



Summation of these two reactions gives

Using $\Delta H_{298.15}^\circ$ of $\text{H}_2\text{O}(\text{l})$, $\text{CO}_3^{--}(\infty \text{H}_2\text{O})$ and $\text{OH}^-(\infty \text{H}_2\text{O})$ from Ref. 6 yields $\Delta H_{298.15}^\circ = -290.64 \text{ kcal. mole}^{-1}$.

References

- (1) O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. 58, 2228(1936).
- (2) JANAP table for $\text{LiOH}(\text{c})$, March 31, 1966.
- (3) S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958). S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeters," UCRL-7992, Oct. 1964.
- (4) C. B. Messer, L. G. Fasolino and C. E. Thalman, J. Am. Chem. Soc. 77, 4524 (1955).
- (5) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes" NSRDS-NBS 2 Natl. Bur. Std., April 1, 1965.
- (6) D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties", NBS Technical Note 270-1, October 1, 1965.

Heat Capacity and Entropy

The low temperature heat capacity, $16.68\text{--}300^\circ\text{K.}$, was measured by O. L. I. Brown and W. M. Latimer, J. Am. Chem. Soc. 58, 2228 (1936). G. I. Janz, E. Neuenchwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963) measured the heat content by drop calorimetry in the temperature range $560\text{--}1150^\circ\text{K.}$, and gave enthalpy and heat capacity equations based on their measurement. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point. The entropy at 16.68°K. was calculated from the extrapolated low temperature C_p data, using the cubic law. The value of $S_{16.68}^\circ = 0.053 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data

T_m were taken from A. Reisman, J. Am. Chem. Soc. 80, 3558 (1958). The enthalpies of transition were estimated from the relative areas of the transitions and the heat of fusion of the differential analysis curve reported by Reisman loc. cit.

Melting Data

T_m was obtained from Reisman loc. cit. and ΔH_m° was taken from Janz et. al. (loc. cit.).

Mar. 31, 1966

 Cl_2O_3

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S ^o -(H ^o -H ₂₉₈)/T	H ^o -H ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298	23.000	30.423	30.423	*000	-264.232	103.687
300	23.080	30.566	30.423	*043	-264.125	102.415
400	26.810	37.732	31.376	2.563	-258.275	141.115
500	30.820	44.131	35.296	5.418	-252.280	110.271
600	35.700	50.167	35.608	8.736	-246.151	89.661
700	44.320	56.387	38.136	12.776	-240.633	74.976
800	44.320	62.305	40.785	17.208	-234.312	64.011
900	44.320	67.525	43.481	21.640	-228.652	55.524
1000	44.320	72.195	46.123	26.072	-223.136	48.767
1100	44.320	76.410	48.688	30.504	-217.755	43.264
1200	44.320	80.275	51.162	34.936	-212.487	38.699
1300	44.320	83.823	53.540	39.368	-207.322	34.854
1400	44.320	87.107	55.822	43.800	-202.248	31.572
1500	44.320	90.165	58.010	48.232	-197.263	28.741
1600	44.320	93.026	60.110	52.664	-192.358	26.275
1700	44.320	95.712	62.126	57.096	-187.474	23.766
1800	44.320	98.246	64.063	61.528	-182.603	21.349
1900	44.320	100.652	65.926	65.960	-177.833	19.196
2000	44.320	102.935	67.719	70.392	-173.135	17.267

$S_{298.15}^o = 30.423 \pm 0.05$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^o 298.15 = -281.63 \pm 0.04$ kcal. mole⁻¹
 $\Delta F_f^o = 10.7 \pm 0.1$ kcal. mole⁻¹
 $T_m = 983.15 \pm 1^\circ K.$

Heat of Formation.

The $\Delta H_f^o 298.15$ was obtained from $\Delta H_f^o 298.15(c)$ by adding ΔH_m^o and the difference between $H_m^o - H_m^o 298.15$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 683.15°K. The heat capacity below 683.15°K. was obtained from the heat capacity of the crystal. Above 683.15°K. the heat capacity was adopted as 44.32 cal. deg.⁻¹ mole⁻¹, based on the enthalpy measurements in the range 996-1150°K. reported by G. J. Janz, E. Neuenchwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See Li₂CO₃(c) table.

Magnesium Carbonate (MgCO_3)
(Crystal)

GFW = 84.32135

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal/mol	ΔG°	Log Kp
0	4.000	4.000	INFINITE	-2.794	-263.933	-263.933	INFINITE
100	5.899	2.576	28.648	-2.607	-264.956	-264.956	565.510
200	13.760	9.356	17.274	-1.884	-265.616	-252.371	275.778
298	18.215	15.740	15.740	0.000	-265.700	-245.742	180.134
300	18.284	15.852	15.740	0.034	-265.701	-245.618	178.033
400	21.476	21.571	16.498	2.029	-265.632	-238.930	130.544
500	23.915	26.631	18.028	4.301	-265.417	-232.276	101.528
600	26.060	31.187	19.848	6.803	-265.093	-225.678	82.293
700	27.760	35.337	21.760	9.577	-264.615	-219.138	68.418
800	29.220	39.142	23.706	12.449	-264.015	-212.649	58.418
900	30.500	42.660	25.619	15.337	-263.696	-206.251	50.095
1000	31.500	45.928	27.488	18.440	-263.259	-199.716	43.648



OPW = 84.32135

(CRYSTALL)

MAGNESIUM CARBONATE (MgCO_3)

$\Delta H_f^\circ = -263.9 \pm 2 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = -265.7 \pm 2 \text{ kcal/mol}$
 $S^\circ_{298.15} = 15.74 \text{ gibbs/mol}$
 $T_d = 675^\circ \text{K}$

Heat of Formation.

The adopted $\Delta H_f^\circ_{298.15} = -265.7 \pm 2 \text{ kcal/mol}$ is the average value derived from the dissociation pressures of $\text{MgCO}_3(\text{c})$ in the temperature range $671\text{--}782^\circ \text{K}$ measured by Marc and from the $\Delta H_f^\circ_{923} = 25.9 \pm 0.6 \text{ kcal/mol}$ determined by Thomasson using a high temperature differential calorimeter. The decomposition of MgCO_3 has been studied in a bomb calorimeter by Roth; this yields $\Delta H_{293}^\circ = 23.8 \text{ kcal/mol}$ when corrected to constant pressure. The value is derived from the small difference between two large heats of combustion, so the uncertainty is probably large. Roth also reported $\Delta H_{363}^\circ = 26.15 \text{ kcal/mol}$ from calorimetric data on the heat of solution in HCl. Berthelot measured the heat of solution of $\text{MgSO}_4(\text{aq})$ with $\text{K}_2\text{CO}_3(\text{aq})$. Analyzing his data we find $\Delta H_{298.15}^\circ = -268.6 \text{ kcal/mol}$.

Discrepancies are apparent in the wide range of the calorimetric results and in the third law drift of the equilibrium data. Possible sources for the drift include lack of true equilibrium (e.g., excess surface energy for MgO) and uncertainty in the high temperature entropy of MgCO_3 (see entropy write-up). Non-standard state behavior of the crystal phases may also be a problem in the calorimetric studies. The data of Thomasson and Cunningham, based on a high temperature differential thermal analysis technique, are probably the most reliable of the calorimetric values; however, there are uncertainties in the absolute energy calibration. The first result of Roth may be dismissed as too discrepant and the remaining two calorimetric values are within $\pm 3 \text{ kcal}$ of the selected heat of formation.

Source	Method	Reaction	T, °K	ΔH_f° (kcal/mol)	$\Delta H_f^\circ_{298.15}$ Drift kcal/mol
1. Marc	Kp	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	671-782	-	28.3 ± 0.9
2. Thomasson	Calorimetric	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	923	25.9	27.7
3. Roth	Calorimetric	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	293	23.8	23.8
Roth	Calorimetric	$\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$	363	26.15	26.10
4. Berthelot	Calorimetric	$\text{K}_2\text{CO}_3(\sim.5\text{m}) + \text{MgSO}_4(\sim.5\text{m}) = \text{MgCO}_3(\text{c}) + \text{K}_2\text{SO}_4(\sim.5\text{m})$	288	1.05	1.55

Sources:

1. R. Marc and A. Simek, Z. Anorg. Chem. **82**, 17 (1913).
2. G. V. Thomasson and D. A. Cunningham, J. Sci. Instr. **41**, 308-10 (1964).
3. W. A. Roth, J. Prakt. Chem. **158**, 117 (1941).
4. Berthelot, Ann. Chim. Phys. **5**, 160-179 (1875).

Heat Capacity and Entropy.

Low temperature heat capacities ($56.3 - 291.6^\circ \text{K}$) were measured by C. T. Anderson, J. Am. Chem. Soc. **56**, 849 (1934). The high temperature heat capacities are derived by a Shomate analysis of smoothed enthalpies reported by K. K. Kelley, Bulletin 584, p. 114, U.S. Bureau of Mines, Washington, D.C. 1960. Kelley obtained the smoothed values from unpublished high temperature ($400\text{--}745^\circ \text{K}$) enthalpy measurements by C. H. Shomate, Berkeley Thermodynamics Laboratory, Region II, Bureau of Mines, Berkeley, California. The data were joined smoothly at 298°K and extrapolated graphically above 743°K . The entropy was obtained from the heat capacities using $S_{56.2}^\circ = 0.57 \text{ eu}$.

Because of the drift in the decomposition pressure data, it is pertinent to assess the uncertainty in the functions. The greatest potential source for error is in the values above room temperature where the increment of entropy is about 20 eu between 298 and 700°K . Unfortunately, no evaluation of the unpublished enthalpies is possible, but an increase of 10% in the entropy increment would reduce the drift to a tolerable level.

Decomposition Data.

T_d is calculated as the temperature at which ΔH_f° equals zero for $\text{MgCO}_3(\text{c}) = \text{MgO}(\text{c}) + \text{CO}_2(\text{g})$.

Cyano Unipositive Ion (CN⁺)

(Ideal Gas) GFW = 26.01730

T, °K	Cp ^a	Gibbs/mol S ^b - (C°-H° ₂₉₈)/T	hcal/mol H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0						
100						
200						
298	7.034	50.986	1.000	429.400	419.940	-307.424
300	7.037	51.029	-0.13	429.412	419.881	-305.863
400	7.240	53.079	51.266	430.027	416.610	-227.625
500	7.514	54.723	1.463	430.591	413.189	-160.605
600	7.788	56.118	2.229	431.119	409.659	-140.216
700	8.027	57.337	3.020	431.617	406.042	-126.772
800	8.225	58.422	3.833	432.097	402.356	-109.918
900	8.385	59.400	4.664	432.558	398.613	-96.796
1000	8.516	60.291	5.509	433.007	394.813	-86.286
1100	8.624	61.108	6.366	433.444	390.973	-77.679
1200	8.716	61.862	7.233	433.872	387.094	-70.499
1300	8.797	62.563	8.109	434.289	383.177	-64.418
1400	8.870	63.218	8.992	434.703	379.231	-59.201
1500	8.937	63.832	9.883	435.112	375.255	-54.675
1600	9.001	64.411	10.779	435.516	371.250	-50.710
1700	9.061	64.958	11.683	435.923	367.221	-47.209
1800	9.119	65.478	12.592	436.324	363.167	-44.004
1900	9.175	65.972	13.506	436.727	359.095	-41.305
2000	9.229	66.444	14.427	437.131	354.998	-38.792
2100	9.281	66.896	15.352	437.535	350.881	-36.517
2200	9.331	67.329	16.283	437.939	346.744	-34.446
2300	9.379	67.745	17.218	438.344	342.590	-32.553
2400	9.425	68.145	18.156	438.750	338.419	-30.817
2500	9.469	68.530	19.103	439.159	334.229	-29.216
2600	9.510	68.903	20.052	439.567	330.024	-27.741
2700	9.550	69.262	21.005	439.974	325.803	-26.372
2800	9.587	69.610	21.962	440.380	321.567	-25.099
2900	9.622	69.947	22.923	440.802	317.317	-23.914
3000	9.656	70.274	23.886	441.215	313.050	-22.806
3100	9.687	70.591	24.854	441.630	308.771	-21.768
3200	9.716	70.899	25.824	442.045	304.481	-20.795
3300	9.743	71.199	26.797	442.460	300.174	-19.880
3400	9.769	71.490	27.772	442.874	295.856	-19.018
3500	9.793	71.773	28.750	443.292	291.525	-18.204
3600	9.815	72.050	29.731	443.708	287.184	-17.434
3700	9.835	72.319	30.713	444.125	282.828	-16.706
3800	9.854	72.581	31.694	444.541	278.467	-16.015
3900	9.872	72.838	32.674	444.958	274.103	-15.360
4000	9.888	73.088	33.657	445.373	269.704	-14.736
4100	9.903	73.332	34.642	445.788	265.303	-14.142
4200	9.917	73.571	35.633	446.202	260.903	-13.576
4300	9.930	73.804	36.625	446.615	256.495	-13.036
4400	9.942	74.033	37.619	447.028	252.086	-12.520
4500	9.953	74.256	38.613	447.439	247.671	-12.026
4600	9.963	74.475	39.609	447.848	243.247	-11.554
4700	9.972	74.690	40.606	448.256	238.822	-11.101
4800	9.980	74.900	41.624	448.665	234.399	-10.666
4900	9.988	75.106	42.627	449.071	229.979	-10.249
5000	9.995	75.307	43.621	449.474	225.553	-9.848
5100	10.001	75.505	44.621	449.877	221.126	-9.463
5200	10.007	75.700	45.622	450.277	216.697	-9.092
5300	10.012	75.890	46.622	450.677	212.263	-8.735
5400	10.017	76.078	47.624	451.074	207.823	-8.390
5500	10.022	76.261	48.626	451.468	203.379	-8.058
5600	10.025	76.442	49.628	451.861	198.938	-7.738
5700	10.029	76.619	50.631	452.251	194.500	-7.428
5800	10.032	76.794	51.634	452.637	189.194	-7.129
5900	10.035	76.965	52.637	453.025	184.855	-6.840
6000	10.037	77.134	53.641	453.409	180.482	-6.560

June 30, 1969

CYANO UNIPOSITIVE ION (CN⁺)

(IDEAL GAS)

GFW = 26.01730

Ground State Configuration [3π]

ΔH₀⁰ = 428.6 ± 3.0 kcal/mol

S_{298.15}⁰ = 50.98 ± 1.5 gibbs/mol

ΔH_f⁰ = 429.4 ± 3.0 kcal/mol

Electronic Levels and Degeneracies

E _i , cm ⁻¹	E _i
0	[6]
[1500]	[1]
[6000]	[2]
[8000]	[3]
[15000]	[2]

ω _e = [1580] cm ⁻¹	ω _e x _e = [12.5] cm ⁻¹	σ = 1
B _e = [1.566] cm ⁻¹	α _e = [0.017] cm ⁻¹	r _e = 1.29 Å

Heat of Formation

Dibeler and Liston (1) have measured the photoionization thresholds for the processes:

ClCN + hv → Cl ⁺ + CN + e ⁻	ΔH ₀ ⁰ = 399.44 ± 0.5 kcal
ClCN + hv → Cl + CN ⁺ + e ⁻	ΔH ₀ ⁰ = 426.65 ± 0.5 kcal

By subtraction we obtain

Cl + CN ⁺ → Cl ⁺ + CN	ΔH ₀ ⁰ = -27.21 ± 0.7 kcal
---------------------------------------------	--------------------------------------------------

Using JANAF values for Cl, Cl⁺ and CN we obtain ΔH_f⁰(CN⁺) = 430.6 ± 3.0 kcal/mol and the ionization potential of CN, g = 327.42 ± 0.7 kcal/mol.

Berkowitz et al. (2) have measured the photoionization thresholds for the processes:

HCN + hv → H ⁺ + CN + e ⁻	ΔH ₀ ⁰ = 438.18 ± 0.3 kcal
HCN + hv → H + CN ⁺	ΔH ₀ ⁰ = 448.09 ± 0.3 kcal

By subtraction we obtain

H + CN ⁺ → H ⁺ + CN	ΔH ₀ ⁰ = -9.91 ± 0.4 kcal
-------------------------------------------	-------------------------------------------------

Using JANAF values for H, H⁺ and CN we obtain ΔH_f⁰(CN⁺) = 426.7 ± 3.0 kcal/mol, and the ionization potential of CN, g = 323.51 ± 0.4 kcal/mol.

We adopt a median value for ΔH_f⁰(CN⁺) = 428.6 ± 3.0 kcal/mol and 325.4 ± 2 kcal/mol for the ionization potential of CN.

Heat Capacity and Entropy

The molecule has eight valence electrons and thus we expect that its molecular constants should fall between those for C₂ and BN. The ground electronic state is either 1₂ or 3₂ and the two levels are likely to be very close. As a consequence the thermodynamic functions are dominated by the 3₂ contribution and so we choose this to be the ground state. The other levels are estimated based on the values of Fougere and Nesbet (3) for C₂ and of Verhaegen et al. (4) for BN. The vibrational constants and bond length are estimated between those for the 3₂ states of BN and C₂. The rotational constants B₀ is obtained from the estimated bond length and α_e is calculated from the other constants assuming a Morse potential function. The enthalpy at 0°K is -2.076 kcal/mol.

References:

1. V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).
2. J. Berkowitz, W. A. Chupka and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969).
3. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. **44**, 285 (1966).
4. G. Verhaegen, W. G. Richards and C. M. Hoser, J. Chem. Phys. **46**, 160 (1967).

CN⁺

Cyanide Uninegative Ion (CN⁻)

GFW = 26.01840

CN⁻Ground State Configuration [1s²] $\Delta H_f^\circ = 15.2 \pm 3 \text{ kcal/mol}$ $S_{298.15}^\circ = 46.81 \pm 0.5 \text{ gibbs/mol}$ $\Delta H_f^\circ = 16 \pm 3 \text{ kcal/mol}$

Electronic Levels and Degeneracies

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[1]
[67000]	[2]

$\omega_e = [2250] \text{ cm}^{-1}$	$\omega_e x_e = [13.8] \text{ cm}^{-1}$	$\sigma = 1$
$B_e = [2.116] \text{ cm}^{-1}$	$\alpha_e = [0.0177] \text{ cm}^{-1}$	$r_e = [1.111] \text{ \AA}$

Heat of Formation

Berkowitz et al. (1) have recently obtained $88 \pm 0.5 \text{ kcal}$ for the electron affinity of CN from the photoionization thresholds of the reactions $\text{HCN} + \text{H}^\bullet + \text{CN}^\bullet$ and $\text{HCN} + \text{H}^\bullet + \text{CN} + \text{e}^-$.

Other values have been reported by Page (2), who reinterpreted his earlier data (3), to yield $73 \pm 1 \text{ kcal/mol}$; Bakulina and Ionov (4) in conjunction with the data of Branscomb and Smith (5) reported $78 \pm 5 \text{ kcal/mol}$ and Inoue (6) who obtained $83 \pm 7 \text{ kcal/mol}$.

We adopt the value given by Berkowitz et al. (1) as being the most well defined in terms of both the precision of measurements and the reactions being studied. This leads to $\Delta H_f^\circ(\text{CN}^\bullet, g) = 15.2 \pm 3 \text{ kcal/mol}$ or $\Delta H_f^\circ(\text{CN}^\bullet, g) = 16 \pm 3 \text{ kcal/mol}$.

Heat Capacity and Entropy

The electronic structure and molecular constants are estimated by analogy with the isoelectronic species CO and N₂. The uncertainties in the constants are generally small since N₂ and CO are quite similar, thus the entropy has an uncertainty of only 0.5 eu. The enthalpy at 0°K is -2.072 kcal/mol .

References:

1. J. Berkowitz, W. A. Chupka, and T. A. Walter, *J. Chem. Phys.* **50**, 1497 (1969).
2. F. M. Page, *J. Chem. Phys.* **43**, 2466 (1966).
3. R. Napper and F. M. Page, *Trans. Faraday Soc.* **59**, 1086 (1963).
4. I. N. Bakulina and H. I. Ionov, *Russ. J. Phys. Chem. (Eng. Transl.)* **33**, 286 (1959).
5. L. M. Branscomb and S. J. Smith, *J. Chem. Phys.* **25**, 598 (1956).
6. M. Inoue, *J. Chim. Phys.* **63**, 1061 (1966).

T, °K	Cp ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	$H^\circ - H_{298}^\circ$	ΔG°	Log Kp
0	6.963	46.813	46.813	16.000	0.000	10.758	7.686
100	6.963	46.856	46.813	15.993	0.013	10.726	7.614
200	6.963	47.002	46.863	15.980	0.017	10.697	7.532
298	7.057	50.435	47.604	15.137	1.415	7.436	3.250
400	7.240	51.741	48.198	14.922	2.132	5.944	2.165
600	7.406	52.669	48.778	14.669	2.464	4.842	1.418
800	7.573	53.869	49.353	14.391	3.613	3.320	0.680
1000	7.735	54.770	49.903	14.093	4.379	1.870	0.478
1200	7.880	55.593	50.434	13.784	5.159	0.789	0.173
1400	8.008	56.350	50.937	13.464	5.924	0.131	0.066
1600	8.120	57.052	51.416	13.137	6.766	-1.394	0.254
1800	8.218	57.706	51.877	12.804	7.578	-2.403	0.404
2000	8.303	58.318	52.315	12.464	8.364	-3.364	0.555
2200	8.377	58.893	52.735	12.115	9.125	-4.279	0.623
2400	8.442	59.436	53.137	11.766	9.861	-5.153	0.704
2600	8.498	59.950	53.523	11.426	10.579	-6.005	0.789
2800	8.548	60.437	53.893	11.096	11.278	-6.779	0.823
3000	8.592	60.900	54.250	10.775	11.956	-7.537	0.867
3200	8.631	61.342	54.594	10.466	12.623	-8.281	0.903
3400	8.666	61.764	54.925	10.166	13.278	-8.951	0.932
3600	8.698	62.168	55.245	9.886	13.923	-9.544	0.955
3800	8.726	62.555	55.555	9.626	14.558	-10.062	0.973
4000	8.752	62.927	55.854	9.386	15.186	-10.514	0.988
4200	8.775	63.285	56.144	9.166	15.806	-10.906	0.999
4400	8.796	63.629	56.426	8.966	16.416	-11.244	1.006
4600	8.814	63.962	56.699	8.786	17.016	-11.534	1.012
4800	8.834	64.283	56.964	8.626	17.606	-11.784	1.014
5000	8.850	64.593	57.222	8.486	18.186	-12.004	1.015
5200	8.866	64.893	57.472	8.366	18.756	-12.194	1.014
5400	8.880	65.184	57.716	8.266	19.316	-12.354	1.012
5600	8.894	65.466	57.954	8.186	19.866	-12.484	1.009
5800	8.906	65.740	58.186	8.126	20.406	-12.594	1.004
6000	8.918	66.006	58.412	8.086	20.936	-12.684	1.000
6200	8.929	66.265	58.633	8.066	21.456	-12.754	0.992
6400	8.940	66.517	58.848	8.066	21.966	-12.804	0.984
6600	8.950	66.762	59.059	8.086	22.466	-12.834	0.976
6800	8.960	67.001	59.265	8.126	22.956	-12.844	0.967
7000	8.969	67.233	59.466	8.186	23.436	-12.834	0.958
7200	8.978	67.461	59.663	8.266	23.906	-12.804	0.948
7400	8.986	67.682	59.856	8.366	24.366	-12.754	0.938
7600	8.994	67.899	60.045	8.486	24.816	-12.684	0.927
7800	9.002	68.111	60.230	8.626	25.256	-12.594	0.916
8000	9.009	68.318	60.412	8.786	25.686	-12.484	0.905
8200	9.017	68.520	60.589	8.966	26.106	-12.354	0.894
8400	9.024	68.719	60.764	9.166	26.516	-12.204	0.882
8600	9.030	68.913	60.935	9.386	26.916	-12.034	0.870
8800	9.037	69.103	61.104	9.626	27.306	-11.844	0.858
9000	9.043	69.289	61.269	9.886	27.686	-11.634	0.846
9200	9.050	69.472	61.431	10.166	28.056	-11.404	0.834
9400	9.056	69.651	61.590	10.466	28.416	-11.154	0.822
9600	9.062	69.827	61.747	10.786	28.766	-10.884	0.810
9800	9.067	70.000	61.901	11.126	29.106	-10.594	0.797
10000	9.073	70.169	62.053	11.486	29.436	-10.284	0.784
10200	9.079	70.336	62.202	11.866	29.756	-9.954	0.772
10400	9.084	70.500	62.349	12.266	30.066	-9.604	0.759
10600	9.090	70.660	62.493	12.686	30.366	-9.234	0.746
10800	9.095	70.819	62.635	13.126	30.656	-8.844	0.734
11000	9.100	70.974	62.775	13.586	30.936	-8.434	0.721
11200	9.105	71.127	62.913	14.066	31.206	-7.994	0.708

June 30, 1969

CN⁻

Sodium Cyanide (NaCN)

(Crystal) Mol. Wt. = 49.00765

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _f
0	1.000	0.000	INFINITE	INFINITE	4.642	-23.493	-23.493	INFINITE
100	8.450	8.450	47.871	-2.742	-23.470	-21.814	-21.814	47.674
200	16.253	16.253	28.315	-2.000	-21.680	-20.227	-20.227	42.652
298	16.415	28.315	28.315	-	0.000	-21.680	-19.229	44.994
300	16.390	28.416	28.416	0.030	-21.672	-19.211	-19.211	43.995
400	16.410	33.161	28.960	1.672	-21.969	-18.397	-18.397	40.052
500	16.432	36.805	30.176	3.315	-21.738	-17.531	-17.531	7.663
600	16.455	39.803	31.538	4.959	-21.549	-16.709	-16.709	6.086
700	16.478	42.341	32.905	6.606	-21.397	-15.915	-15.915	4.969
800	16.502	44.543	34.225	8.255	-21.273	-15.140	-15.140	4.136
900	16.526	46.488	35.482	9.906	-21.176	-14.380	-14.380	3.492
1000	16.550	48.231	36.671	11.560	-21.108	-13.629	-13.629	2.979
1100	16.576	49.809	37.795	13.216	-21.064	-12.885	-12.885	2.560
1200	16.602	51.253	38.857	14.875	-21.036	-12.148	-12.148	2.128
1300	16.628	52.582	39.862	16.536	-21.020	-11.416	-11.416	1.685
1400	16.653	53.816	40.815	18.200	-21.012	-10.684	-10.684	1.239
1500	16.678	54.965	41.721	19.867	-21.006	-9.941	-9.941	0.785
1600	16.703	56.043	42.583	21.536	-21.000	-9.194	-9.194	0.329
1700	16.728	57.056	43.404	23.208	-21.000	-8.441	-8.441	-0.220
1800	16.752	58.013	44.190	24.882	-21.000	-7.685	-7.685	-0.769
1900	16.776	58.919	44.941	26.558	-21.000	-6.924	-6.924	-1.305
2000	16.800	59.780	45.662	28.237	-21.000	-6.161	-6.161	-1.831

SODIUM CYANIDE (NaCN)

(CRYSTAL)

MOL. WT. = 49.00765

CNNa

$$S_{298.15}^{\circ} = [28.32 \pm 0.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 835^{\circ} \text{ K.}$$

$$\Delta H_f^{\circ} 0 = -23.49 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -21.68 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{\circ} = [2.1] \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{\circ} 298.15 (\text{to dimer}) = [41.3] \text{ kcal. mole}^{-1}$$

$$\Delta H_g^{\circ} 298.15 (\text{to monomer}) = 44.21 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The enthalpy change for the reaction $\text{NaCN}(c) \rightarrow \text{NaCN}(\infty \text{ H}_2\text{O})$ was reported to be $0.29 \pm 0.20 \text{ kcal. mole}^{-1}$ by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RS-2, National Bureau of Standards, April 1, 1965. Incorporating this data with the heats of formation for $\text{Na}^+(\infty \text{ H}_2\text{O})$, -57.39 , and $\text{CN}^-(\infty \text{ H}_2\text{O})$, $36.0 \text{ kcal. mole}^{-1}$, reported by D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, October 1, 1965, National Bureau of Standards, the value of $\Delta H_f^{\circ} 298.15$ for $\text{NaCN}(c)$ was derived and adopted.

G. Lord and A. A. Woolf, J. Chem. Soc. 2546 (1954), determined the value, $\Delta H_f^{\circ} 298.15(\text{NaCN}, c) = -21.4 \text{ kcal. mole}^{-1}$, by solution calorimetry. This value is in agreement with the adopted one.

Heat Capacity and Entropy.

The low temperature heat capacities, $101.6-345.8^{\circ} \text{ K.}$, were reported by C. E. Messer and W. T. Ziegler, J. Am. Chem. Soc. 63, 2705 (1941). The C_p values above 345.8° K. were estimated by graphical extrapolation. $S_{298.15}^{\circ}$ was derived from low temperature heat capacities, based on $S_{100}^{\circ} = 8.4 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ which was estimated by comparison with the $S_{298.15}^{\circ}$ values for NaCl, KCl, and KCN crystals.

Transition Data.

The transition temperatures, T_{t2} and T_{t1} , were determined by C. E. Messer and W. T. Ziegler, loc. cit. The corresponding enthalpies of transition were reported to be 0.15 and $0.70 \text{ kcal. mole}^{-1}$, respectively. However, these quantities were incorporated with C_p values used to evaluate $H^{\circ}-H_{298.15}^{\circ}$. Therefore ΔH_f° 's are not listed.

N₂ Lifting Data.

see NaCN(1) table for details.

Heat Sublimation.

The difference between $\Delta H_f^{\circ} 298.15$ for $(\text{NaCN})_2(g)$ and $2\text{NaCN}(c)$ is $\Delta H_g^{\circ} 298.15$ (to dimer) and for $\text{NaCN}(g)$ and $\text{NaCN}(c)$ is $\Delta H_g^{\circ} 298.15$ (to monomer).

CNNa

T, °K.	C _p	$S^{\circ} - (H^{\circ} - H_{298}^{\circ})/T$	ΔH_f°	ΔF_f°	Log K _f
0					
100	16.415	29.096	0.000	- 20.160	13.347
200					
298					
300	16.390	30.097	0.030	- 20.152	13.256
400	16.410	34.822	1.672	- 20.449	9.588
500	16.432	38.486	3.315	- 20.218	7.366
600	19.000	41.484	4.759	- 20.029	5.000
700	19.000	44.413	6.959	- 19.624	4.868
800	19.000	46.930	8.759	- 19.249	4.109
900	19.000	49.188	10.559	- 18.906	3.530
1000	19.000	51.190	12.259	- 18.589	3.075
1100	19.000	53.001	14.459	- 18.302	2.709
1200	19.000	54.654	16.359	- 18.030	2.324
1300	19.000	56.175	18.259	- 17.778	1.969
1400	19.000	57.583	20.159	- 17.546	1.641
1500	19.000	58.894	22.059	- 17.334	1.330
1600	19.000	60.120	23.959	- 17.146	1.039
1700	19.000	61.272	25.859	- 16.983	0.776
1800	19.000	62.356	27.759	- 16.846	0.534
1900	19.000	63.385	29.659	- 16.734	0.310
2000	19.000	64.360	31.559	- 16.643	0.105
2100	19.000	65.287	33.459	- 16.578	- 0.083
2200	19.000	66.170	35.359	- 16.539	- 0.293
2300	19.000	67.015	37.259	- 16.525	- 0.513
2400	19.000	67.824	39.159	- 16.534	- 0.748
2500	19.000	68.599	41.059	- 16.567	- 1.000
2600	19.000	69.345	42.959	- 16.625	- 1.261
2700	19.000	70.062	44.859	- 16.707	- 1.533
2800	19.000	70.753	46.759	- 16.812	- 1.817
2900	19.000	71.419	48.659	- 16.940	- 2.113
3000	19.000	72.063	50.559	- 17.091	- 2.420

Dec. 31, 1960; Mar. 31, 1966

$$S_{298.15}^{\circ} = [29.996] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = [-20.160] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = [2.1] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = [35.39] \text{ kcal. mole}^{-1}$$

$$T_m = 835^{\circ} \text{ K.}$$

$$T_b = [1803]^{\circ} \text{ K.}$$

Heat of Formation.

$\Delta H_f^{\circ} 298.15(1)$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated by comparison with those for NaCN(c), KCN(c) and KCN(l). A glass transition temperature is assumed at 600°K. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature was reported by M. Truthe, Z. anorg. Chem. 78, 129 (1912). ΔH_m° was estimated such that the derived third law value for ΔH_v° (NaCN, l) agrees with the second law value. See NaCN(g) table for details.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction $\text{NaCN}(l) = \text{NaCN}(g)$ becomes zero. The difference between ΔH_f° for NaCN(g) and NaCN(l) at T_b is ΔH_v° .

Sodium Cyanide (NaCN)

(Ideal Gas)

Mol. Wt. = 49.00765

CNNA

MOL. WT. = 49.00765

SODIUM CYANIDE (NaCN)

(IDEAL GAS)

Point Group $C_{\infty v}$ $S_{298.15} = [59.14] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Group State Quantum Weight = 1

 $\Delta H_f^\circ = 22.46 \pm 0.50 \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ 298.15 = 22.53 \pm 0.50 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

 $\omega_e, \text{ cm.}^{-1}$ $\frac{\omega_e}{[400](1)}$

239 (2)

2176 (1)

Bond Distance: Na-C = $[1.992] \text{ \AA}$ C-N = $[1.16] \text{ \AA}$ Bond Angle: Na-C-N = $[180]^\circ$ Rotational Constant: B = $[0.18272] \text{ cm.}^{-1}$ $\sigma = 1$

Heat of Formation

The vapor pressures of NaCN(l) at temperatures 805-1353°K. were measured by C. K. Ingold, J. Chem. Soc. 123, 885 (1923). According to the investigation reported by R. F. Porter, J. Chem. Phys. 35, 318 (1961), the vapor consists of NaCN and (NaCN)₂. Based on his data the dimer/monomer ratios at temperatures 805-1353°K. (1078.2-1826.2°K.) were calculated to be 0.29-0.09. Hence the respective partial pressures for NaCN(g) and (NaCN)₂(g) were derived. By the second and third law methods, the values of $\Delta H_f^\circ 298.15$ (1 → monomer) were evaluated to be 43.43 and 42.69 kcal. mole⁻¹, respectively. The heat of formation ($\Delta H_f^\circ 298.15$) for NaCN(g) was calculated from $\Delta H_f^\circ 298.15$ (NaCN, c) and the third law value for ΔH_f° .

Heat Capacity and Entropy

The molecular structure of NaCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C-N bond distance was assumed to be the same as that in KCN(g) and the Na-C bond distance was taken from G. E. Leroy, Ph. D. Dissertation, Harvard University, 1961, which was calculated. The vibrational frequencies, ν_2 and ν_3 , were measured by G. E. Leroy and W. Klemperer, J. Chem. Phys. 35, 774 (1961) from infrared absorption spectra. The value of ν_1 was calculated by valence force method described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is $1.53187 \times 10^{-38} \text{ g. cm.}^2$.

Dec. 31, 1960; Mar. 31, 1966

CNNA

CNN RADICAL (CN₂)

(IDEAL GAS)

OFW = 40.02455

Point Group C_{∞v}
 $\Delta H_f^\circ = [139.5 \pm 30] \text{ kcal/mol}$
 $\Delta H_f^\circ = [139.7 \pm 30] \text{ kcal/mol}$
 $\Delta H_f^\circ = 55.35 \text{ gibbs/mol}$
 Ground State Quantum Weight = 3

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}
 1241 (1)
 393 (2)
 2847 (1)

Bond Distance: C-N = [1.15] Å

Bond Angle: C-N-N = 180°

Rotational Constant: $B_0 = [0.450368] \text{ cm}^{-1}$ $\sigma = 1$

Heat of Formation

The heat of formation is calculated from the estimated heat of reaction $\Delta H_f^\circ = 255 \pm 30 \text{ kcal/mol}$ for $\text{CNN}(\text{g}) \rightarrow \text{C}(\text{g}) + 2\text{N}(\text{g})$. Since CNN radical can dissociate to give C + N₂ or CN + N, the molecule must have more energy than either CN or N₂. It is assumed that the extra bond will be quite weak, for this we estimate $30 \pm 30 \text{ kcal/mol}$ which gives $\Delta H_f^\circ = 255 \pm 30 \text{ kcal/mol}$ for the first path and $\Delta H_f^\circ = 204 \pm 30 \text{ kcal/mol}$ for the second. We adopt the former value.

Heat Capacity and Entropy

D. E. Milligan and M. E. Jacox, J. Chem. Phys. 44, 2850 (1966), have measured three fundamental vibrational frequencies for CNN radical (g) in the infrared and ultraviolet spectra by matrix-isolation, and proposed a linear molecular configuration with a \sum ground state which has been confirmed by E. Wasserman, L. Barash and W. A. Yager, J. Am. Chem. Soc. 81, 2075 (1959), in the electron paramagnetic resonance observations. Also Milligan and Jacox suggested a "C≡N-N" bond structure, based on the agreement between the C-N and N-N stretching force constants (calculated from observed vibrational frequencies in the CNN radical) and the typical C≡N and N-N stretching force constants. In addition, they estimated the bond distances $r_{\text{C-N}} = 1.15\text{Å}$ and $r_{\text{N-N}} = 1.25\text{Å}$ from the proposed structure. The principal moment of inertia is $6.2148 \times 10^{-39} \text{ g cm}^2$.

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ - (C^\circ - H^\circ_{\text{ref}})/T}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{\text{ref}}}$	ΔH_f°	Log Kp
0	+0.00	INFINITE	-2.479	139.545	INFINITE
100	7.403	45.837	63.598	139.541	-303.337
200	9.100	51.517	56.250	139.596	-150.838
298	10.105	55.354	+0.000	139.700	-100.605
300	10.120	55.355	+0.019	139.702	-99.073
400	10.803	58.427	55.760	139.807	-74.522
500	11.323	60.856	56.548	139.892	-59.240
600	11.745	62.999	57.452	139.956	-48.046
700	12.104	64.837	58.378	139.996	-41.762
800	12.419	66.417	59.311	140.010	-37.049
900	12.693	67.953	60.372	140.031	-32.048
1000	12.933	69.302	61.018	140.031	-28.648
1100	13.144	70.545	61.828	140.024	-25.865
1200	13.320	71.699	62.603	140.011	-23.547
1300	13.475	72.776	63.346	139.992	-21.645
1400	13.613	73.776	64.054	139.972	-19.405
1500	13.756	74.720	64.734	139.948	-16.448
1600	13.864	75.612	65.386	139.924	-13.353
1700	13.959	76.455	66.013	139.898	-10.209
1800	14.041	77.250	66.615	139.876	-7.084
1900	14.115	78.017	67.196	139.843	-4.010
2000	14.180	78.762	67.755	139.815	-1.029
2100	14.238	79.436	68.295	139.787	1.925
2200	14.290	80.039	68.816	139.756	4.834
2300	14.336	80.573	69.316	139.726	7.700
2400	14.377	81.046	69.809	139.696	10.523
2500	14.414	81.434	70.283	139.665	13.315
2600	14.447	81.750	70.742	139.632	16.084
2700	14.476	82.000	71.187	139.600	18.829
2800	14.505	82.273	71.620	139.568	21.549
2900	14.530	82.482	72.061	139.532	24.246
3000	14.552	82.655	72.451	139.496	26.916
3100	14.573	82.803	72.850	139.460	29.563
3200	14.593	82.931	73.235	139.423	32.187
3300	14.610	83.065	73.607	139.383	34.791
3400	14.626	83.197	73.967	139.343	37.370
3500	14.640	83.326	74.348	139.302	39.921
3600	14.654	83.453	74.700	139.258	42.446
3700	14.669	83.579	75.044	139.215	44.946
3800	14.680	83.693	75.371	139.170	47.421
3900	14.689	83.813	75.710	139.122	49.873
4000	14.700	83.928	76.033	139.074	52.303
4100	14.709	84.048	76.368	139.023	54.718
4200	14.718	84.168	76.695	138.970	57.118
4300	14.726	84.282	77.020	138.916	59.503
4400	14.734	84.391	77.357	138.861	61.873
4500	14.741	84.501	77.548	138.802	64.211
4600	14.748	84.613	77.733	138.743	66.528
4700	14.754	84.726	77.924	138.683	68.829
4800	14.760	84.831	78.108	138.617	71.114
4900	14.766	84.937	78.294	138.551	73.384
5000	14.771	85.043	78.479	138.483	75.638
5100	14.776	85.149	78.659	138.411	77.877
5200	14.781	85.255	78.835	138.341	80.101
5300	14.785	85.361	79.009	138.263	82.311
5400	14.789	85.467	79.184	138.186	84.506
5500	14.794	85.573	79.359	138.104	86.689
5600	14.797	85.679	79.529	138.022	88.859
5700	14.801	85.785	79.699	137.939	90.919
5800	14.804	85.891	79.869	137.856	92.969
5900	14.808	85.997	80.039	137.775	94.999
6000	14.811	86.103	80.209	137.691	96.999

June 30, 1966

NCN Radical (CN₂)

(Ideal Gas) GFW = 40.02455

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	+0.00	INFINITE	- 2.465	102.639	INFINITE	
100	7.294	44.683	52.531	102.640	102.639	
200	9.098	50.280	55.114	102.677	102.604	
298	10.515	54.194	57.671	102.800	101.963	
300	10.537	54.259	57.671	102.800	101.963	
400	11.251	57.437	60.019	102.802	100.694	
500	12.252	60.059	62.421	102.805	98.174	
600	12.840	62.391	64.266	103.307	95.366	
700	13.248	64.402	65.425	103.459	92.530	
800	13.578	66.035	66.431	103.598	89.674	
900	13.789	67.403	67.287	103.726	86.801	
1000	13.970	69.255	68.284	103.828	83.914	
1100	14.112	70.604	61.163	103.921	81.017	
1200	14.225	71.837	62.001	104.001	78.114	
1300	14.318	72.960	62.685	104.059	75.204	
1400	14.391	74.043	63.166	104.106	72.287	
1500	14.452	75.038	64.300	104.176	69.370	
1600	14.504	75.972	65.000	104.218	66.453	
1700	14.557	76.853	65.672	104.254	63.537	
1800	14.601	77.685	66.316	104.282	60.620	
1900	14.635	78.475	66.916	104.305	57.703	
2000	14.662	79.225	67.432	104.327	54.786	
2100	14.685	79.940	68.106	104.344	51.869	
2200	14.705	80.623	68.659	104.354	48.952	
2300	14.722	81.270	69.100	104.363	46.035	
2400	14.736	81.890	69.524	104.370	43.118	
2500	14.748	82.503	70.210	104.369	40.201	
2600	14.746	83.081	70.694	104.367	37.284	
2700	14.737	83.638	71.163	104.364	34.367	
2800	14.721	84.176	71.618	104.358	31.450	
2900	14.700	84.697	72.056	104.349	28.533	
3000	14.785	85.194	72.490	104.337	25.616	
3100	14.792	85.676	72.907	104.324	22.699	
3200	14.799	86.149	73.314	104.308	19.782	
3300	14.806	86.605	73.710	104.288	16.865	
3400	14.811	87.047	74.097	104.264	13.948	
3500	14.816	87.476	74.472	104.244	11.031	
3600	14.821	87.893	74.839	104.218	8.114	
3700	14.825	88.300	75.197	104.190	5.197	
3800	14.829	88.695	75.567	104.160	2.280	
3900	14.833	89.085	75.922	104.128	- 0.637	
4000	14.836	89.456	76.274	104.093	- 3.554	
4100	14.839	89.822	76.641	104.056	- 6.471	
4200	14.842	90.180	76.997	104.016	- 9.388	
4300	14.845	90.528	77.345	103.974	- 12.305	
4400	14.848	90.869	77.685	103.930	- 15.222	
4500	14.850	91.204	78.019	103.883	- 18.139	
4600	14.853	91.531	78.088	103.834	- 21.056	
4700	14.855	91.850	78.378	103.783	- 23.973	
4800	14.857	92.163	78.662	103.728	- 26.890	
4900	14.859	92.470	78.940	103.672	- 29.807	
5000	14.860	92.769	79.214	103.615	- 32.724	
5100	14.862	93.064	79.482	103.550	- 35.641	
5200	14.864	93.352	79.746	103.486	- 38.558	
5300	14.866	93.635	80.006	103.419	- 41.475	
5400	14.868	93.915	80.261	103.350	- 44.392	
5500	14.868	94.186	80.512	103.275	- 47.309	
5600	14.869	94.454	80.758	103.200	- 50.226	
5700	14.870	94.717	81.001	103.121	- 53.143	
5800	14.871	94.976	81.239	103.039	- 56.060	
5900	14.873	95.231	81.471	102.954	- 58.977	
6000	14.874	95.480	81.706	102.866	- 61.894	

June 30, 1968

NCN RADICAL (CN₂)

(IDEAL GAS)

GFW = 40.02455

Point Group D_{∞h}
 $\Delta H_f^\circ = [102.6 \pm 25] \text{ kcal/mol}$
 $\Delta H_f^\circ = 54.194 \text{ gibbs/mol}$
 $\Delta H_f^\circ = [102.6 \pm 25] \text{ kcal/mol}$
 $\Delta H_f^\circ = 54.194 \text{ gibbs/mol}$
 Ground State Quantum Weight = 3

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	Degeneracy
808 (1)	1
425 (2)	2
1475 (1)	1

Bond Distance: C-N = 1.232 Å

Bond Angle: N-C-N = 180°

Rotational Constant: B₀ = 0.3969 cm⁻¹

Heat of Formation

The heat of formation of NCN radical (g), $\Delta H_f^\circ = 102.6 \pm 25 \text{ kcal/mol}$, was calculated from the heat of reaction $\Delta H_r^\circ = 294 \pm 25 \text{ kcal/mol}$ for $\text{N}_2 + \text{C} \rightarrow 2\text{N}(\text{g}) + \text{C}(\text{g})$ which was estimated as twice the C-N bond dissociation energy (147 kcal/mol). The value of C-N bond dissociation energy was derived from the heat of combustion for n-butyl-isobutyridine amine, determined by G. E. Costes and L. E. Sutton, J. Chem. Soc. 1187 (1948).

Heat Capacity and Entropy

G. Herzberg and D. N. Travis, Can. J. Phys. 42, 1658 (1964), have found NCN radical (g) is a linear symmetric molecule with a Σ_g^- ground state in the rotational spectra by a flash photolysis technique, and determined the bond distance $r_{\text{C-N}} = 1.232 \text{ Å}$ and rotational constant $B_0 = 0.3969 \text{ cm}^{-1}$ which have been adopted in the tabulation. Also the structure "N-C-N" has been suggested by Herzberg and Travis, based on the bond distance of 1.232 Å, which is in good agreement with the C-N bond length observed in the HNCN, HNCS and CH₃NCS. The principal moment of inertia is $7.061 \times 10^{-39} \text{ g cm}^2$.

D. E. Milligan, M. E. Jacox and A. M. Basa, J. Chem. Phys. 43, 3149 (1965), have found two infrared-active vibrational fundamentals of NCN(g) at 423 and 1475 cm⁻¹ in the infrared and ultraviolet spectra by a matrix-isolation method. They also estimated the symmetric stretching frequency ($\nu_1 = 808 \text{ cm}^{-1}$) by valence force calculation.

E. Wasserman, L. Barash and M. A. Yager, J. Am. Chem. Soc. 87, 2075 (1965), have confirmed the NCN radical(g) is a linear molecule with a triplet ground state by electron paramagnetic resonance.

CN₂

T, °K.	C _p	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	0.000	INFINITE	-4.374	-268.788	-268.788	INFINITE
100	14.471	10.514	35.814	2.867	-271.441	-247.556	133.127
200	22.500	23.387	56.406	5.056	-271.150	-236.753	103.477
298	26.530	33.173	33.173	0.000	-270.260	-250.496	183.610
300	26.590	33.338	33.174	0.049	-270.258	-250.373	182.397
400	29.900	41.421	34.254	2.867	-271.441	-247.556	133.127
500	33.590	48.520	36.406	6.056	-271.150	-236.753	103.477
600	39.030	55.153	38.983	9.702	-270.456	-229.910	83.745
700	44.830	61.597	41.755	13.890	-269.272	-223.240	69.609
800	50.650	66.889	44.594	17.937	-268.371	-216.743	59.211
900	56.730	71.593	47.322	21.655	-267.641	-210.331	51.075
1000	62.630	75.729	49.947	25.782	-266.640	-204.013	44.507
1100	68.500	79.956	52.484	30.220	-265.376	-197.813	39.302
1200	74.580	84.065	54.946	34.944	-264.340	-191.821	34.753
1300	80.280	87.960	57.337	39.811	-263.302	-186.043	30.410
1400	85.650	91.625	59.657	44.893	-262.306	-180.426	26.730
1500	90.800	95.127	61.907	49.930	-261.393	-174.662	23.534
1600	95.330	98.422	64.087	54.937	-260.766	-169.246	20.796
1700	100.150	101.550	66.169	60.096	-259.495	-164.069	18.380
1800	104.260	104.525	68.246	65.302	-258.496	-159.127	16.249
1900	107.800	107.401	70.231	70.450	-257.760	-154.450	14.357
2000	110.070	109.070	72.136	75.428	-257.250	-150.028	12.668

Dec. 31, 1960; Mar. 31, 1966

$S_{298.15}^o = 33.17 \pm 0.2$ cal. deg.⁻¹ mole⁻¹
 $T_f = 723.15^\circ\text{K.}$
 $T_m = 1123.15^\circ\text{K.}$

$\Delta H_f^o = -268.79 \pm 0.05$ kcal. mole⁻¹
 $\Delta H_f^o = -270.26 \pm 0.05$ kcal. mole⁻¹
 $\Delta H_c^o = 0.185$ kcal. mole⁻¹
 $\Delta H_m^o = 7.080$ kcal. mole⁻¹

Heat of Formation.

The heat of formation was obtained from the heat of solution $\Delta H_{\text{sol}}^o = -6.36$ kcal. mole⁻¹ and the heats of formation for Na⁺(aq) and CO₃²⁻(aq), -57.53 and -161.84 kcal. mole⁻¹, respectively. The heat of solution was taken from J. P. Rupert, H. P. Hopkins, Jr., and C. A. Wulff, *J. Phys. Chem.*, **69**, 3059-62 (1965). The ionic heats of formation were taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm "Selected Values of Chemical Thermodynamic Properties" NBS Technical Note 270-1, October 1, 1965.

A value of ΔH_f^o 298.15 = -270.9 kcal. mole⁻¹ has been selected by D. D. Wagman, Natl. Bur. Std. Rept. No. 8628, 87, Jan. 1965.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.8-292.1°K., were measured by C. T. Anderson, *J. Am. Chem. Soc.*, **55**, 3621 (1933). In the temperature range 473.15-873.15°K. Popov and Galchenko (Source 1) measured the heat capacities (by heat conduction calorimetry) and observed two transformations, one at about 623°K. and the other at about 750°K. Popov and Ginzburg (Source 2) measured enthalpies in the temperature range 480-1350°K. and tabulated their data only in the range 476-872°K. Ginzburg (Source 3) has given heat capacity equations based on the data from Source 1 and 2 and has tabulated thermodynamic functions in the range 500-1500°K. There appear to be inconsistencies among the data, equations and functions. Rolin and Recapet (Source 4) also measured the enthalpy in the temperature range 645-1322°K. Janz, Neunschwander and Kelly (Source 5) have given an enthalpy equation based on their heat content measured data in the range 707-1127°K. May (Source 6) has tabulated smoothed measured enthalpy values in the range 400-1500°K. All the above information was used in a Shomate analysis in order to smooth the enthalpies and calculate heat capacities. The values from the low and high temperature sources join smoothly at 298°K. The heat capacity was graphically extrapolated above the melting point.

The entropy was calculated at 54.80° using the Debye and Einstein function $D(\frac{138}{T}) + 2E(\frac{266}{T})$ given by Anderson, loc. cit. The value of $S_{54.6}^o = 3.943$ cal. deg.⁻¹ mole⁻¹.

Source

- 1 M. M. Popov and G. L. Galchenko, *Zh. Obshch. Khim.*, **21**, 2220 (1951).
- 2 M. M. Popov and D. M. Ginzburg, *Zh. Obshch. Khim.*, **26**, 971-80 (1956).
- 3 D. M. Ginzburg, *Zh. Obshch. Khim.*, **25**, 968-70 (1956).
- 4 M. Rolin and J. M. Recapet, *Bull. Soc. chim.*, 2504 (1964).
- 5 G. J. Janz, E. Neunschwander and F. J. Kelly, *Trans. Faraday Soc.*, **59**, 841 (1963).
- 6 M. N. May, *Tappi*, **35**, 511 (1952).

Transition Data.

T_f was taken from Ginzburg loc. cit. and ΔH_f^o was obtained from the above reported enthalpy measurements by means of Shomate function analysis. The heat of transition at 593.15°K. has been incorporated in the heat capacity.

Melting Data.

T_m was taken from Ginzburg loc. cit. and ΔH_m^o was obtained from the above reported enthalpy measurements by means of Shomate function analysis.

Sodium Carbonate (Na_2CO_3)

(Liquid)

Mol. Wt. = 105.98895



MOL. WT. = 105.98895

(LIQUID)

SODIUM CARBONATE (Na_2CO_3)

$$S_{298.15}^\circ = 37.14 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^\circ 298.15 = -265.21 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 7.090 \text{ kcal. mole}^{-1}$$

$$T_m = 1123.15^\circ\text{K.}$$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was obtained from $\Delta H_f^\circ 298.15(c)$ by adding ΔH_m° and the difference between $H_m^\circ - H_m^\circ 298.15$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 723.15°K. The heat capacity below 723.15°K. was obtained from the heat capacity of the crystal. Above 723.15°K. the heat capacity was adopted as $45.30 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, based on the enthalpy measurements in the range $1127\text{--}1210^\circ\text{K.}$ reported by G. J. Janz, E. Neumannschwander and P. J. Kelly, Trans. Faraday Soc. 59, 841 (1963). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{Na}_2\text{CO}_3(c)$ table.

T, °K.	C_p°	$S^\circ - (H^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _f
0						
100						
200						
298	26.530	37.143	37.143	•000	- 246.625	180.781
300	26.590	37.307	37.144	•049	- 246.509	179.581
400	29.900	45.391	38.224	2.667	- 246.189	151.253
500	35.890	52.485	40.376	•054	- 235.665	102.135
600	39.030	59.116	42.952	9.698	- 265.405	82.771
700	44.830	65.564	45.723	13.889	- 220.623	68.988
800	45.300	71.620	48.590	18.424	- 264.218	58.704
900	45.300	76.956	51.451	22.954	- 261.287	50.750
1000	45.300	81.729	54.245	27.484	- 259.684	44.422
1100	45.300	86.046	56.943	32.014	- 258.527	39.272
1200	45.300	89.988	59.595	36.544	- 257.655	34.636
1300	45.300	93.614	62.018	41.074	- 301.984	30.593
1400	45.300	96.971	64.397	45.604	- 300.300	26.976
1500	45.300	100.096	66.674	50.134	- 296.634	23.859
1600	45.300	103.020	68.895	54.664	- 296.984	21.147
1700	45.300	105.766	70.946	59.194	- 295.343	18.767
1800	45.300	108.355	72.953	63.724	- 293.719	16.664
1900	45.300	110.805	74.881	68.254	- 292.108	14.702
2000	45.300	113.128	76.736	72.784	- 290.509	13.117
2100	45.300	115.338	78.522	77.314	- 288.917	11.609
2200	45.300	117.446	80.244	81.844	- 287.342	10.246
2300	45.300	119.459	81.905	86.374	- 285.774	9.008
2400	45.300	121.387	83.511	90.904	- 284.220	7.879
2500	45.300	123.236	85.063	95.434	- 282.676	6.847



T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	6.000	∞	∞	2.072	27.200	27.200	INFINITE
100	6.615	39.613	53.461	1.379	26.826	26.826	92.609
200	6.995	42.995	56.811	0.800	26.016	26.016	124.711
298	6.965	47.214	60.113	0.000	26.417	32.783	24.029
300	6.965	47.257	60.144	0.013	26.414	32.823	23.910
400	7.013	49.265	62.488	0.111	26.318	34.075	19.109
500	7.121	50.641	64.006	1.417	26.296	37.144	16.235
600	7.276	52.152	64.851	2.437	26.332	39.311	14.318
700	7.450	53.287	64.182	3.673	26.409	41.468	12.946
800	7.624	54.293	64.759	5.027	26.514	43.612	11.914
900	7.786	55.250	65.314	6.497	26.637	45.744	11.108
1000	7.931	56.028	56.845	8.163	26.771	47.859	10.459
1100	8.057	56.700	51.151	9.993	26.912	49.962	9.926
1200	8.168	57.496	51.634	11.794	27.062	52.049	9.479
1300	8.263	58.134	52.295	13.616	27.218	54.126	9.099
1400	8.346	58.769	52.736	15.446	27.376	56.189	8.771
1500	8.417	59.346	53.136	17.285	27.537	58.241	8.495
1600	8.478	59.893	53.502	19.130	27.700	60.284	8.234
1700	8.535	60.409	53.950	21.080	27.865	62.315	8.011
1800	8.583	60.898	54.332	23.136	28.032	64.337	7.811
1900	8.626	61.357	54.691	25.297	28.201	66.349	7.631
2000	8.664	61.807	55.026	27.561	28.372	68.353	7.469
2100	8.698	62.230	55.359	29.930	28.543	70.346	7.321
2200	8.728	62.635	55.680	32.401	28.719	72.335	7.185
2300	8.756	63.024	55.991	34.974	28.894	74.311	7.061
2400	8.781	63.397	56.292	37.652	29.074	76.282	6.946
2500	8.804	63.756	56.584	40.431	29.254	78.247	6.840
2600	8.825	64.102	56.866	43.313	29.438	80.202	6.741
2700	8.844	64.435	57.140	46.296	29.623	82.153	6.649
2800	8.863	64.757	57.407	49.380	29.810	84.103	6.563
2900	8.880	65.069	57.666	52.563	30.001	86.056	6.483
3000	8.895	65.370	57.917	55.846	30.194	88.007	6.407
3100	8.910	65.662	58.163	59.229	30.388	89.957	6.336
3200	8.924	65.945	58.401	62.701	30.586	91.795	6.269
3300	8.937	66.220	58.634	66.263	30.786	93.707	6.206
3400	8.949	66.487	58.861	69.916	30.988	95.606	6.145
3500	8.961	66.746	59.083	73.662	31.192	97.509	6.086
3600	8.973	66.999	59.299	77.510	31.399	99.404	6.034
3700	8.984	67.245	59.511	81.461	31.608	101.286	5.982
3800	8.994	67.485	59.717	85.516	31.818	103.164	5.933
3900	9.004	67.718	59.919	89.674	32.031	105.039	5.886
4000	9.014	67.946	60.117	93.936	32.247	106.908	5.841
4100	9.024	68.169	60.311	98.301	32.464	108.774	5.798
4200	9.033	68.387	60.501	102.766	32.684	110.630	5.756
4300	9.042	68.599	60.687	107.334	32.906	112.483	5.717
4400	9.050	68.806	60.869	111.999	33.130	114.333	5.679
4500	9.059	69.011	61.047	116.762	33.356	116.177	5.642
4600	9.068	69.210	61.223	121.621	33.584	118.012	5.607
4700	9.076	69.405	61.395	126.574	33.814	119.845	5.573
4800	9.084	69.596	61.566	131.621	34.046	121.672	5.540
4900	9.092	69.782	61.733	136.762	34.280	123.497	5.506
5000	9.100	69.967	61.892	142.000	34.516	125.315	5.477
5100	9.107	70.148	62.052	147.334	34.755	127.132	5.448
5200	9.115	70.325	62.210	152.766	34.995	128.941	5.419
5300	9.123	70.498	62.365	158.294	35.237	130.741	5.391
5400	9.130	70.667	62.517	163.919	35.480	132.542	5.364
5500	9.138	70.836	62.667	169.642	35.727	134.356	5.336
5600	9.145	71.001	62.814	175.464	35.974	136.179	5.312
5700	9.153	71.163	62.959	181.384	36.225	137.919	5.288
5800	9.160	71.322	63.102	187.402	36.476	139.698	5.264
5900	9.167	71.478	63.242	193.518	36.729	141.492	5.240
6000	9.175	71.633	63.381	199.731	36.985	143.249	5.218

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CARBON MONOXIDE (CO)

(IDEAL GAS)

MOL. WT. = 28.01055

Ground State Configuration $1\Sigma^+$

$$\Delta H_f^0 = -27.20 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 47.21 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = -26.42 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$\omega_e = 2169.52 \text{ cm.}^{-1}$$

$$\omega_e x_e = 13.453 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$B_0 = 1.9302 \text{ cm.}^{-1}$$

$$\omega_e = 0.01746 \text{ cm.}^{-1}$$

$$r_0 = 1.1281 \text{ Å}$$

Heat of Formation.

The enthalpy change ($\Delta H_f^{298.15}$) for the reaction: $\text{CO(g)} + 1/2 \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$ was reported to be -67.856 ± 0.029 kcal. mole⁻¹, based on molecular weight of $\text{CO}_2 = 44.010$, by F. D. Rossini, J. Research Nat. Bur. Standards 65, 407 (1959). It was recalculated to be -67.858 ± 0.03 kcal. mole⁻¹, using molecular weight of $\text{CO}_2 = 44.011$, for internal consistency. From the value of $\Delta H_f^{298.15}$, the heat of formation ($\Delta H_f^{298.15}$) for CO(g) was derived to be -26.417 ± 0.04 kcal. mole⁻¹, which yields $D_0(\text{CO}) = 11.09$ e.v.

The $D_0(\text{CO})$ value has been proposed to be 6.92 to 11.1 e.v. in the past few decades in order to explain data collected from spectroscopic, flame, shock-wave, detonation, and electron-impact studies. Recent evaluations by L. Brewer and A. Searcy, Ann. Rev. Phys. Chem. 1, 259 (1956); M. A. Fineman and A. W. Petrocelli, J. Chem. Phys. 35, 25 (1962); and C. P. Olesse and W. B. Water II, J. Chem. Phys. 32, 137 (1963) favored the value 11.1 e.v., reported by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 1953.

The heat of combustion of CO(g) was also determined by J. H. Abery and E. Griffiths, Proc. Roy. Soc. (London) [A] 141, 1 (1933), R. W. Feunung and P. T. Cotton, ibid., [A] 141, 17 (1933), and W. A. Roth and H. Bause, Arch. Eisenhütten 6, 43 (1932-33).

Heat Capacity and Entropy.

The functions adopted here were obtained from J. Balzer, L. G. Svedoff and H. L. Johnston, Ohio State University, TR 316-6, May 1, 1951, assuming the thermodynamic functions for the naturally occurring isotopic mixture to be the same as those for $\text{C}^{12}\text{O}^{16}(\text{g})$. The spectroscopic constants employed for calculation were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., 1950. The tabulated functions include the second order corrections to the rigid-rotator and harmonic-oscillator molecular model for vibrational anharmonicity, rotational stretching and rotational-vibrational interaction.

The spectroscopic constants listed above are for the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander and O. T. Sorenberg, Rev. Mod. Phys. 30, 585 (1958).

Thermodynamic properties for CO from 70 to 300°K., with pressures to 300 atmospheres were reported by J. O. Hunt and R. B. Stewart, NBS-TN-202, National Bureau of Standards, 1953. Calculations of the vapor pressure and heats of vaporization and sublimation of CO and CO_2 below one atmosphere were reported by J. C. Mulline, B. S. Kirk and W. T. Ziegler, U. S. Atomic Energy Commission NP-13662 (1963).

Carbon Oxide Sulfide (COS)

(Ideal Gas) Mol. Wt. = 60.077

COS

MOL. WT. = 60.077

(IDEAL GAS)

CARBON OXIDE SULFIDE (COS)

Log K_p

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	7.077	46.387	INFINITE	33.111	33.111	INFINITE
100	8.478	51.643	1.676	32.948	32.948	76.911
200	9.491	55.195	5.06	32.969	32.930	49.900
298	9.916	57.323	9.00	32.980	32.939	29.016
300	9.940	55.323	0.18	33.082	39.429	28.649
400	10.959	56.390	1.046	33.735	41.774	22.823
500	11.686	60.920	2.201	34.223	43.726	19.112
600	12.249	63.102	3.398	34.438	45.587	16.404
700	12.700	65.025	4.647	35.003	47.358	14.785
800	13.068	66.746	5.936	35.397	50.368	13.759
900	13.370	68.303	7.258	35.807	50.615	12.290
1000	13.621	69.725	8.608	36.418	50.859	11.115
1100	13.849	71.040	9.981	36.430	51.104	10.153
1200	14.058	72.245	11.373	36.442	51.345	9.351
1300	14.153	73.372	12.761	36.457	51.586	8.672
1400	14.280	74.428	14.203	36.470	51.825	8.090
1500	14.390	75.414	15.636	36.484	52.064	7.586
1600	14.485	76.346	17.050	36.494	52.304	7.144
1700	14.569	77.227	18.459	36.508	52.542	6.767
1800	14.643	78.062	19.864	36.520	52.779	6.408
1900	14.710	78.855	21.461	36.532	53.014	6.098
2000	14.770	79.611	22.935	36.544	53.251	5.819
2100	14.824	80.333	24.415	36.556	53.485	5.566
2200	14.872	81.028	25.890	36.563	53.723	5.326
2300	14.920	81.686	27.390	36.568	53.953	5.126
2400	14.962	82.322	28.884	36.574	54.183	4.934
2500	15.002	82.934	30.362	36.581	54.420	4.757
2600	15.038	83.523	31.880	36.587	54.651	4.594
2700	15.078	84.090	33.400	36.593	54.881	4.430
2800	15.103	84.640	34.890	36.600	55.115	4.271
2900	15.137	85.170	36.411	36.607	55.343	4.117
3000	15.167	85.684	37.926	36.614	55.572	4.048
3100	15.196	86.182	39.484	36.730	55.799	3.934
3200	15.223	86.665	40.945	36.755	56.024	3.860
3300	15.250	87.134	42.489	36.781	56.250	3.726
3400	15.275	87.589	44.015	36.808	56.481	3.630
3500	15.300	88.032	45.544	36.837	56.712	3.541
3600	15.324	88.464	47.075	36.866	56.934	3.456
3700	15.347	88.894	48.604	36.894	57.159	3.376
3800	15.370	89.309	49.930	36.920	57.379	3.306
3900	15.392	89.693	51.682	36.944	57.600	3.228
4000	15.414	90.063	53.223	36.969	57.818	3.159
4100	15.436	90.464	54.765	36.995	58.042	3.094
4200	15.457	91.200	57.857	37.012	58.267	3.023
4300	15.478	91.956	59.405	37.033	58.496	2.915
4400	15.498	92.635	60.956	37.053	58.712	2.861
4500	15.516	93.249	62.509	37.074	58.924	2.809
4600	15.537	93.846	64.067	37.096	59.136	2.759
4700	15.557	94.428	65.620	37.118	59.344	2.710
4800	15.576	95.000	67.179	37.140	59.554	2.666
4900	15.595	95.556	68.739	37.162	59.764	2.622
5000	15.614	96.100	70.302	37.184	59.974	2.579
5100	15.633	96.634	71.864	37.206	60.183	2.537
5200	15.651	97.156	73.428	37.228	60.392	2.499
5300	15.670	97.668	75.000	37.250	60.601	2.461
5400	15.688	98.174	76.569	37.271	60.810	2.425
5500	15.706	98.677	78.141	37.292	61.021	2.389
5600	15.724	99.174	79.714	37.313	61.228	2.356
5700	15.742	99.668	81.289	37.334	61.436	2.326
5800	15.760	100.159	82.866	37.355	61.641	2.292
5900	15.777	100.647	84.445	37.376	61.841	2.260
6000	15.795	101.132	86.027	37.397	62.042	2.226

March 31, 1961

 $\Delta H_f^0 = -33.11 \pm 0.25$ kcal. mole⁻¹ $\Delta H_f^0 = -33.08 \pm 0.25$ kcal. mole⁻¹Point group C_{∞v} $S_{298.15}^0 = 55.323$ cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(ω, cm. ⁻¹)	(g)
859 (1)	859 (1)
524 (2)	524 (2)
2064 (1)	2064 (1)

Rotational Constant, B₀₀₀ = 0.20287 cm.⁻¹

σ = 1

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.⁻¹):

α ₁ = 0.0006044	χ ₁₁ = -4.0	A ₀₀₀ = 0
α ₂ = 0.0003539	χ ₂₂ = -0.4	C ₀₀₀ = 0
α ₃ = 0.001838	χ ₃₃ = -7.0	D ₀₀₀ = 4.37 × 10 ⁻⁸
ε ₂₂ = 3.2	χ ₁₃ = -4.5	

Heat of Formation

E. Ferras and H. Wesemann, *Angew. Chem.* **45**, 795 (1932), report equilibrium constants from 823° to 873°K for the reaction CO₂(g) + H₂O(g) = COS(g) + H₂O(g). These yield ΔH_f 700 = 8.19 ± 0.23 kcal, whence ΔH_f 298.15 for COS is -33.08 ± 0.25 kcal. mole⁻¹. The same authors report equilibrium constants for the reaction COS(g) + H₂(g) = CS₂(g) + H₂O(g), but regard these as less reliable than the others. The resulting value of -26.39 kcal. mole⁻¹ for ΔH_f 298.15 of COS has been disregarded.

Heat Capacity and Entropy

J. S. Gordon (private communication, February 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.* **22**, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants have been taken from C. A. Burrus and W. Gordy, *Phys. Rev.* **93**, 897 (1954), H. J. Callomon, D. C. McKean, and H. W. Thompson, *Proc. Roy. Soc. (London)* **A208**, 341 (1951), **A222**, 431 (1954), M. W. P. Strandberg, T. Wentink, and R. L. Kuhl, *Phys. Rev.* **75**, 270 (1949), C. H. Townes, A. N. Holden, and P. R. Merritt, *Phys. Rev.* **74**, 1113 (1948), and T. Wentink, *J. Chem. Phys.* **30**, 105 (1959). The thermodynamic functions below 298.15°K have been calculated for the rigidly rotating harmonic oscillator.

Point Group D_{∞h}
S_{298.15} = 51.07 ± 0.03 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = -93.965 ± 0.011 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -94.054 ± 0.011 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

λ , cm. ⁻¹
1342.86 (1)
667.50 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å
Bond Angle: O-C-O = 180°
Rotational Constant: B₀ = 0.39038 cm.⁻¹
σ⁺ = 2

Heat of Formation

The enthalpy change (ΔH_f⁰ 298.15) of the reaction C(s, graphite) + O₂(g) = CO₂(g) has been measured by P. H. Dewey and D. R. Harper, *J. Res. Natl. Bur. Std.* **21**, 457 (1936), R. S. Jessup, *ibid.* **21**, 491 (1936), and E. J. Prosen and F. D. Rossini, *ibid.*, **33**, 439 (1944). Based on these data, the heat of formation (ΔH_f⁰ 298.15) for CO₂(g) was reported to be -94.0518 ± 0.0108 kcal. mole⁻¹, using molecular weight of CO₂ = 44.010, by E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Res. Natl. Bur. Standards* **33**, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole⁻¹, based on molecular weight of CO₂ = 44.011, for internal consistency.

Heat Capacity and Entropy

The functions adopted here were obtained from H. W. Woolley, *J. Research Nat. Bur. Standards* **52**, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., *J. Chem. Phys.* **30**, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtney, *Mem. soc. roy. Liege* **18**, 496 (1957) and V. R. Stull, P. J. Wyatt and G. N. Flass, *J. Chem. Phys.* **57**, 1442 (1952). The high-resolution infrared spectrum of 0.8 - enriched CO₂ was examined in the region 5400-1620 cm.⁻¹, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.⁻¹ by G. V. Barney, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B₀, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B₀ which was derived from B₀ using B_e-B₀ = 0.0011 cm.⁻¹ given in G. Herzberg, loc. cit. The principal moment of inertia is I = 7.1495 × 10⁻³⁹ g. cm.²

Heat capacities of CO₂(g) at high pressures were reported by M. F. Vukalovich, V. V. Altunin and A. N. Gureev, *Teploenergetika*, **12** (7), 58 (1965); K. Krueger, *Ver. Deut. Ingr. Z.*, **105** (32) 1620 (1964), and M. F. Vukalovich and A. N. Gureev, *Teploenergetika*, **11** (6), 80 (1964).

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S ⁰ -(F ⁰ -H ₂₉₈ ⁰)/T	H ⁰ -H ₂₉₈ ⁰ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	6.900	∞	∞	-93.965	-93.965	INFINITE
100	42.758	48.108	-2.238	-93.997	-94.100	205.645
200	7.734	51.869	-0.816	-94.028	-94.191	102.922
298	8.874	51.072	-0.000	-94.054	-94.265	69.095
300	8.895	51.127	-0.016	-94.055	-94.267	68.670
400	9.877	53.830	-0.948	-94.070	-94.335	54.400
500	10.666	56.122	-1.987	-94.091	-94.399	41.260
600	11.310	58.126	-3.087	-94.124	-94.458	34.405
700	11.850	59.910	-4.245	-94.169	-94.510	29.506
800	12.307	61.426	-5.466	-94.220	-94.566	25.620
900	12.697	62.692	-6.702	-94.270	-94.596	22.970
1000	12.980	64.344	-7.984	-94.321	-94.628	20.680
1100	13.243	65.594	-9.266	-94.371	-94.658	18.806
1200	13.466	66.566	-10.532	-94.419	-94.681	17.243
1300	13.653	67.303	-11.785	-94.465	-94.700	15.920
1400	13.815	68.859	-13.362	-94.515	-94.716	14.785
1500	13.953	69.817	-14.750	-94.562	-94.728	13.801
1600	14.074	70.722	-16.152	-94.607	-94.739	12.940
1700	14.177	71.598	-17.565	-94.650	-94.746	12.180
1800	14.265	72.445	-18.988	-94.691	-94.751	11.510
1900	14.342	73.165	-20.418	-94.742	-94.751	10.898
2000	14.424	73.903	-21.857	-94.788	-94.751	10.353
2100	14.489	74.658	-23.303	-94.834	-94.746	9.860
2200	14.520	75.334	-24.757	-94.885	-94.744	9.411
2300	14.550	75.951	-26.223	-94.931	-94.744	9.000
2400	14.609	76.554	-27.674	-94.991	-94.724	8.625
2500	14.692	77.153	-29.141	-95.048	-94.714	8.280
2600	14.734	77.730	-30.613	-95.107	-94.698	7.960
2700	14.801	78.296	-32.084	-95.170	-94.683	7.660
2800	14.871	78.854	-33.560	-95.237	-94.668	7.380
2900	14.881	79.344	-35.049	-95.305	-94.639	7.132
3000	14.873	79.848	-36.535	-95.377	-94.615	6.892
3100	14.902	80.336	-38.024	-95.451	-94.587	6.668
3200	14.956	80.810	-39.516	-95.520	-94.560	6.458
3300	15.015	81.270	-41.015	-95.591	-94.531	6.260
3400	15.078	81.717	-42.507	-95.666	-94.495	6.074
3500	15.097	82.151	-44.006	-95.784	-94.462	5.898
3600	15.030	82.574	-45.508	-95.874	-94.421	5.732
3700	15.075	83.388	-47.020	-95.968	-94.374	5.574
3800	15.119	84.197	-48.516	-96.066	-94.326	5.426
3900	15.179	85.258	-50.027	-96.169	-94.272	5.283
4000	15.097	83.780	-51.538	-96.263	-94.237	5.149
4100	15.119	84.162	-53.051	-96.367	-94.186	5.020
4200	15.139	84.536	-54.566	-96.471	-94.136	4.898
4300	15.179	85.258	-56.082	-96.583	-94.072	4.780
4400	15.197	85.607	-57.601	-96.694	-94.015	4.670
4500	15.216	85.949	-59.122	-96.807	-93.954	4.563
4600	15.234	86.284	-60.644	-96.923	-93.895	4.460
4700	15.254	86.931	-62.166	-97.040	-93.836	4.366
4800	15.272	87.451	-63.695	-97.160	-93.746	4.266
4900	15.290	87.928	-65.223	-97.281	-93.678	4.178
5000	15.306	87.557	-66.753	-97.404	-93.603	4.091
5100	15.327	87.860	-68.285	-97.530	-93.528	4.008
5200	15.349	88.158	-69.817	-97.659	-93.451	3.928
5300	15.371	88.451	-71.355	-97.783	-93.361	3.850
5400	15.393	88.738	-72.893	-97.912	-93.260	3.775
5500	15.415	89.021	-74.438	-98.042	-93.190	3.703
5600	15.437	89.299	-75.976	-98.173	-93.104	3.633
5700	15.459	89.572	-77.522	-98.308	-92.998	3.560
5800	15.481	89.841	-79.068	-98.438	-92.918	3.491
5900	15.503	90.106	-80.617	-98.572	-92.820	3.438
6000	15.525	90.367	-82.168	-98.707	-92.724	3.377

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Carbon Oxide Sulfide (COS)

(Ideal Gas) Mol. Wt. = 60.077

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	2.373	33.111	INFINITE	
100	7.077	46.367	1.676	32.438	33.111	
200	8.812	53.183	0.000	31.766	32.438	
300	9.916	55.323	0.000	31.082	31.766	
400	10.959	56.390	1.066	30.395	31.082	
500	11.688	56.519	2.061	29.703	30.395	
600	12.249	57.438	3.368	28.987	29.703	
700	12.700	58.025	4.647	28.258	28.987	
800	13.068	58.746	5.936	27.507	28.258	
900	13.370	59.326	7.258	26.736	27.507	
1000	13.651	59.725	8.608	25.959	26.736	
1100	13.829	61.034	9.981	25.104	25.959	
1200	14.005	62.767	11.373	24.186	25.104	
1300	14.153	63.540	12.781	23.204	24.186	
1400	14.280	64.260	14.203	22.166	23.204	
1500	14.390	64.930	15.636	21.082	22.166	
1600	14.485	65.561	17.080	20.054	21.082	
1700	14.569	66.152	18.533	19.082	20.054	
1800	14.643	66.704	19.994	18.166	19.082	
1900	14.710	67.226	21.461	17.304	18.166	
2000	14.770	67.714	22.935	16.496	17.304	
2100	14.824	68.173	24.415	15.742	16.496	
2200	14.874	68.604	25.900	15.036	15.742	
2300	14.920	69.007	27.390	14.378	15.036	
2400	14.962	69.382	28.884	13.766	14.378	
2500	15.002	69.734	30.382	13.200	13.766	
2600	15.038	70.063	31.884	12.678	13.200	
2700	15.073	70.374	33.390	12.198	12.678	
2800	15.106	70.666	34.899	11.758	12.198	
2900	15.137	70.941	36.411	11.356	11.758	
3000	15.167	71.198	37.926	10.992	11.356	
3100	15.196	71.436	39.444	10.666	10.992	
3200	15.223	71.655	40.963	10.378	10.666	
3300	15.250	71.854	42.483	10.128	10.378	
3400	15.275	72.034	44.003	9.916	10.128	
3500	15.300	72.195	45.524	9.742	9.916	
3600	15.324	72.337	47.045	9.606	9.742	
3700	15.347	72.460	48.566	9.508	9.606	
3800	15.370	72.565	50.087	9.444	9.508	
3900	15.392	72.653	51.608	9.411	9.444	
4000	15.414	72.723	53.129	9.400	9.411	
4100	15.436	72.776	54.650	9.410	9.400	
4200	15.457	72.813	56.171	9.440	9.410	
4300	15.477	72.835	57.692	9.490	9.440	
4400	15.496	72.843	59.213	9.560	9.490	
4500	15.516	72.837	60.734	9.650	9.560	
4600	15.537	72.817	62.255	9.760	9.650	
4700	15.557	72.783	63.776	9.890	9.760	
4800	15.576	72.735	65.297	10.040	9.890	
4900	15.595	72.673	66.818	10.210	10.040	
5000	15.614	72.597	68.339	10.400	10.210	
5100	15.633	72.508	69.860	10.610	10.400	
5200	15.651	72.406	71.381	10.840	10.610	
5300	15.670	72.291	72.902	11.090	10.840	
5400	15.688	72.163	74.423	11.360	11.090	
5500	15.706	72.023	75.944	11.650	11.360	
5600	15.724	71.870	77.465	11.960	11.650	
5700	15.742	71.704	78.986	12.290	11.960	
5800	15.760	71.525	80.507	12.640	12.290	
5900	15.777	71.333	82.028	13.010	12.640	
6000	15.795	71.128	83.549	13.400	13.010	

March 31, 1961

CARBON OXIDE SULFIDE (COS)

(IDEAL GAS)

MOL. WT. = 60.077

$$\Delta H_f^o = -33.11 \pm 0.25 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = -33.08 \pm 0.25 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 55.323 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Point Group C_{∞v}

Vibrational Levels and Multiplicities

(<i>u</i>), cm. ⁻¹
859 (1)
524 (2)
2064 (1)

Rotational Constant, B₀₀₀ = 0.20297 cm.⁻¹

σ = 1

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.⁻¹):

$$\alpha_1 = 0.0006044 \quad \chi_1 = -4.0 \quad A_{000} = 0$$

$$\alpha_2 = 0.0003539 \quad \chi_2 = -0.4 \quad C_{000} = 0$$

$$\alpha_3 = 0.001838 \quad \chi_3 = -7.0 \quad D_{000} = 4.37 \times 10^{-8}$$

$$B_{22} = 3.2 \quad \chi_{22} = -11.5$$

$$B_{33} = 4.5 \quad \chi_{33} = -4.5$$

Heat of Formation

E. Terres and H. Wesemann, *Angew. Chem.* 45, 795 (1932), report equilibrium constants from 623° to 873°K for the reaction $\text{CO}_2(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{COS}(\text{g}) + \text{H}_2\text{O}(\text{g})$. These yield $\Delta H_f^o 700 = 8.19 \pm 0.25 \text{ kcal.}$ whence $\Delta H_f^o 298.15$ for COS is $-33.08 \pm 0.25 \text{ kcal. mole}^{-1}$. The same authors report equilibrium constants for the reaction $\text{COS}(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$, but regard these as less reliable than the others. The resulting value of $-28.39 \text{ kcal. mole}^{-1}$ for $\Delta H_f^o 298.15$ of COS has been disregarded.

Heat Capacity and Entropy

J. S. Gordon (private communication, February 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.* 22, 1442 (1954), which takes anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The constants have been taken from C. A. Burrus and W. Dordy, *Phys. Rev.* 93, 897 (1954), H. J. Callomon, D. C. McKean, and H. W. Thompson, *Proc. Roy. Soc. (London)* A208, 341 (1951), A222, 431 (1954), M. W. P. Strandberg, T. Wentink, and R. L. Kynl, *Phys. Rev.* 75, 270 (1949), C. H. Townes, A. N. Holden, and F. R. Merritt, *Phys. Rev.* 74, 1113 (1948), and T. Wentink, *J. Chem. Phys.* 30, 105 (1959). The thermodynamic functions below 298.15°K have been calculated for the rigidly rotating harmonic oscillator.

Carbon Dioxide (CO₂)

(Ideal Gas) Mol. Wt. = 44.00995

CARBON DIOXIDE (CO₂)

(IDEAL GAS)

MOL. WT. = 44.00995

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.000	INFINITE	- 2.238	- 93.965	- 93.965	INFINITE
100	6.981	42.758	90.188	- 93.997	- 94.100	205.645
200	7.734	47.769	91.849	- 94.028	- 94.191	102.922
298	8.674	51.072	93.000	- 94.054	- 94.265	69.095
300	8.896	51.127	93.072	- 94.055	- 94.267	68.670
400	9.477	53.830	94.434	- 94.070	- 94.335	51.540
500	10.466	56.122	95.987	- 94.091	- 94.399	41.260
600	11.310	58.126	97.981	- 94.124	- 94.458	34.405
700	12.029	59.850	99.985	- 94.156	- 94.516	29.180
800	12.667	61.522	94.706	- 94.218	- 94.556	25.830
900	12.667	62.992	55.546	- 94.270	- 94.596	22.970
1000	12.980	64.344	56.159	- 94.321	- 94.628	20.680
1100	13.243	65.594	57.143	- 94.371	- 94.658	18.806
1200	13.466	66.841	58.200	- 94.419	- 94.686	17.200
1300	13.656	68.085	59.315	- 94.469	- 94.701	15.920
1400	13.815	69.329	60.485	- 94.515	- 94.716	14.785
1500	13.953	69.817	59.984	- 94.562	- 94.728	13.801
1600	14.074	70.722	60.627	- 94.607	- 94.739	12.940
1700	14.177	71.948	61.418	- 94.650	- 94.750	12.180
1800	14.269	73.391	62.363	- 94.690	- 94.759	11.504
1900	14.352	75.048	63.463	- 94.728	- 94.767	10.908
2000	14.424	73.903	62.648	- 94.762	- 94.771	10.383
2100	14.489	74.608	63.512	- 94.793	- 94.774	9.860
2200	14.547	75.294	64.267	- 94.821	- 94.776	9.340
2300	14.600	75.931	64.935	- 94.846	- 94.775	8.820
2400	14.648	76.554	65.503	- 94.869	- 94.774	8.300
2500	14.692	77.153	65.986	- 94.889	- 94.771	7.780
2600	14.734	77.730	66.486	- 94.906	- 94.766	7.260
2700	14.772	78.284	66.999	- 94.921	- 94.759	6.740
2800	14.807	78.824	67.525	- 94.935	- 94.750	6.220
2900	14.841	79.344	67.999	- 94.947	- 94.739	5.700
3000	14.873	79.848	67.670	- 94.957	- 94.725	5.180
3100	14.902	80.336	68.071	- 94.965	- 94.709	4.660
3200	14.928	80.807	68.493	- 94.971	- 94.691	4.140
3300	14.956	81.270	68.933	- 94.976	- 94.671	3.620
3400	14.982	81.717	69.215	- 94.979	- 94.649	3.100
3500	15.006	82.151	69.578	- 94.980	- 94.625	2.580
3600	15.030	82.574	69.933	- 94.979	- 94.599	2.060
3700	15.053	82.986	70.280	- 94.976	- 94.571	1.540
3800	15.075	83.388	70.620	- 94.971	- 94.540	1.020
3900	15.097	83.780	70.953	- 94.964	- 94.506	0.500
4000	15.119	84.162	71.278	- 94.954	- 94.470	0.000
4100	15.139	84.536	71.597	- 94.941	- 94.431	- 0.480
4200	15.159	84.901	71.909	- 94.925	- 94.389	- 0.960
4300	15.179	85.258	72.216	- 94.906	- 94.344	- 1.440
4400	15.197	85.607	72.516	- 94.884	- 94.296	- 1.920
4500	15.216	85.949	72.811	- 94.859	- 94.245	- 2.400
4600	15.234	86.284	73.100	- 94.831	- 94.191	- 2.880
4700	15.254	86.611	73.384	- 94.799	- 94.134	- 3.360
4800	15.272	86.933	73.663	- 94.764	- 94.074	- 3.840
4900	15.290	87.248	73.937	- 94.726	- 94.011	- 4.320
5000	15.306	87.557	74.206	- 94.685	- 93.944	- 4.800
5100	15.327	87.860	74.471	- 94.641	- 93.873	- 5.280
5200	15.349	88.159	74.731	- 94.594	- 93.799	- 5.760
5300	15.371	88.451	74.988	- 94.544	- 93.721	- 6.240
5400	15.393	88.738	75.239	- 94.491	- 93.639	- 6.720
5500	15.415	89.021	75.488	- 94.435	- 93.554	- 7.200
5600	15.437	89.299	75.732	- 94.376	- 93.465	- 7.680
5700	15.459	89.572	75.972	- 94.314	- 93.371	- 8.160
5800	15.481	89.841	76.209	- 94.248	- 93.271	- 8.640
5900	15.503	90.106	76.442	- 94.178	- 93.165	- 9.120
6000	15.525	90.367	76.672	- 94.104	- 93.054	- 9.600

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Point Group D_{∞h}
 $S_{298.15}^0 = 51.07 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = -93.965 \pm 0.011 \text{ kcal. mole}^{-1}$
 $\Delta F_f^0 = -94.054 \pm 0.011 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

λ , cm. ⁻¹
1342.86 (1)
667.30 (2)
2349.30 (1)

Bond Distance: C-O = 1.16 Å
 Bond Angle: O-C-O = 180°
 Rotational Constant: B₀ = 0.39038 cm.⁻¹
 $\sigma^- = 2$

Heat of Formation

The enthalpy change (ΔH_f^0) of the reaction C(s, graphite) + O₂(g) = CO₂(g) has been measured by P. H. Dewey and D. R. Harper, *J. Res. Natl. Bur. Std.* **21**, 457 (1938), R. S. Jessup, *ibid.* **21**, 491 (1938), and E. J. Frosen and F. D. Rossini, *ibid.*, **23**, 439 (1944). Based on these data, the heat of formation (ΔH_f^0) for CO₂(g) was reported to be -94.0518 ± 0.0108 kcal. mole⁻¹, using molecular weight of CO₂ = 44.010, by E. J. Frosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards* **33**, 447 (1944). This value was recalculated to be -94.054 ± 0.011 kcal. mole⁻¹, based on molecular weight of CO₂ = 44.011, for internal consistency.

Heat Capacity and Entropy

The functions adopted here were obtained from H. W. Woolley, *J. Research Nat. Bur. Standards* **52**, 289 (1954) who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by T. Wentnik, Jr., *J. Chem. Phys.* **30**, 105 (1959). Slightly different sets of spectroscopic constants were obtained by C. P. Courtney, *Mem. soc. roy. Liege* **19**, 496 (1957) and V. R. Stull, P. J. Wyatt and O. N. Plass, *J. Chem. Phys.* **37**, 1442 (1962). The high-resolution infrared spectrum of O₁₈-enriched CO₂ was examined in the region 5400-1620 cm.⁻¹, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm.⁻¹ by C. V. Berny, Ph. D. Thesis, University of Washington, 1962.

The molecular structure was reported by O. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc. 1945. The rotational constant, B₀, was obtained from H. W. Woolley, loc. cit. The value of bond distance, r_e, was calculated from B₀ which was derived from B₀, using B₀-B₀ = 0.0011 cm.⁻¹ given in O. Herzberg, loc. cit. The principal moment of inertia is I = 7.1485 X 10⁻³⁹ g. cm.²

Heat capacities of CO₂(g) at high pressures were reported by M. P. Vukalovich, V. V. Altunin and A. N. Gureev, *Teplotnergetika*, **12** (7), 56 (1965); K. Krueger, *Ver. Deut. Ingr. Z.*, **106** (32) 1650 (1964), and M. P. Vukalovich and A. N. Gureev, *Teplotnergetika*, **11** (6), 80 (1964).

CO₂

Carbon Dioxide Unequivocal Ion (CO₂⁻)

(Ideal Gas) GFW = 44.0105

T, °K	Cp ^a	gibbs/mol S ^b - (G ^c - H ^c)/T	H ^c - H ^c ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log Kp
0						
100	8.746	57.489	+0.00	-105.500	-106.137	77.401
200	8.759	57.489	+0.16	-105.510	-106.141	77.324
300	8.769	57.489	+0.59	-105.520	-106.145	77.244
400	8.776	57.489	+0.94	-105.530	-106.148	77.164
500	10.226	62.362	1.915	-106.612	-106.261	46.447
600	10.864	64.284	2.971	-107.186	-106.138	38.661
700	11.369	66.000	4.084	-107.772	-105.915	33.068
800	11.811	67.549	5.245	-108.365	-105.611	28.451
900	12.149	68.960	6.401	-108.964	-105.231	25.554
1000	12.417	70.255	7.672	-109.566	-104.784	22.900
1100	12.632	71.449	8.925	-110.172	-104.278	20.718
1200	12.807	72.555	10.197	-110.781	-103.714	18.889
1300	12.950	73.586	11.485	-111.395	-103.099	17.333
1400	13.068	74.551	12.787	-112.010	-102.439	15.991
1500	13.166	75.456	14.090	-112.631	-101.733	14.822
1600	13.249	76.308	15.419	-113.254	-100.987	13.794
1700	13.318	77.113	16.748	-113.878	-100.200	12.882
1800	13.378	77.876	18.083	-114.507	-99.377	12.066
1900	13.429	78.601	19.423	-115.141	-98.520	11.352
2000	13.473	79.291	20.768	-115.776	-97.630	10.668
2100	13.512	79.949	22.118	-116.417	-96.703	10.004
2200	13.546	80.579	23.470	-117.065	-95.753	9.512
2300	13.575	81.182	24.827	-117.712	-94.768	9.005
2400	13.600	81.759	26.187	-118.360	-93.750	8.586
2500	13.625	82.316	27.547	-119.027	-92.720	8.106
2600	13.646	82.850	28.910	-119.692	-91.651	7.704
2700	13.664	83.366	30.276	-120.361	-90.564	7.331
2800	13.681	83.863	31.643	-121.035	-89.445	6.982
2900	13.696	84.342	33.017	-121.714	-88.300	6.658
3000	13.710	84.808	34.382	-122.399	-87.140	6.348
3100	13.722	85.258	35.754	-123.087	-85.952	6.060
3200	13.734	85.694	37.127	-123.781	-84.748	5.788
3300	13.744	86.116	38.501	-124.480	-83.517	5.531
3400	13.753	86.526	39.876	-125.182	-82.262	5.286
3500	13.762	86.926	41.251	-125.882	-80.997	5.059
3600	13.770	87.313	42.628	-126.604	-79.700	4.838
3700	13.777	87.691	44.005	-127.322	-78.385	4.630
3800	13.784	88.058	45.383	-128.043	-77.050	4.431
3900	13.790	88.416	46.767	-128.766	-75.701	4.242
4000	13.796	88.766	48.141	-129.497	-74.341	4.061
4100	13.802	89.106	49.521	-130.231	-72.941	3.888
4200	13.807	89.439	50.902	-130.968	-71.538	3.723
4300	13.811	89.764	52.283	-131.710	-70.133	3.564
4400	13.815	90.082	53.664	-132.456	-68.718	3.411
4500	13.819	90.392	55.046	-133.204	-67.302	3.263
4600	13.824	90.696	56.428	-133.957	-65.879	3.123
4700	13.827	90.993	57.811	-134.713	-64.446	2.987
4800	13.831	91.284	59.194	-135.473	-62.994	2.856
4900	13.833	91.570	60.577	-136.236	-61.522	2.731
5000	13.837	91.849	61.960	-137.002	-59.982	2.609
5100	13.840	92.123	63.344	-137.773	-58.426	2.491
5200	13.842	92.392	64.728	-138.546	-56.853	2.377
5300	13.845	92.656	66.113	-139.321	-55.267	2.267
5400	13.847	92.914	67.497	-140.101	-53.671	2.160
5500	13.849	93.168	68.882	-140.883	-52.057	2.057
5600	13.852	93.418	70.267	-141.668	-50.430	1.956
5700	13.854	93.663	71.652	-142.457	-48.798	1.860
5800	13.856	93.904	73.038	-143.248	-47.155	1.765
5900	13.857	94.141	74.423	-144.043	-45.504	1.673
6000	13.859	94.374	75.809	-144.840	-43.848	1.584

June 30, 1966; Dec. 31, 1966

CARBON DIOXIDE UNEQUIVOCAL ION (CO₂⁻) (IDEAL GAS) GFW = 44.0105

Point group [C_{2v}]

S_{298.15}⁰ = [57.5] gibbs/mol

Ground State Quantum Weight = [2]

ΔH₀⁰ = [-104.1 ± 27] kcal/mol

ΔH_{298.15}⁰ = [-105.5 ± 27] kcal/mol

Vibrational Frequencies and Degeneracies

ω cm ⁻¹
[1400] (1)
[800] (1)
1671 (1)

Bond Distance: C-O = [1.25] Å

Bond Angle: O-C-O = 127° ± 8°

Product of the Moments of Inertia: I_AI_BI_C = [2.1296] × 10⁻¹¹⁶ g³ cm⁶

σ = [2]

Heat of Formation

The heat of formation, ΔH₂₉₈⁰(CO₂⁻, g) = -105.5 ± 27 kcal/mol, is estimated from ΔH₂₉₈⁰ = 88.6 ± 10 kcal/mol for HCO₂⁻(g) → H(g) + CO₂⁻(g), using the ΔH₂₉₈⁰(HCO₂⁻, g) = -142 ± 17 kcal/mol and ΔH₂₉₈⁰(H, g) = 52.1 kcal/mol. The value of ΔH₂₉₈⁰ is assumed to be the same as that for HCOOH(g) → H(g) + COOH(g). The values of ΔH₂₉₈⁰(HCOOH, g) and ΔH₂₉₈⁰(H, g) = -90.5 and 52.1 kcal/mol, respectively, are from "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Std. Tech. Note 270-1, Washington, D. C., Oct. 1965, and the value of ΔH₂₉₈⁰(COOH, g) = -54 ± 3 kcal/mol, is from S. W. Benson, J. Chem. Ed. 42, 502 (1965). The value of ΔH₂₉₈⁰(HCO₂⁻, g) is estimated from an approximate lattice energy calculation for sodium formate. The derived electron affinity of CO₂(g) is 11.5 kcal/mol (0.5 eV) with an estimated uncertainty range of 0-40 kcal/mol.

Heat Capacity and Entropy

The correlations of A. D. Walsh, J. Chem. Soc. 1953, 2268, predict a bent molecular structure for CO₂⁻ based on its 17 valence electrons. K. O. Hartman and I. C. Hsataune, J. Chem. Phys. 44, 1913 (1966), measured the asymmetric C-O stretching frequency and derived the bond angle of 127° ± 8° from the infrared spectrum of matrix-isolated CO₂⁻. They also estimated the bond distance C-O and the symmetric stretching and the bending vibrational frequencies by the valence force method. These molecular constants are adopted in the tabulation. The three principal moments of inertia are I_A = 0.4511 × 10⁻³⁵, I_B = 6.6491 × 10⁻³⁵ and I_C = 7.1002 × 10⁻³⁵ g cm².

D. W. Overall and D. H. Whiffen, Mol. Phys. 4, 135 (1961), have derived a bond angle of 134° which is in good agreement with the value selected. This result was obtained from electron spin resonance for the CO₂⁻ radical trapped in sodium formate.

Carbon Phosphide (CP)

(Ideal Gas) Mol. Wt. = 42.986

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-2.083	110.731	110.731	INFINITE
100	6.957	44.923	-1.982	111.321	107.089	-234.031
200	6.981	48.848	-1.982	111.621	102.719	-112.241
298	7.149	51.661	0.000	111.700	98.337	-72.072
300	7.154	51.705	0.013	111.700	98.244	-71.568
400	7.406	54.845	0.133	111.650	89.366	-39.638
500	7.741	55.996	1.502	111.520	89.306	-39.634
600	7.989	56.930	2.289	111.328	84.879	-30.916
700	8.184	58.177	3.098	111.079	80.490	-25.129
800	8.335	59.280	3.925	110.790	76.830	-19.349
900	8.456	60.166	4.764	110.480	73.480	-13.600
1000	8.545	60.864	5.614	110.150	70.465	-8.810
1100	8.619	61.982	6.473	110.080	63.547	-12.625
1200	8.679	62.735	7.338	109.660	61.441	-11.135
1300	8.728	63.432	8.208	109.843	58.764	-9.675
1400	8.768	64.086	9.082	109.843	56.880	-8.244
1500	8.805	64.686	9.962	109.586	55.080	-7.864
1600	8.835	65.256	10.844	109.451	51.608	-7.049
1700	8.861	65.792	11.729	109.314	49.248	-6.331
1800	8.884	66.299	12.616	109.174	46.895	-5.694
1900	8.905	66.778	13.504	108.860	44.542	-5.057
2000	8.923	67.237	14.397	108.860	42.212	-4.413
2100	8.940	67.673	15.290	108.745	39.884	-4.151
2200	8.955	68.089	16.185	108.598	37.559	-3.731
2300	8.969	68.486	17.081	108.451	35.244	-3.349
2400	8.982	68.865	17.977	108.304	32.944	-2.994
2500	8.994	69.237	18.877	108.153	30.630	-2.678
2600	9.005	69.590	19.777	108.001	28.330	-2.381
2700	9.016	69.930	20.678	107.849	26.037	-2.107
2800	9.026	70.258	21.581	107.698	23.771	-1.854
2900	9.036	70.578	22.487	107.547	21.521	-1.618
3000	9.045	70.881	23.388	107.389	19.196	-1.398
3100	9.054	71.178	24.293	107.234	16.926	-1.193
3200	9.063	71.465	25.199	107.077	14.659	-1.001
3300	9.071	71.744	26.105	106.919	12.397	-0.821
3400	9.079	72.017	27.011	106.760	10.140	-0.654
3500	9.087	72.279	27.921	106.600	7.890	-0.493
3600	9.095	72.535	28.830	106.439	5.642	-0.342
3700	9.102	72.784	29.740	106.277	3.401	-0.201
3800	9.109	73.027	30.651	106.115	1.166	-0.067
3900	9.117	73.265	31.562	105.954	-1.075	0.060
4000	9.124	73.495	32.474	105.785	-3.297	0.180
4100	9.131	73.720	33.387	105.619	-5.524	0.294
4200	9.137	73.940	34.300	105.450	-7.739	0.403
4300	9.144	74.155	35.214	105.280	-9.961	0.506
4400	9.151	74.366	36.127	105.111	-12.171	0.608
4500	9.157	74.571	37.044	104.943	-14.383	0.698
4600	9.164	74.772	37.960	104.764	-16.589	0.788
4700	9.170	74.970	38.877	104.590	-18.789	0.874
4800	9.176	75.166	39.794	104.415	-20.984	0.955
4900	9.182	75.352	40.712	104.235	-23.177	1.035
5000	9.189	75.538	41.631	104.056	-25.367	1.109
5100	9.195	75.720	42.550	103.873	-27.560	1.181
5200	9.201	75.898	43.470	103.691	-29.743	1.250
5300	9.207	76.074	44.390	103.508	-31.926	1.316
5400	9.213	76.248	45.311	103.320	-34.105	1.381
5500	9.219	76.415	46.233	103.132	-36.266	1.444
5600	9.225	76.581	47.155	102.942	-38.437	1.500
5700	9.231	76.744	48.078	102.750	-40.605	1.557
5800	9.237	76.905	49.000	102.558	-42.768	1.612
5900	9.243	77.063	49.925	102.361	-44.924	1.662
6000	9.248	77.218	50.850	102.164	-47.083	1.715

June 30, 1962

CARBON PHOSPHIDE (CP)

(IDEAL GAS)

MOL. WT. = 42.986

$$\Delta H_f^0 = 110.7 \pm 23.1 \text{ kcal. mole}^{-1}$$
$$\Delta H_f^{298.15} = 111.7 \pm 23.1 \text{ kcal. mole}^{-1}$$
$$S_{298.15}^0 = 51.66 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Configuration Σ^+

Electronic Level and Multiplicity

$$\frac{\epsilon_i}{0} \quad \frac{g_i}{2}$$

$$\omega_e x_e = 1259.67 \text{ cm.}^{-1}$$

$$r_e = 1.562 \text{ \AA}$$

$$\alpha_e = 0.00597 \text{ cm.}^{-1}$$

$$\sigma_e = 1$$

$$E_e = 0.7986 \text{ cm.}^{-1}$$

Heat of Formation.

$\Delta H_f^{298.15}$ was calculated from the dissociation energy (D_0^0) given by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall (1953). H. Barwald, G. Herzberg, and L. Herzberg, Ann. Physik 20, 569 (1934) reported a $D_0^0 = 6.9$ e.v. A. G. Gaydon (loc. cit.) reports that a linear Birge-Sponer extrapolation for $\chi^2 \sum (V_0 - 9)$ gives a $D_0^0 = 6.9$ e.v. and that a linear Birge-Sponer extrapolation of the excited states $A^1\Pi$ and $B^1\Sigma^+$ favored a similar value. Using the spectral data of H. Barwald et al. (loc. cit.), Gaydon concludes that D_0^0 is 6 ± 1 e.v. The uncertainty reported by Gaydon (loc. cit.) ± 1 e.v. corresponds to an uncertainty of ± 23.1 kcal. mole⁻¹ for the $\Delta H_f^{298.15}$. The 6.9 e.v. of H. Barwald et al. (loc. cit.) would give a $\Delta H_f^{298.15} = 90.6$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The molecular constants were taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York (1950).

Carbon Monosulphide (CS)

(Ideal Gas) Mol. Wt. = 44.077

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	6.900	INFINITE	2.081	54.224	54.224	INFINITE
100	6.957	42.667	1.387	54.740	50.791	-110.999
200	6.912	47.422	0.860	54.866	48.736	-110.999
298	7.122	50.299	0.000	55.000	42.684	-31.287
300	7.126	50.343	0.013	54.999	42.607	-31.038
400	7.401	52.429	0.739	54.380	38.508	-21.039
500	7.690	54.112	1.494	53.878	34.598	-15.122
600	7.939	55.537	2.276	53.425	30.785	-11.213
700	8.137	56.776	3.080	53.004	27.069	-8.451
800	8.293	57.873	3.902	52.604	23.425	-6.044
900	8.415	58.858	4.737	52.225	19.952	-4.865
1000	8.512	59.749	5.584	51.865	17.791	-3.888
1100	8.589	60.564	6.439	51.521	15.838	-3.107
1200	8.651	61.314	7.301	51.230	14.099	-2.458
1300	8.703	62.009	8.169	51.000	13.469	-1.911
1400	8.746	62.656	9.041	50.825	12.920	-1.444
1500	8.783	63.260	9.918	50.698	12.444	-1.040
1600	8.814	63.828	10.798	50.613	12.027	-0.688
1700	8.841	64.363	11.681	50.563	11.662	-0.378
1800	8.865	64.869	12.566	50.539	11.342	-0.104
1900	8.886	65.349	13.453	50.534	11.064	0.140
2000	8.904	65.805	14.343	50.548	10.827	0.359
2100	8.921	66.240	15.234	50.577	10.627	0.557
2200	8.937	66.656	16.127	50.620	10.460	0.735
2300	8.951	67.053	17.022	50.675	10.325	0.898
2400	8.964	67.435	17.917	50.740	10.220	1.046
2500	8.976	67.801	18.814	50.815	10.140	1.182
2600	8.987	68.151	19.713	50.900	10.080	1.307
2700	8.998	68.492	20.612	50.995	10.030	1.423
2800	9.008	68.820	21.512	51.100	10.000	1.530
2900	9.018	69.136	22.413	51.215	10.000	1.628
3000	9.027	69.442	23.316	51.340	10.000	1.720
3100	9.036	69.738	24.219	51.475	10.000	1.806
3200	9.044	70.025	25.123	51.620	10.000	1.886
3300	9.052	70.303	26.028	51.775	10.000	1.960
3400	9.060	70.574	26.933	51.940	10.000	2.030
3500	9.067	70.837	27.839	52.115	10.000	2.096
3600	9.075	71.092	28.747	52.300	10.000	2.158
3700	9.082	71.341	29.654	52.495	10.000	2.216
3800	9.089	71.583	30.563	52.700	10.000	2.271
3900	9.095	71.819	31.472	52.915	10.000	2.322
4000	9.102	72.050	32.382	53.140	10.000	2.371
4100	9.109	72.274	33.292	53.375	10.000	2.418
4200	9.115	72.494	34.204	53.620	10.000	2.463
4300	9.121	72.709	35.115	53.875	10.000	2.503
4400	9.128	72.918	36.028	54.140	10.000	2.543
4500	9.134	73.124	36.941	54.415	10.000	2.580
4600	9.140	73.324	37.855	54.690	10.000	2.616
4700	9.146	73.521	38.769	54.965	10.000	2.650
4800	9.152	73.714	39.684	55.240	10.000	2.682
4900	9.157	73.902	40.599	55.515	10.000	2.713
5000	9.163	74.087	41.515	55.790	10.000	2.743
5100	9.169	74.269	42.432	56.065	10.000	2.771
5200	9.175	74.447	43.350	56.340	10.000	2.797
5300	9.180	74.622	44.267	56.615	10.000	2.824
5400	9.186	74.793	45.185	56.890	10.000	2.849
5500	9.191	74.962	46.104	57.165	10.000	2.873
5600	9.197	75.128	47.023	57.440	10.000	2.895
5700	9.202	75.291	47.943	57.715	10.000	2.917
5800	9.208	75.451	48.864	58.000	10.000	2.938
5900	9.213	75.608	49.785	58.275	10.000	2.958
6000	9.219	75.763	50.706	58.550	10.000	2.977

Dec. 31, 1960 Dec. 31, 1962

CARBON MONOSULPHIDE (CS)

(IDEAL GAS)

Mol. Wt. = 44.077

$$\Delta H_f^0 = 54.2 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = 55.0 \pm 5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 50.3 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Configuration $\sum +$

Electronic Level and Multiplicity

E, cm. ⁻¹	g _i
0	1

$$\omega_e = 1285.08 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$\alpha_e = 0.00592 \text{ cm.}^{-1}$$

$$r_e = 1.535 \text{ Å}$$

Heat of Formation.

A. Lagerqvist, H. Westerlund, C. V. Wright and R. P. Barrow, Arkiv for Fysik **14**, 387 (1958) examined the UV band system of CS and made a new extrapolation of the ground state vibrational levels to find $D_0^0 = 7.85 \text{ e.v.}$, which leads to $\Delta H_f^{298} \text{ CS} = 55 \pm 5.0 \text{ kcal. mole}^{-1}$. H. Schaffer and H. Wiedemeier, Paper presented at the XVIIIth IUPAC Congress Montreal (1961). Have measured $\Delta H_f^{298.15} \text{ CS(g)}$ by an equilibrium method and found $58 \pm 3 \text{ kcal. mole}^{-1}$. E. Gallegos and R. W. Kiser, J. Phys. Chem. **65**, 1177 (1961) obtained a value of $\Delta H_f^{298.15} \text{ CS(g)} = 55.0 \text{ kcal. mole}^{-1}$ from the heat of formation of CS^+ and the ionization potential of CS. C. J. Fincham and R. A. Bergman, J. Metals, **9**, 680 (1957) measured the equilibrium between CS_2 and sulphur containing ores. Combining these with similar experiments for H_2S the heat of formation of CS at 298 is calculated to be $59.0 \text{ kcal. mole}^{-1}$. The gases assumed are CS_2 , CS, S, S₂, H₂, H₂S, and HS — because of the complex equilibria and the use of outside data for the H_2S equilibrium, the assumption of $P_{\text{H}_2} = 1 \text{ atm.}$ and the uncertainty in HS values, this value was given no weight.

Heat Capacity and Entropy.

A. Lagerqvist, et al., loc. cit., give the vibrational constants. The rotational constants are from the microwave measurements of R. C. Mockler and R. Bird, Phys. Rev. **98**, 1837 (1955).

Carbon Disulfide (CS₂)

(Ideal Gas) Mol. Wt. = 76.143

CS₂CARBON DISULFIDE (CS₂)

(IDEAL GAS)

MOL. WT. = 76.143

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	7.000	0.000	INFINITE	2.551	27.287	27.287	INFINITE
100	7.004	47.019	2.551	26.146	26.146	26.146	2.551
200	9.461	52.776	1.004	28.128	19.866	21.616	21.616
298	10.875	56.832	0.000	27.880	15.991	11.721	11.721
300	10.895	56.899	0.000	27.874	15.917	11.595	11.595
400	11.850	61.166	0.200	26.570	12.975	8.521	8.521
500	12.480	62.880	0.375	25.692	8.413	3.677	3.677
600	12.974	65.200	0.549	24.874	5.036	1.834	1.834
700	13.346	67.230	0.716	24.166	1.835	0.573	0.573
800	13.636	69.000	0.875	23.533	0.000	0.000	0.000
900	13.858	70.451	1.025	22.985	-2.374	-4.005	-4.005
1000	14.033	72.121	1.166	22.520	-4.163	-9.10	-9.10
1100	14.172	73.463	1.303	22.122	-4.325	-14.595	-14.595
1200	14.283	74.703	1.437	21.774	-4.482	-20.116	-20.116
1300	14.375	75.850	1.568	21.472	-4.639	-25.660	-25.660
1400	14.450	76.911	1.696	21.211	-4.795	-31.222	-31.222
1500	14.513	77.917	1.821	21.022	-4.957	-36.799	-36.799
1600	14.567	78.856	1.943	20.897	-5.113	-42.388	-42.388
1700	14.612	79.740	2.062	20.825	-5.269	-47.986	-47.986
1800	14.650	80.576	2.178	20.805	-5.425	-53.591	-53.591
1900	14.682	81.370	2.291	20.836	-5.581	-59.201	-59.201
2000	14.716	82.124	2.401	20.916	-5.737	-64.816	-64.816
2100	14.742	82.843	2.508	21.048	-5.894	-70.436	-70.436
2200	14.766	83.529	2.612	21.230	-6.051	-76.060	-76.060
2300	14.786	84.176	2.712	21.461	-6.208	-81.688	-81.688
2400	14.806	84.816	2.808	21.740	-6.365	-87.320	-87.320
2500	14.824	85.420	2.901	22.065	-6.522	-92.956	-92.956
2600	14.839	86.002	2.991	22.436	-6.679	-98.596	-98.596
2700	14.857	86.552	3.078	22.851	-6.836	-104.239	-104.239
2800	14.872	87.076	3.162	23.310	-6.993	-109.884	-109.884
2900	14.880	87.576	3.243	23.814	-7.150	-115.532	-115.532
3000	14.892	88.159	3.321	24.363	-7.307	-121.182	-121.182
3100	14.902	88.618	3.396	24.956	-7.464	-126.833	-126.833
3200	14.913	89.091	3.468	25.594	-7.621	-132.484	-132.484
3300	14.923	89.586	3.537	26.276	-7.778	-138.135	-138.135
3400	14.931	89.994	3.603	27.001	-7.935	-143.786	-143.786
3500	14.940	90.429	3.667	27.768	-8.092	-149.437	-149.437
3600	14.948	90.880	3.729	28.576	-8.249	-155.087	-155.087
3700	14.956	91.259	3.788	29.424	-8.406	-160.738	-160.738
3800	14.963	91.576	3.844	30.311	-8.563	-166.388	-166.388
3900	14.971	92.037	3.897	31.236	-8.720	-172.038	-172.038
4000	14.977	92.426	3.948	32.201	-8.877	-177.688	-177.688
4100	14.984	92.796	3.997	33.206	-9.034	-183.338	-183.338
4200	14.991	93.157	4.044	34.251	-9.191	-188.988	-188.988
4300	14.997	93.506	4.089	35.336	-9.348	-194.638	-194.638
4400	15.003	93.855	4.133	36.461	-9.505	-200.288	-200.288
4500	15.009	94.192	4.176	37.626	-9.662	-205.938	-205.938
4600	15.015	94.522	4.217	38.831	-9.819	-211.588	-211.588
4700	15.021	94.841	4.256	40.076	-9.976	-217.238	-217.238
4800	15.026	95.151	4.293	41.361	-10.133	-222.888	-222.888
4900	15.031	95.471	4.328	42.686	-10.290	-228.538	-228.538
5000	15.037	95.775	4.361	44.051	-10.447	-234.188	-234.188
5100	15.042	96.073	4.392	45.456	-10.604	-239.838	-239.838
5200	15.047	96.365	4.421	46.901	-10.761	-245.488	-245.488
5300	15.052	96.653	4.448	48.386	-10.918	-251.138	-251.138
5400	15.057	96.933	4.473	49.911	-11.075	-256.788	-256.788
5500	15.062	97.209	4.497	51.476	-11.232	-262.438	-262.438
5600	15.066	97.481	4.519	53.081	-11.389	-268.088	-268.088
5700	15.071	97.747	4.540	54.726	-11.546	-273.738	-273.738
5800	15.075	98.007	4.559	56.411	-11.703	-279.388	-279.388
5900	15.080	98.267	4.576	58.136	-11.860	-285.038	-285.038
6000	15.085	98.521	4.591	59.901	-12.017	-290.688	-290.688

June 30, 1961

CS₂

SILICON CARBIDE, ALPHA (SiC)

(CRYSTAL)

OPW = 40.09715

$$\Delta H_f^0 = -16.9 \pm 1.5 \text{ kcal/mol}$$

$$\Delta H_{298.15}^0 = -17.1 \pm 1.5 \text{ kcal/mol}$$

$$S_{298.15}^0 = 3.94 \pm 0.03 \text{ gibbs/mol}$$

$$T_d = [3245]^\circ \text{K}$$

Heat of Formation

The heat of formation is calculated from $\Delta H_{298}^0 = -591.9 \text{ kcal/mol}$ for $\text{SiC}(\alpha) + 4P_2(g) \rightarrow \text{SiP}_4(g) + CP_4(g)$ based on the tentative value of $\Delta H_{298}^0 = -223.1 \text{ kcal/mol}$ for $CP_4(g)$. Greenberg¹ determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey² obtained by oxygen bomb calorimetry yield a ΔH_f^0 which is over 2 kcal more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained mass spectrometrically by Drowart³ are in close agreement with the selected ΔH_f^0 , but Knudsen weight loss data of Grieverson⁴ and solubility-activity data of Kirkwood⁵ yield values less negative by 2 and 3 kcal, respectively. The results are summarized below.

The data of Drowart show a significant drift while those of Grieverson do not, but the latter should be corrected for $C_{Si}(g)$ and $C_{Si}(g)$ which are present in amounts of about 4 and 3%, respectively, at 2000°K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin⁶ and Ghoatagore⁷ yield apparent pressures which are smaller by factors of 1/30 to 1/1000.

Source	Method	Reaction	Range, °K	No. of Points	ΔH_{298}^0 (kcal/mol)	Drift ΔH_{298}^0 (kcal/mol)
Greenberg (1966)	P_2 Calorimetry	A	298	—	-591.9	-17.1
Humphrey (1952)	O_2 Calorimetry	B	303	—	-292.0	-19.6
Drowart (1958)	Mass Spec.	C	2149-2318	7	136.940.7	124.61 -5.640.3 -16.9(-17.6)*
Grieverson (1960)	Knudsen Wt. Loss	C	1785-2004	10	122.940.7	122.66 -0.240.4 -15.0
Kirkwood (1961)	Soln. in Pb	D	1693	1	—	25.66 - -14.1
A) $\text{SiC}(\alpha) + 4P_2(g) \rightarrow \text{SiP}_4(g) + CP_4(g)$						
B) $\text{SiC}(\alpha) + 2O_2(g) \rightarrow \text{SiO}_2(\text{low-temp}) + CO_2(g)$						
*Value in parentheses is based on authors' data for $\text{Si}(1) \rightarrow \text{Si}(g)$ rather than JANAF value.						

Heat Capacity and Entropy

Low temperature heat capacities are from data (54-296°K) of Humphrey² and are in good agreement with earlier data (54-295°K) of Kelley⁸. The entropy is obtained from C_p using $S_0^0 = 0.038 \text{ eu}$. C_p above room temperature is based on enthalpy data of Humphrey² (389-1789°K), Walker⁹ (373-1073°K) and Magnus¹⁰ (372-1172°K). Maximum deviations of the data from the selected values are 1.4, 2 and -1.7%, respectively; these occur in the range 370-621°K. Kirillin¹¹ obtained enthalpy data (1114-2843°K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.7% iron impurity, these data deviate by -1.1-5% from the selected values. Enthalpies (793-1790°K) of Fieldhouse¹² are high by 1-8% while those of Maksimenko¹³ were not available for analysis.

Transition Data

$\text{SiC}(\alpha)$, also called hexagonal II or 6H, is one of the more common of many hexagonal forms which arise from various possible stacking sequences of the hexagonal SiC layers.¹⁴ The properties of these phases are so similar that they have not been adequately differentiated thermodynamically. It has frequently been assumed that cubic $\text{SiC}(\beta)$ transforms to α at about 2300°K, but this seems unlikely since both phases have been prepared over temperature ranges of 1700-3000°K.¹⁴ Heat of formation and equilibrium data indicate that α is less stable up to 2000°K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data

The decomposition temperature is calculated as the value at which the total pressure reaches one atm for vapor consisting of $C_{Si}(4.3 \text{ mol } \%)$, $\text{Si}(32.0\%)$, $\text{Si}_2(21.2\%)$, $\text{Si}_2(1.9\%)$, $\text{CSi}(0.2\%)$, and $\text{Si}_3(0.25\%)$. The tables predict decomposition to graphite and pure liquid silicon at about 3280°K; however, Scafe¹⁵ observed peritectic decomposition to graphite and solution containing 19 atom percent of carbon at 3103±40°K. In contrast, Drolloff¹⁶ reported the peritectic at 2813±40°K and 27 percent carbon. Badami¹⁷ has shown that decomposition in vacuum at lower temperatures (2400°K) leads to graphite.

References

1. E. Greenberg et al., Argonne National Laboratory, ANL-7175, 138 (1966); ANL-7020, 169 (1965).
2. J. Drowart, *Compt. Rend. Acad. Sci. Paris*, **259**, 1015 (1964); *Ann. Chim. Phys.*, **19**, 1089 (1952).
3. J. Drowart, G. DeMaria and M. G. Inghram, *J. Chem. Phys.*, **29**, 1015 (1958); J. Drowart and G. DeMaria, pp 16-23 in reference (14).
4. P. Grieverson and C. B. Alcock, "Special Ceramics," Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208, Haywood & Co., London, 1960.
5. D. H. Kirkwood and J. Chipman, *J. Phys. Chem.*, **65**, 1082 (1961).
6. V. Voronin, N. J. Makarov and B. P. Rudin, *Izvestiya Otd. Khim. Silikatov* 1 Okladov, Akad. Nauk SSSR, Sb. Statei **1965**, 203-208.
7. K. N. Ghoatagore, Solid-State Electronics **9**, 178 (1966).
8. K. K. Kelley, *J. Am. Chem. Soc.*, **53**, 1137 (1931).
9. B. E. Walker, C. T. Ewing and R. R. Miller, *J. Chem. Eng. Data*, **7**, 595 (1962).
10. A. Magnue, *Ann. Physik*, **10**, 303 (1923); Ya. Chelchovskoi, *Topolofis. Vysokikh Temperatur*, Akad. Nauk SSSR **2**, 9 (1964).
11. I. B. Pikhovskii and A. G. Hodge, AD-150854 (1958).
12. M. S. Maksimenko and J. S. Polubelova, *Trudy Leningrad. Tekhnol. Inst. im. Lenaveta* **33**, 30 (1965).
13. J. R. O'Connor and J. Smiltens, editors, "Silicon Carbide," Pergamon Press, London, 1960.
14. R. Scafe and G. A. Slack, *J. Chem. Phys.*, **30**, 1551 (1959); pp 24-30 in ref. (14).
15. R. T. Drolloff, U. S. Dept. Comm. Clearinghouse, PB Rept. 171,385, 28 pp (1960).
16. D. V. Badami, *Nature*, **195**, 569 (1962).

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

T, °K	C _p	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
0	0.000	0.000	INFINITE	0.782	17.261	17.261	INFINITE
100	1.019	3.349	7.002	0.755	17.312	17.235	37.666
200	3.896	1.820	4.879	0.512	17.428	17.110	10.697
298	6.415	3.970	3.970	0.000	17.500	16.937	12.415
300	6.455	4.010	3.970	0.012	17.501	16.934	12.336
400	8.150	6.118	4.246	0.749	17.517	16.741	9.147
500	9.235	8.061	4.818	1.622	17.507	16.547	7.233
600	9.888	9.815	5.507	2.585	17.400	16.358	5.058
700	10.265	11.393	6.074	3.469	17.422	16.320	4.048
800	10.485	12.835	6.574	4.280	17.455	15.984	3.249
900	11.301	14.146	7.099	5.003	17.440	15.602	3.037
1000	11.573	15.351	7.605	5.640	17.426	15.621	3.414
1100	11.798	16.465	8.088	6.116	17.415	15.425	3.046
1200	12.000	17.500	8.548	6.548	17.407	15.282	2.780
1300	12.193	18.466	8.982	6.935	17.404	15.085	2.536
1400	12.292	19.372	9.390	7.280	17.402	14.905	2.327
1500	12.415	20.224	9.778	7.595	17.406	14.726	2.146
1600	12.524	21.029	10.144	7.887	17.414	14.548	1.987
1700	12.618	21.788	10.491	8.156	17.431	14.372	1.846
1800	12.708	22.515	10.815	8.403	17.452	14.200	1.720
1900	12.786	23.205	11.113	8.629	17.476	14.032	1.606
2000	12.858	23.862	11.383	8.835	17.501	13.868	1.502
2100	12.923	24.491	11.628	9.022	17.526	13.708	1.407
2200	12.981	25.097	11.850	9.191	17.551	13.552	1.321
2300	13.033	25.677	12.051	9.344	17.575	13.400	1.242
2400	13.080	26.228	12.232	9.482	17.598	13.252	1.169
2500	13.137	26.764	12.395	9.606	17.620	13.108	1.101
2600	13.182	27.280	12.541	9.717	17.641	12.968	1.038
2700	13.226	27.777	12.671	9.815	17.661	12.832	0.980
2800	13.263	28.256	12.787	9.900	17.679	12.700	0.927
2900	13.299	28.726	12.890	9.972	17.695	12.572	0.878
3000	13.334	29.177	12.980	10.031	17.709	12.448	0.833
3100	13.367	29.615	13.057	10.078	17.721	12.328	0.791
3200	13.398	30.035	13.122	10.113	17.731	12.211	0.751
3300	13.428	30.438	13.177	10.137	17.739	12.097	0.712
3400	13.456	30.824	13.222	10.151	17.745	11.985	0.674
3500	13.483	31.194	13.258	10.156	17.749	11.874	0.637
3600	13.509	31.549	13.285	10.152	17.750	11.764	0.601
3700	13.534	31.890	13.304	10.139	17.748	11.655	0.565
3800	13.557	32.217	13.315	10.118	17.744	11.547	0.530
3900	13.580	32.530	13.319	10.089	17.737	11.440	0.495
4000	13.602	32.830	13.315	10.053	17.727	11.334	0.460

Mar. 31, 1967

$$\Delta H_f^\circ = -17.3 \pm 1.5 \text{ kcal/mol}$$
$$\Delta H_f^{298.15} = -17.5 \pm 1.5 \text{ kcal/mol}$$

Heat of Formation.

The heat of formation is calculated from $\Delta H_f^{298} = -591.5$ kcal/mol for $\text{SiC}(\beta) + \text{P}_2(\text{g}) \rightarrow \text{SiP}_4(\text{g}) + \text{C}_2(\text{g})$, based on the tentative value of $\Delta H_f^{298} = -223 \pm 1$ kcal/mol for $\text{C}_2(\text{g})$. Greenberg¹ determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey² obtained by oxygen bomb calorimetry yield a ΔH_f° which is over 3 kcal more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained with the Knudsen weight loss method by Davis³ are in good agreement with the selected ΔH_f° , but similar data of Grisevson⁴ and solubility-activity data of Rein⁵ and d'Entremont⁶ yield values less negative by 1.6 to 2.5 kcal. The results are summarized below. Other equilibrium data⁵ relating SiC and SiO₂ are not included, pending the revision of tables for SiO₂.

The data of Davis show a serious drift, while those of Grisevson do not; but the latter should be corrected for $\text{C}_2\text{Si}(\text{g})$ and $\text{CSi}_2(\text{g})$ which are present in amounts of about 4 and 3%, respectively, at 2000°K. Silicon carbide may have a small vaporization coefficient; since rates of free evaporation reported by Voronin⁷ and Ghoshtagore⁸ yield apparent pressures which are smaller by factors of 1/30 to 1/10000.

Source	Method	Reaction	Range, T°K	No. of Points	ΔH_f^{298} (kcal/mol)	Drift (eu)	ΔH_f^{298} (kcal/mol)
Greenberg (1956)	P ₂ Calorimetry	A	298	-	-591.5	-	-17.5
Humphrey (1952)	O ₂ Calorimetry	B	303	-	-290.9	-	-20.6
Davis (1961)	Knudsen Wt. Loss	C	2117-2171	8	167.28	126.10	-19.13
Grisevson (1960)	" "	D	1808-1973	6	123.340.3	122.65	-0.440.2
Rein (1963)	Soln. in C-Fe	D	1823-1873	2	32.0	27.43	-2.5
d'Entremont (1963)	Soln. in Ag	D	1693	1	-	27.31	-15.7
A) $\text{SiC}(\beta) + \text{P}_2(\text{g}) \rightarrow \text{SiP}_4(\text{g}) + \text{C}_2(\text{g})$							
B) $\text{SiC}(\beta) + 2\text{O}_2(\text{g}) \rightarrow \text{SiO}_2(\text{low quartz}) + \text{CO}_2(\text{g})$							
C) $\text{SiC}(\beta) \rightarrow \text{C}(\text{graph}) + \text{Si}(\text{g})$							
D) $\text{SiC}(\beta) \rightarrow \text{C}(\text{graph}) + \text{Si}(\text{l})$							

*Value in parentheses is based on author's data for Si(l) → Si(g) rather than JANAF value.

Heat Capacity and Entropy.

Low temperature heat capacities are from data (54-296°K) of Humphrey². The entropy is obtained from Op^9 using $S_{298}^\circ = 0.041$ eu. C_p above room temperature is based on Humphrey's enthalpy data (389-1693°K), which show a maximum deviation of $\pm 1.1\%$ from the selected functions. Humphrey's sample contained about 1% of α -SiC and about 0.6% of other impurities. Kirillin⁹ obtained enthalpy data (1114-2843°K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.73% iron impurity, these data deviate by -1.1% from the selected values.

Transition Data.

$\text{SiC}(\beta)$, also called cubic or 3C, has a structure of the diamond or zinc blende type¹⁰. The cubic phase differs from the many hexagonal forms only in the order of the stacking sequence of the hexagonal SiC layers. It has frequently been assumed that β transforms into α at about 2300°K, but this seems unlikely, since both phases have been prepared over temperature ranges of 1700-3000°K. Heat of formation and equilibrium data indicate that β is more stable up to 2000°K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data.

The decomposition temperature is calculated as the value at which the total pressure reaches one atm for vapor consisting of $\text{C}_2\text{Si}(45.4 \text{ mol } \%), \text{Si}(32.1\%), \text{CSi}_2(20.1\%), \text{Si}_2(1.8\%), \text{CSi}(0.28\%), \text{CSi}_3(0.23\%)$. The tables predict decomposition to graphite and pure liquid silicon at about 3337°K; however, Scaell¹¹ observed peritectic decomposition to graphite and solution containing 19 atom percent of carbon at 3103-340°K. In contrast, Dolloff¹² reported the peritectic at 2813-40°K and 27 percent carbon.

References.

1. Z. Greenberg et al., Argonne National Laboratory, ANL-7175, 138 (1956); ANL-7020, 169 (1955).
2. G. L. Humphrey, S. Todd, J. P. Coughlin and E. G. King, U.S. Bur. Mines RI 4868 (1952).
3. S. O. Davis, D. F. Anthrop and A. W. Searcy, J. Chem. Phys. 34, 659 (1961).
4. P. Grisevson and C. B. Alcock, "Special Ceramics," Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208, Haywood & Co., London, 1960.
5. R. H. Rein and J. Chipman, J. Phys. Chem. 67, 839 (1963).
6. J. C. d'Entremont and J. Chipman, J. Phys. Chem. 67, 499 (1963).
7. N. I. Voronin, N. L. Makarova and B. P. Yudin, Izvest. v Otd. Khim. Silykatov 1 Okladov, Akad. Nauk SSSR, Sb. Statei 1965, 203-8.
8. R. N. Ghoshtagore, Solid-State Electronics 9, 178 (1966).
9. V. A. Kirillin, A. E. Sheindlin and V. Ya. Chekhovskoi, Teplofiz. Vysokikh Temperatur, Akad. Nauk SSSR 2, 9 (1964).
10. J. R. O'Connor and J. Smitens, editors, "Silicon Carbide," Pergamon Press, London, 1960.
11. R. I. Scaell, U. S. Chem. Phys. 30, 1551 (1959); pp 24-30 in ref. 10.
12. R. T. Dolloff, U. S. Dept. Comm., Clearinghouse, PB Rept. 171,365, 28 pp (1960).

Silicon Carbide (SiC)

(Ideal Gas) GFW = 40.09715

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	0.000	INFINITE	2.215	170.806	170.806	INFINITE
100	6.958	42.719	57.917	171.423	167.264	-365.555
200	7.441	47.617	51.671	171.773	162.951	-176.065
298	9.182	50.892	50.892	172.000	158.573	-116.237
300	9.216	50.949	50.892	172.004	158.489	-115.459
400	10.574	53.513	51.273	172.250	153.948	-84.113
500	10.857	56.219	53.030	172.466	149.347	-65.279
600	10.810	58.180	52.597	172.595	144.709	-52.710
700	10.594	59.140	51.760	172.681	139.056	-39.998
800	10.300	60.000	50.800	172.725	133.375	-31.754
900	9.761	60.302	55.401	172.736	126.139	-27.568
1000	9.420	63.323	56.143	172.736	126.139	-27.568
1100	9.332	64.235	56.438	172.736	126.139	-27.568
1200	9.483	65.062	57.489	172.736	126.139	-27.568
1300	9.850	65.820	58.173	172.736	126.139	-27.568
1400	9.855	65.820	58.173	172.736	126.139	-27.568
1500	9.462	67.173	59.223	171.049	103.306	-15.052
1600	9.477	67.784	59.739	170.741	98.799	-13.495
1700	9.497	68.360	60.229	170.428	94.416	-12.138
1800	9.520	68.900	60.690	170.100	89.919	-10.998
1900	9.544	69.400	61.120	169.760	85.192	-9.991
2000	9.567	69.860	61.518	169.410	80.192	-9.091
2100	9.591	70.376	61.877	169.050	74.880	-8.272
2200	9.614	70.823	62.269	168.680	69.240	-7.528
2300	9.635	71.240	62.600	168.300	63.280	-6.830
2400	9.655	71.620	62.880	167.910	57.010	-6.170
2500	9.674	72.055	63.159	167.510	50.440	-5.561
2600	9.692	72.435	63.397	167.100	43.570	-4.991
2700	9.708	72.801	63.623	166.680	36.300	-4.451
2800	9.723	73.140	63.840	166.250	28.630	-3.941
2900	9.737	73.450	64.040	165.810	20.560	-3.451
3000	9.749	73.726	64.210	165.360	12.090	-2.981
3100	9.761	74.146	65.332	164.510	42.997	-3.031
3200	9.771	74.456	65.612	164.228	39.406	-2.691
3300	9.781	74.740	65.855	163.948	35.919	-2.372
3400	9.791	75.000	66.060	163.660	32.530	-2.071
3500	9.799	75.333	66.408	163.380	28.675	-1.791
3600	9.806	75.609	66.660	163.135	27.375	-1.662
3700	9.813	75.878	66.906	162.890	26.439	-1.562
3800	9.820	76.130	67.130	162.640	25.740	-1.476
3900	9.826	76.360	67.330	162.390	25.240	-1.396
4000	9.831	76.544	67.508	162.150	24.840	-1.323
4100	9.837	76.687	67.631	161.910	24.540	-1.256
4200	9.841	76.784	67.712	161.660	24.240	-1.194
4300	9.846	76.835	67.755	161.410	23.940	-1.136
4400	9.850	76.880	67.790	161.160	23.640	-1.084
4500	9.853	77.003	68.077	160.910	23.340	-1.029
4600	9.857	78.020	68.878	160.660	22.744	-1.212
4700	9.860	78.232	69.075	160.410	22.444	-1.136
4800	9.863	78.400	69.240	160.160	22.144	-1.064
4900	9.866	78.530	69.390	159.910	21.844	-1.004
5000	9.868	78.642	69.543	159.660	21.544	-0.943
5100	9.870	78.738	69.685	159.410	21.244	-0.886
5200	9.872	78.829	70.004	159.160	20.944	-0.833
5300	9.874	78.910	70.150	158.910	20.644	-0.783
5400	9.876	79.000	70.290	158.660	20.344	-0.733
5500	9.877	79.080	70.420	158.410	20.044	-0.683
5600	9.878	79.160	70.550	158.160	19.744	-0.633
5700	9.880	79.240	70.680	157.910	19.444	-0.583
5800	9.882	79.320	70.810	157.660	19.144	-0.533
5900	9.884	79.400	70.940	157.410	18.844	-0.483
6000	9.885	79.480	71.070	157.160	18.544	-0.433

Mar. 31, 1967

SILICON CARBIDE (SiC)

(IDEAL GAS)

GFW = 40.09715

Ground State Configuration [1²Σ]ΔHf°₀ = 170.8 ± 8 kcal/molS°_{298.15} = [50.9] gibbs/molΔHf°_{298.15} = 172 ± 8 kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i	E _i , cm ⁻¹	g _i
0	[1]	[8000]	[2]
[1000]	[6]	[14000]	[2]
[5000]	[3]	[18000]	[1]

ω_eX_e = [5] cm⁻¹ω_e = [1226] cm⁻¹B_e = [0.6933] cm⁻¹r_e = [1.7] Å

Heat of Formation.

Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibrium over the systems SiC-graphite and boron-silicon-graphite¹. Third law analysis of the partial pressures of Si and SiC yields the results summarized below. The adopted value, ΔHf°₂₉₈ = 172 ± 8, is the mean of the two results and the uncertainty reflects the possible effect of an error of up to 4 eu in the functions. The corresponding dissociation energy is D°₀ = 106.5 ± 8 kcal/mol.

Source	Method	Range, T°K	No. of Points	ΔHf° ₂₉₈ (kcal/mol)*	Drift (eu)	ΔHf° ₂₉₈ (kcal/mol)
Drowart (1959)	Mass Spec.	2181-2316	3	27.144	65.94	173.6
Verhaegen (1964)	"	2249-2344	3	48.744	82.67	170.4

*For the reaction C(graphite) + Si(g) = SiC(g)

Heat Capacity and Entropy.

The ground state is assumed to be ¹Σ_g, as suggested by Weltner and McLeod³. By analogy with C₂, there should be a low-lying ³Π excited state; this would dominate the thermodynamic functions at temperatures above 2000°K if the level lies below 5000 cm⁻¹. The ³Π level is assumed to lie at 1000 cm⁻¹, intermediate between the value⁴ observed for C₂ and that estimated for Si₂ (see JANAF table). Additional excited states, ³Σ_g, ¹Π, ¹Δ, and ¹Σ_g, are estimated by comparison with those observed or predicted⁴ for C₂. The estimates for the electronic levels are relatively uncertain and probably yield an upper limit for the entropy at temperatures where SiC(g) is significant. A probable lower limit for the electronic contribution may be obtained by increasing the ³Π level to 7000 cm⁻¹ and omitting the other excited states. This would reduce the entropy by 3.5 and 2.0 eu at 2000 and 4000°K.

The vibrational frequency is that estimated by Weltner³ from a valence bond calculation using k = 7.44 x 10⁵ dyn/cm obtained from C₂Si. The constants ω_eX_e, ω_e and r_e are estimated by interpolation between those^{6,4} for the ³Π_u states of Si₂ and C₂. Use of constants based on the ³Π_g state is consistent with the assumption that this state dominates the electronic partition function at high temperatures. B_e is calculated from r_e.

References.

1. J. Drowart, G. DeMaria and M. G. Inghram, J. Chem. Phys. **29**, 1015 (1958).
2. G. Verhaegen, P. E. Stafford and J. Drowart, J. Chem. Phys. **40**, 1622 (1964).
3. W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. **31**, 235 (1964).
4. E. A. Ballik and D. A. Ramsay, Astrophys. J. **137**, 64 (1963).
5. P. F. Fougere and R. K. Nesbet, J. Chem. Phys. **44**, 285 (1966).
6. A. E. Douglas, Can. J. Phys. **33**, 801 (1955).

CSI

Disilicon Carbide (SiC₂)
(Ideal Gas) GFW = 68.18315

DISILICON CARBIDE (CSi₂)

(IDEAL GAS)

OPW = 68.1815

Point Group [D_{∞h}]
S_{298.15}° = [57.9] gibbs/mol
ΔH_{f,0}° = 127.1 ± 6 kcal/mol
ΔH_{f,298.15}° = 128 ± 6 kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	E _i
0	[1]
[12000]	[6]
[19000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
[670] (1)	
[275] (2)	
[1600] (1)	

Bond Distance: C-Si = [1.75] Å
Bond Angle: C-Si-Si = [180°]
Rotational Constant: B₀ = [0.0980] cm⁻¹
σ = [2]

Heat of Formation

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the SiC-graphite¹, SiC-silicon² and boron-carbon-silicon³ systems. Third law analysis of the partial pressures of CSi₂ and Si yields the concordant values 127.4, 127.9 and 128.6 kcal/mol. Two of the drifts are rather large, but they are opposite in sign so that no consistent entropy difference is apparent between the data and the tabulated functions. The drifts may be related to the low condensation coefficient for CSi₂ suggested by Drowart¹. Rates of free evaporation reported by Voronin⁴ yield apparent pressures which are lower by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of ΔH_{f,298}° = 128 ± 6 kcal/mol includes allowance for an error in the entropy of up to 3 eu.

Source	Method	Reaction	Range, °K	No. of Points	ΔH _{f,298} ° (kcal/mol)	Drift (eu)	ΔH _{f,298} ° (kcal/mol)
Drowart (1958)	Mass Spec.	A	2149-2316	7	-104±7	-86.0	7.4±3.0
Drowart (1960)	"	B	1825-2160	7	141±3	134.4	-3.4±1.7
Verhaegen (1964)	"	A	2083-2344	6	-68±25	-86.8	-9±12
A) C(graph) + 2 Si(g) = CSi ₂ (g) B) SiC(α) + Si(l) = CSi ₂ (g)							

Heat Capacity and Entropy

Weitner and McLeod⁵ observed a band system in absorption at 5300 Å in matrix isolation and assigned this tentatively to the transition ¹Π_u - X¹Σ⁺ of CSi₂. This assignment is adopted, although the evidence is not at all conclusive. A ³Π_u excited state is assumed to lie at 12000 cm⁻¹, presumably arising from the same molecular orbital configuration as the ¹Π_u state. A linear, symmetric structure is assumed, as suggested by Weitner. The bond distance is estimated by comparison with Si₂, C₂ and C₃. Vibrational frequencies are estimated from a valence bond calculation using κ₁ = 7.46 x 10⁵ and κ₂/κ₁² = 0.11 x 10⁵ dyne/cm. The stretching force constant is taken from C₂Si₂, while the bending force constant is from C₂Si and the ¹Π_u excited state of C₃. The moment of inertia is 28.56 x 10⁻³⁹ g cm².

References

1. J. Drowart, G. DeMaris and M. G. Ingraham, J. Chem. Phys. **22**, 1015 (1958).
2. J. Drowart and G. DeMaris, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, New York, 1960.
3. O. Vorhaegen, P. E. Stafford and J. Drowart, J. Chem. Phys. **40**, 1622 (1964).
4. N. I. Voronin, N. L. Mukarova and B. F. Yudin, Insulated. v Otd. Khim. Silikatov 1 Oklasov, Akad. Nauk SSSR, Sb. Statist. 1965, 203-8.
5. W. Weitner, Jr., and D. McLeod, Jr., J. Chem. Phys. **41**, 235 (1964); **45**, 3096 (1966).

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K ^e
0	0.000	INFINITE	INFINITE	-	127.068	127.068	INFINITE
100	8.204	47.977	87.846	-2.722	127.068	127.068	2.000
200	11.334	57.681	107.881	-1.065	127.068	127.068	2.000
298	11.334	57.681	107.881	-1.065	128.000	113.430	63.440
300	11.351	57.951	107.881	-1.021	127.999	113.742	62.861
400	12.082	61.322	109.000	-1.195	127.913	109.000	59.555
500	12.830	64.080	109.217	-2.431	127.742	104.291	45.586
600	13.057	66.422	109.227	-3.717	127.514	99.420	36.287
700	13.391	68.461	109.227	-5.040	127.242	94.993	29.658
800	13.652	70.267	109.227	-6.392	126.935	90.406	24.698
900	13.857	71.887	109.227	-7.764	126.600	85.861	20.850
1000	14.019	73.356	109.227	-9.162	126.240	81.359	17.780
1100	14.149	74.698	109.227	-10.571	125.856	76.882	15.275
1200	14.254	75.934	109.227	-11.991	125.450	72.448	13.194
1300	14.341	77.078	109.227	-13.421	125.021	68.047	11.440
1400	14.416	78.144	109.227	-14.859	124.573	63.683	9.941
1500	14.482	79.141	109.227	-16.304	124.104	59.351	8.647
1600	14.543	80.077	109.227	-17.755	123.615	55.049	7.519
1700	14.604	80.961	109.227	-19.213	123.109	50.789	6.555
1800	14.666	81.797	109.227	-20.676	122.587	46.572	5.699
1900	14.733	82.592	109.227	-22.146	122.046	42.406	4.949
2000	14.806	83.349	109.227	-23.623	121.487	38.289	4.299
2100	14.887	84.076	109.227	-25.107	120.908	34.222	3.749
2200	14.978	84.768	109.227	-26.601	120.309	30.205	3.289
2300	15.078	85.436	109.227	-28.103	119.690	26.238	2.909
2400	15.186	86.080	109.227	-29.614	119.051	22.321	2.599
2500	15.307	86.703	109.227	-31.141	118.384	18.454	2.349
2600	15.436	87.306	109.227	-32.678	117.699	14.637	2.149
2700	15.578	87.891	109.227	-34.229	116.996	10.869	1.999
2800	15.719	88.460	109.227	-35.793	116.276	7.152	1.899
2900	15.869	89.014	109.227	-37.373	115.542	3.485	1.839
3000	16.025	89.555	109.227	-38.967	114.793	-0.228	1.819
3100	16.184	90.083	109.227	-40.578	114.029	-3.965	1.839
3200	16.348	90.599	109.227	-42.204	113.251	-7.702	1.889
3300	16.507	91.104	109.227	-43.847	112.460	-11.439	1.959
3400	16.667	91.600	109.227	-45.506	111.656	-15.176	2.039
3500	16.825	92.085	109.227	-47.180	110.838	-18.912	2.119
3600	16.980	92.561	109.227	-48.870	110.005	-22.649	2.199
3700	17.130	93.028	109.227	-50.576	109.158	-26.386	2.279
3800	17.274	93.487	109.227	-52.296	108.296	-30.123	2.359
3900	17.411	93.938	109.227	-54.031	107.420	-33.860	2.439
4000	17.541	94.380	109.227	-55.778	106.529	-37.597	2.519
4100	17.663	94.815	109.227	-57.538	105.624	-41.334	2.599
4200	17.776	95.242	109.227	-59.311	104.704	-45.071	2.679
4300	17.880	95.661	109.227	-61.093	103.769	-48.808	2.759
4400	17.975	96.073	109.227	-62.886	102.819	-52.545	2.839
4500	18.061	96.478	109.227	-64.688	101.854	-56.282	2.919
4600	18.137	96.876	109.227	-66.498	100.874	-60.019	2.999
4700	18.204	97.267	109.227	-68.315	99.879	-63.756	3.079
4800	18.263	97.651	109.227	-70.139	98.869	-67.493	3.159
4900	18.312	98.028	109.227	-71.967	97.844	-71.230	3.239
5000	18.352	98.398	109.227	-73.801	96.804	-74.967	3.319
5100	18.385	98.742	109.227	-75.638	95.749	-78.704	3.399
5200	18.409	99.119	109.227	-77.477	94.679	-82.441	3.479
5300	18.426	99.470	109.227	-79.319	93.594	-86.178	3.559
5400	18.436	99.815	109.227	-81.162	92.494	-89.915	3.639
5500	18.440	100.153	109.227	-83.006	91.379	-93.652	3.719
5600	18.437	100.485	109.227	-84.850	90.249	-97.389	3.799
5700	18.429	100.812	109.227	-86.694	89.104	-101.126	3.879
5800	18.415	101.132	109.227	-88.536	87.944	-104.863	3.959
5900	18.397	101.447	109.227	-90.377	86.769	-108.599	4.039
6000	18.374	101.756	109.227	-92.215	85.584	-112.336	4.119

Mar. 31, 1967

GFW = 59.91115

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^b	ΔG ^c	Log K ^p
0	∞	∞	∞	∞	∞	∞	∞
100	3.577	3.054	1.101	-43.697	-43.697	-43.697	19.410
200	3.577	3.054	1.461	-43.697	-43.697	-43.697	18.609
298	8.680	5.791	1.461	-43.697	-43.697	-43.697	18.609
300	8.680	5.791	1.461	-43.697	-43.697	-43.697	18.609
400	8.680	5.791	1.461	-43.697	-43.697	-43.697	18.609
500	8.680	5.791	1.461	-43.697	-43.697	-43.697	18.609
600	11.358	12.727	3.053	-43.697	-43.697	-43.697	15.413
700	11.719	14.509	4.209	-43.697	-43.697	-43.697	13.133
800	11.927	16.067	5.348	-43.697	-43.697	-43.697	11.424
900	12.087	17.502	6.592	-43.697	-43.697	-43.697	10.005
1000	12.232	18.763	8.074	-43.697	-43.697	-43.697	8.653
1100	12.379	19.955	9.839	-43.697	-43.697	-43.697	7.424
1200	12.535	21.039	12.069	-43.697	-43.697	-43.697	6.284
1300	12.702	22.049	14.817	-43.697	-43.697	-43.697	5.176
1400	12.881	22.997	18.084	-43.697	-43.697	-43.697	4.128
1500	13.071	23.892	21.877	-43.697	-43.697	-43.697	3.187
1600	13.272	24.742	26.223	-43.697	-43.697	-43.697	2.348
1700	13.481	25.553	31.167	-43.697	-43.697	-43.697	1.613
1800	13.699	26.329	36.834	-43.697	-43.697	-43.697	1.000
1900	13.923	27.076	43.305	-43.697	-43.697	-43.697	0.546
2000	14.154	27.796	50.621	-43.697	-43.697	-43.697	0.216
2100	14.390	28.492	58.800	-43.697	-43.697	-43.697	0.000
2200	14.631	29.167	67.843	-43.697	-43.697	-43.697	-0.216
2300	14.876	29.823	77.775	-43.697	-43.697	-43.697	-0.440
2400	15.125	30.461	88.611	-43.697	-43.697	-43.697	-0.672
2500	15.377	31.084	100.364	-43.697	-43.697	-43.697	-0.912
2600	15.631	31.692	113.051	-43.697	-43.697	-43.697	-1.159
2700	15.889	32.287	126.689	-43.697	-43.697	-43.697	-1.414
2800	16.148	32.869	141.293	-43.697	-43.697	-43.697	-1.676
2900	16.410	33.440	156.877	-43.697	-43.697	-43.697	-1.944
3000	16.673	34.001	173.461	-43.697	-43.697	-43.697	-2.216
3100	16.938	34.552	191.064	-43.697	-43.697	-43.697	-2.492
3200	17.204	35.094	209.704	-43.697	-43.697	-43.697	-2.772
3300	17.472	35.628	229.397	-43.697	-43.697	-43.697	-3.056
3400	17.740	36.153	250.153	-43.697	-43.697	-43.697	-3.344
3500	18.010	36.671	271.980	-43.697	-43.697	-43.697	-3.636
3600	18.280	37.182	294.894	-43.697	-43.697	-43.697	-3.932
3700	18.552	37.687	318.904	-43.697	-43.697	-43.697	-4.232
3800	18.824	38.185	344.024	-43.697	-43.697	-43.697	-4.536
3900	19.097	38.678	370.264	-43.697	-43.697	-43.697	-4.844
4000	19.371	39.165	397.634	-43.697	-43.697	-43.697	-5.156

TITANIUM CARBIDE (TiC)

(CRYSTAL)

GFW = 59.91115

ΔH_f²⁹⁸ = -43.7 ± 1 kcal/mol

ΔH_f^{298,15} = -44.0 ± 1 kcal/mol

ΔH_m²⁹⁸ = [17] kcal/mol

S_{298,15} = 5.79 ± 0.05 gibbs/mol

T_m = 3290 ± 15°K

Heat of Formation

The adopted ΔH_f²⁹⁸ is derived from ΔH_f²⁹⁸ = -275.72 kcal/mol for reaction (a) determined by Humphrey (1) who burned TiC(c) in an oxygen bomb calorimeter. The author reported that the combustion product TiO₂ was >95 per cent rutile and <5 per cent anatase, the heat of formation is calculated assuming the above distribution. The uncertainty adopted is due mainly to the uncertainty in TiO₂(rutile).

Using atomic absorption spectroscopy Vidale (2) determined that the pressure (log P_{Ti} = -7.269) of Ti(g) at 1866°K was equal to the pressure of TiC(c) at 2220°K. Using this data for reaction (b) we obtain a ΔH_f²⁹⁸ = -43.02 kcal/mol. Lowell and Williams (3) measured the ΔH_f²⁹⁸ = -43.3 ± 4 kcal/mol of TiC(c) directly using a high temperature calorimeter, which reduces to ΔH_f²⁹⁸ = -37.7 ± 4 kcal/mol.

Fujishiro and Gokcen (4) determined the equilibrium pressure of Ti(g) in reaction (d) in the temperature range 2383-2593°K. Third law analysis of the data yields a ΔH_f²⁹⁸ = -31.6 kcal/mol. Brantley and Beckman (5) measured equilibrium pressures of CO for reaction (e) in the temperature range 1276 - 1428°K. Third law analysis of the data yields a ΔH_f²⁹⁸ = -61.9 kcal/mol.

Heat Capacity and Entropy

Low temperature heat capacities (55 - 295°K) have been taken from Kelley (6). Naylor (7) measured heat contents from 360 to 1738°K and Levison (8) from 1274 to 2799°K. High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 2799°K the heat capacity is graphically extrapolated. The entropy is based on S₂₉₈ - S₀ = 0.065 eu.

Melting Data

See liquid table.

Reference	Method	Reaction	T°K	ΔH _f ²⁹⁸ kcal/mol	ΔH _f ²⁹⁸ kcal/mol
1	Calorimetry	(a) TiC(c) + 70 ₂ (g) + CO ₂ (g) + TiO ₂ (rutile)	298	-275.72	-44.00
2	Equilibrium	(b) TiC(c) + Ti(c) + C(c)		156.02	-43.02
3	Calorimetry	(c) TiC(c) + C(c) + TiC(c)		-37.74	-37.7
4	Equilibrium	(d) TiC(c) + C(graph) + Ti(g)	2383-2593	169.5±10.3	-10.0±4.1
5	Equilibrium	(e) TiO ₂ (rutile) + 3C(graph) + TiC(c) + 2CO(g)	1276-1428	48.07±1.83	-61.90

References

- G. L. Humphrey, J. Am. Chem. Soc. **73**, 2261 (1951).
- G. L. Vidale, General Electric Co., R61SD147, Contract AF 33(616)-5841, August, 1961.
- C. E. Lowell and W. S. Williams, Rev. Sci. Instr. **32**, 1120-1123 (1961).
- S. Fujishiro and N. A. Gokcen, J. Phys. Chem. **65**, 161 (1961).
- L. R. Brantley and A. O. Beckman, J. Am. Chem. Soc. **52**, 3956 (1930).
- K. K. Kelley, Ind. Eng. Chem. **36**, 865 (1944).
- B. F. Naylor, J. Am. Chem. Soc. **68**, 370 (1946).
- L. S. Levinson, J. Chem. Phys. **42**, 2891 (1965).

(Liquid) $\Delta H_f^\circ = 59.91115$

T, K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{\text{gibbs/mol}}{-(G^\circ - H_{\text{fus}}^\circ)/T}$	$H^\circ - H_{\text{fus}}^\circ$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
100							
200	8.060	11.329	11.329	.000	- 25.892	- 26.681	19.557
298							
300	8.111	11.379	11.379	.015	- 25.892	- 26.686	19.640
400	8.144	11.444	11.444	.045	- 25.890	- 26.953	19.726
500	10.745	12.240	12.358	1.941	- 25.795	- 27.234	11.604
600	11.388	18.265	13.177	3.053	- 25.727	- 27.529	10.027
700	11.719	20.047	14.034	4.209	- 25.682	- 27.833	8.590
800	11.827	21.060	15.066	5.166	- 25.650	- 28.146	7.362
900	11.877	21.615	15.619	6.592	- 25.621	- 28.469	6.309
1000	12.232	24.321	16.512	7.608	- 25.745	- 28.754	6.284
1100	12.379	25.493	17.276	9.039	- 25.826	- 29.051	5.772
1200	12.535	26.577	18.007	10.284	- 26.869	- 29.301	5.336
1300	12.762	27.537	18.705	11.325	- 26.870	- 29.305	4.917
1400	12.941	28.401	19.374	12.104	- 26.870	- 29.305	4.567
1500	13.071	29.430	20.015	14.123	- 26.887	- 29.608	4.358
1600	13.272	30.280	20.630	15.440	- 26.903	- 30.109	4.113
1700	13.481	31.091	21.222	16.777	- 26.923	- 30.310	3.897
1800	13.699	31.867	21.792	18.136	- 26.948	- 30.705	3.709
1900	13.924	32.614	22.394	19.519	- 26.970	- 31.100	3.542
2000	14.154	33.338	22.873	20.921	- 31.455	- 30.787	3.360
2100	14.390	34.030	23.388	22.348	- 31.465	- 30.709	3.196
2200	15.000	34.705	23.887	23.799	- 31.455	- 30.676	3.047
2300	15.000	35.372	24.372	25.272	- 31.382	- 30.608	2.900
2400	15.000	36.038	24.841	26.764	- 31.282	- 30.528	2.767
2500	15.000	36.693	25.303	28.299	- 31.288	- 30.579	2.673
2600	15.000	37.211	25.750	29.799	- 31.237	- 30.553	2.568
2700	15.000	37.777	26.185	31.299	- 31.187	- 30.528	2.471
2800	15.000	38.323	26.609	32.799	- 31.188	- 30.528	2.381
2900	15.000	38.841	27.024	34.299	- 31.082	- 30.497	2.297
3000	15.000	39.358	27.426	35.799	- 31.087	- 30.460	2.219
3100	15.000	39.869	27.817	37.299	- 31.003	- 30.440	2.146
3200	15.000	40.326	28.201	38.799	- 30.961	- 30.425	2.078
3300	15.000	40.735	28.575	40.299	- 30.923	- 30.420	2.014
3400	15.000	41.101	28.941	41.799	- 30.885	- 30.454	1.954
3500	15.000	41.670	29.299	43.299	- 30.845	- 30.382	1.897
3600	15.000	42.092	29.648	44.799	- 132.435	- 30.106	1.858
3700	15.000	42.503	29.990	46.299	- 132.373	- 27.284	1.810
3800	15.000	42.903	30.325	47.799	- 132.365	- 24.462	1.765
3900	15.000	43.293	30.652	49.299	- 132.293	- 21.640	1.722
4000	15.000	43.673	30.973	50.799	- 132.273	- 18.784	1.674
4100	15.000	44.043	31.287	52.299	- 132.269	- 15.907	1.648
4200	15.000	44.405	31.595	53.799	- 132.279	- 13.068	1.680
4300	15.000	44.758	31.897	55.299	- 132.303	- 10.282	1.529
4400	15.000	45.102	32.193	56.799	- 132.338	- 7.554	1.380
4500	15.000	45.440	32.484	58.299	- 132.388	- 4.554	1.221

Dec. 31, 1960; Dec. 31, 1964; June 30, 1968

TITANIUM CARBIDE (TiC)

(LIQUID)

GFW = 59.91115

 $S_{298.15}^\circ = [11.329]$ gibbs/mol $\Delta H_f^\circ_{298.15} = [-25.892 \pm 1]$ kcal/mol $\Delta H_m^\circ = [17]$ kcal/mol $T_m = 3290 \pm 15^\circ\text{K}$

Heat of Formation

The heat of formation is obtained from $\Delta H_f^\circ_{298}(c)$ by adding ΔH_m° and the difference between H_{Ti}° and H_{TiC}° for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200°K the heat capacity is obtained from that of the crystal, above 2200°K it is assumed constant and estimated as 15 gibbs/mol or 7.5 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The adopted T_m is taken from the phase diagram of the system Ti-C, at the composition 50% Ti and 50% C, reported by E. Rudy and D. P. Harmon, Aerojet-General Corporation, BSN No. 84-6899-735001, Contract AF-33(611), April 1, 1966. Earlier reports by E. Friederich and L. Sittig, Z. Anorg. Chem. 144, 171(1925) and C. Agte and K. Moers, Z. Anorg. Chem. 193, 233 (1931), gave a T_m of $3430 \pm 100^\circ\text{K}$ and $3410 \pm 90^\circ\text{K}$, respectively. ΔH_m° is derived from an estimated $\Delta S_m = 2.5$ gibbs/g-atom, as suggested by O. Kubaschewski, E. L. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1967.

CTI

Zirconium Carbide (ZrC)

(Crystal) Mol. Wt. = 103.231

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	3.055	1.394	14.394	1.394	-46.832	-46.832	-46.832	INFINITE
200	6.661	4.773	8.728	0.791	-46.957	-46.957	-46.957	102.142
298	9.058	7.964	7.964	0.000	-47.000	-47.000	-46.104	50.777
300	9.089	8.020	7.964	0.017	-46.998	-46.998	-46.188	33.446
400	10.565	10.565	10.565	0.000	-46.896	-46.896	-45.703	15.096
500	11.265	11.257	9.088	2.088	-46.800	-46.800	-45.976	15.976
600	11.802	15.362	9.067	3.241	-46.727	-46.727	-45.492	16.570
700	12.181	17.215	10.867	4.443	-46.675	-46.675	-45.280	14.140
800	12.445	18.859	11.765	5.675	-46.640	-46.640	-45.094	12.319
900	12.625	20.346	12.625	6.719	-46.618	-46.618	-44.933	10.303
1000	12.760	21.674	13.475	8.148	-46.609	-46.609	-44.773	9.772
1100	12.961	22.899	14.277	9.495	-46.615	-46.615	-44.524	8.846
1200	13.045	24.031	15.043	10.785	-46.589	-46.589	-44.285	8.065
1300	13.129	25.078	15.775	12.094	-46.593	-46.593	-44.010	7.398
1400	13.209	26.047	16.475	13.321	-46.571	-46.571	-43.712	6.827
1500	13.297	26.960	17.144	14.473	-46.560	-46.560	-43.493	6.351
1600	13.381	27.829	17.785	15.571	-46.561	-46.561	-43.171	5.897
1700	13.465	28.643	18.400	16.613	-46.576	-46.576	-42.890	5.514
1800	13.549	29.415	18.991	17.604	-46.575	-46.575	-42.604	5.173
1900	13.633	30.150	19.559	18.553	-46.572	-46.572	-42.317	4.867
2000	13.717	30.851	20.106	19.460	-46.584	-46.584	-42.028	4.592
2100	13.801	31.523	20.634	20.324	-46.575	-46.575	-41.737	4.343
2200	13.885	32.167	21.144	21.154	-46.582	-46.582	-41.280	4.101
2300	13.969	32.786	21.637	21.943	-46.571	-46.571	-40.752	3.872
2400	14.053	33.382	22.114	22.694	-46.595	-46.595	-40.224	3.663
2500	14.137	33.957	22.576	23.424	-46.591	-46.591	-39.694	3.470
2600	14.221	34.514	23.024	24.128	-46.582	-46.582	-39.166	3.292
2700	14.305	35.052	23.460	24.808	-46.506	-46.506	-38.634	3.127
2800	14.389	35.574	23.883	25.473	-46.502	-46.502	-38.101	2.974
2900	14.473	36.090	24.295	26.126	-46.503	-46.503	-37.565	2.831
3000	14.557	36.572	24.696	26.767	-46.503	-46.503	-37.032	2.696
3100	14.641	37.051	25.087	27.397	-46.503	-46.503	-36.501	2.573
3200	14.725	37.517	25.468	28.015	-46.503	-46.503	-35.967	2.456
3300	14.809	37.971	25.840	28.624	-46.506	-46.506	-35.433	2.347
3400	14.893	38.415	26.204	29.224	-46.511	-46.511	-34.901	2.243
3500	14.977	38.848	26.559	29.811	-46.511	-46.511	-34.373	2.146
3600	15.061	39.271	26.906	30.384	-46.513	-46.513	-33.844	2.055
3700	15.145	39.684	27.246	30.943	-46.513	-46.513	-33.311	1.967
3800	15.229	40.089	27.572	31.489	-46.517	-46.517	-32.780	1.885
3900	15.313	40.486	27.894	32.024	-46.517	-46.517	-32.253	1.807
4000	15.397	40.875	28.222	32.549	-46.517	-46.517	-31.730	1.734
4100	15.481	41.256	28.537	33.064	-46.522	-46.522	-31.208	1.663
4200	15.565	41.630	28.844	33.570	-46.524	-46.524	-30.683	1.593
4300	15.649	41.997	29.146	34.067	-46.524	-46.524	-30.163	1.533
4400	15.733	42.358	29.442	34.556	-46.526	-46.526	-29.650	1.473
4500	15.817	42.713	29.733	35.040	-46.526	-46.526	-29.138	1.415
4600	15.901	43.061	30.019	35.519	-46.526	-46.526	-28.621	1.360
4700	15.985	43.404	30.300	35.994	-46.526	-46.526	-28.109	1.307
4800	16.069	43.741	30.577	36.467	-46.526	-46.526	-27.604	1.254
4900	16.153	44.074	30.854	36.937	-46.526	-46.526	-27.101	1.202
5000	16.237	44.401	31.117	37.404	-46.526	-46.526	-26.601	1.151

MOL. WT. = 103.231

(CRYSTAL)

ZIRCONIUM CARBIDE (ZrC)

$$\Delta H_f^0 = -46.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -47.0 \pm 3 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [19] \text{ kcal. mole}^{-1}$$

$$T_m = 3605 \pm 125^\circ \text{K}$$

$$S_{298.15}^0 = 7.964 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

Heat of Formation.

$\Delta H_f^{298.15} = -47.16 \pm 1.5 \text{ kcal. mole}^{-1}$ was calculated from the standard free energy of formation of $-38.9 \pm 1.5 \text{ kcal. mole}^{-1}$ at 2675°K . reported by B. D. Pollock, J. Phys. Chem. **65**, 731 (1961). Using spectrophotometric data reported by G. L. Vidale, Missile and Space Vehicle Department, General Electric R61SD147, August, 1961, we calculated $\Delta H_f^{298.15} = -46.9 \pm 1 \text{ kcal. mole}^{-1}$. These values were averaged with $\Delta H_f^{298.15} = 47.0 \pm 0.6 \text{ kcal. mole}^{-1}$ reported by A. D. Nab, U. S. Bureau of Mines R16518 (1964). The equilibria data reported by C. H. Prescott Jr., J. Am. Chem. Soc. **48**, 2534 (1926) and V. S. Kutsiev, B. P. Omont, and V. A. Epel'baum, Doklady Akad. Nauk SSSR **104**, 567 (1955) were considered but not used.

Heat Capacity and Entropy.

Heat content data over the range 470.8° to 1174.4°K . were taken from a preliminary report by R. Mezaki, T. P. Jambois, A. K. Gangopadhyay, and J. L. Margrave, Univ. of Wisconsin, Madison, Wisconsin, "Thermodynamic Properties of Inorganic Substances VIII. The High Temperature Heat Contents of Zirconium Carbide and Tantalum Carbide". These data were smoothed by means of the Shomate plot into low temperature data reported by E. F. Westrum Jr. and G. Peick, J. Chem. Eng. Data, **8**, 176 (1963). High temperature data reported by D. S. Neel, C. D. Pears, S. Ogleby Jr., Southern Research Institute, Birmingham, Alabama, Technical Documentary Report No. WADD 60-924, p. 134, February 1962, and R. A. McDonald, F. L. Oettinger, and H. Prophet, CPFA Publication No. 44(u), p. 213, February 1964 were then used to obtain the heat capacity above 1174°K .

Melting Data.

Melting points were measured by C. Agte and H. Alkethum, Z. tech. Physik **11**, 182 (1936) and E. Friederich and L. Sittig, Z. Anorg. Chem., **144**, 169 (1925). The value of $3605 \pm 125^\circ \text{K}$. by Agte and Alkethum was chosen. Friederich and Sittig obtained a measurement of 3300°K . but estimated 3500°K . because of the clouding formation of ZrO_2 . Wayne L. Norvell, J. Phys. Chem., **68**, 954 (1964) quoted a value of 3460°C taken from E. K. Storms, Los Alamos Scientific Lab Report LAMS-2674, (1962). The heat of melting is derived from an estimated $\Delta S_m = 2.5 \text{ cal. deg}^{-1} \text{ gm. atom}^{-1}$.

Zirconium Carbide (ZrC)

CZr

(Liquid) Mol. Wt. = 103.231

ZIRCONIUM CARBIDE (ZrC)

(LIQUID)

MOL. WT. = 103.231

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH°	ΔF°	Log K _P
0						
100						
200						
298	9.058	12.815	0.000	-28.366	-29.026	21.275
300	9.089	12.871	0.017	-28.384	-29.030	21.147
400	10.419	15.684	0.968	-28.284	-29.260	15.066
500	11.265	18.108	2.066	-28.186	-29.515	12.600
600	11.802	20.213	3.241	-28.113	-29.788	10.850
700	12.181	22.006	4.443	-28.061	-30.072	9.388
800	12.425	23.510	5.675	-28.026	-30.365	8.294
900	12.644	25.024	6.929	-28.004	-30.655	7.444
1000	12.760	26.524	8.108	-27.995	-30.950	6.764
1100	12.861	27.950	9.485	-28.001	-31.246	6.208
1200	13.045	28.882	10.955	-28.075	-31.542	5.735
1300	13.213	30.005	12.404	-28.090	-31.838	5.359
1400	13.313	30.905	13.811	-28.050	-32.102	5.022
1500	13.297	31.820	15.137	-29.036	-32.316	4.679
1600	13.381	32.680	16.071	-29.067	-32.519	4.414
1700	13.465	33.494	17.413	-29.102	-32.723	4.181
1800	13.549	34.261	18.764	-29.139	-32.927	3.973
1900	13.633	35.001	20.123	-29.179	-33.131	3.779
2000	13.717	35.702	21.490	-29.220	-33.336	3.619
2100	13.801	36.374	22.866	-29.261	-33.540	3.466
2200	13.885	37.018	24.240	-29.308	-33.744	3.312
2300	13.969	37.634	25.611	-29.357	-33.956	3.164
2400	14.053	38.223	26.963	-29.407	-34.160	3.021
2500	14.137	38.788	28.284	-29.458	-34.367	2.893
2600	14.221	39.329	29.584	-29.510	-34.570	2.788
2700	14.305	39.853	30.854	-29.563	-34.774	2.681
2800	14.389	40.361	32.094	-29.617	-34.978	2.582
2900	14.473	40.854	33.314	-29.672	-35.183	2.487
3000	14.557	41.334	34.514	-29.728	-35.387	2.404
3100	14.641	41.801	35.694	-29.785	-35.590	2.324
3200	14.725	42.251	36.854	-29.843	-35.793	2.249
3300	14.809	42.684	37.994	-29.902	-35.996	2.179
3400	14.893	43.101	39.114	-29.962	-36.199	2.113
3500	14.977	43.504	40.224	-30.023	-36.402	2.051
3600	15.061	43.894	41.314	-30.085	-36.605	1.992
3700	15.145	44.278	42.394	-30.148	-36.808	1.936
3800	15.229	44.659	43.464	-30.212	-37.012	1.884
3900	15.313	45.029	44.524	-30.277	-37.216	1.834
4000	15.400	45.389	45.574	-30.343	-37.420	1.787
4100	15.480	45.739	46.614	-30.410	-37.624	1.742
4200	15.560	46.079	47.644	-30.478	-37.828	1.699
4300	15.640	46.409	48.664	-30.547	-38.032	1.658
4400	15.720	46.729	49.674	-30.617	-38.236	1.618
4500	15.800	47.039	50.674	-30.688	-38.440	1.582
4600	15.880	47.339	51.664	-30.760	-38.644	1.547
4700	15.960	47.629	52.644	-30.833	-38.848	1.513
4800	16.040	47.909	53.614	-30.907	-39.052	1.481
4900	16.120	48.179	54.574	-30.982	-39.256	1.451
5000	16.200	48.439	55.524	-31.058	-39.460	1.410
5100	16.280	48.689	56.464	-31.135	-39.664	1.372
5200	16.360	48.929	57.394	-31.213	-39.868	1.336
5300	16.440	49.159	58.314	-31.292	-40.072	1.301
5400	16.520	49.379	59.224	-31.372	-40.276	1.267
5500	16.600	49.589	60.124	-31.453	-40.480	1.234
5600	16.680	49.789	61.014	-31.535	-40.684	1.202
5700	16.760	49.979	61.894	-31.618	-40.888	1.171
5800	16.840	50.159	62.764	-31.702	-41.092	1.141
5900	16.920	50.329	63.624	-31.787	-41.296	1.111
6000	17.000	50.489	64.474	-31.873	-41.500	1.081

Mar. 31, 1962; June 30, 1964; Dec. 31, 1964

CZr

CARBON, DIATOMIC (C₂)

(IDEAL GAS)

GFW = 24.0223

$$\Delta H_f^\circ = 198.2 \pm 0.9 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 200.2 \pm 0.9 \text{ kcal/mol}$$

Symmetry number = 2

$$S_{298.15}^\circ = 47.827 \pm 0.01 \text{ gibbs/mol}$$

Carbon, Diatomic (C₂)
(Ideal Gas)

$$GFW = 24.0223$$

T, °K	C _p ^o	S ^o - (C _p ^o - H _{298.15} ^o)/T	H _{298.15} ^o - H _T ^o	ΔH _f ^o	Log K _p
0	0.000	INFINITE	2.528	198.200	INFINITE
100	7.114	37.918	1.832	198.868	426.429
200	9.669	43.548	1.005	199.539	208.844
298	10.312	47.627	0.000	200.224	136.953
300	10.301	47.690	0.019	200.235	136.040
400	9.476	50.544	48.022	200.733	99.536
500	8.877	52.587	48.740	201.010	77.565
600	8.604	54.178	49.519	201.125	62.936
700	8.509	55.314	50.251	201.133	52.422
800	8.593	56.128	50.941	201.125	44.520
900	8.743	57.636	51.687	200.941	38.520
1000	8.955	59.338	52.328	200.786	33.443
1100	9.230	61.149	52.931	200.603	29.455
1200	9.571	63.068	53.509	200.397	26.226
1300	9.981	65.095	54.061	200.166	23.516
1400	10.455	67.232	54.583	199.916	21.127
1500	10.989	69.476	55.025	199.707	19.046
1600	11.577	71.823	55.485	199.482	17.230
1700	12.214	74.272	55.923	199.217	15.526
1800	12.894	76.818	56.338	198.952	13.916
1900	13.611	79.455	56.724	198.720	12.396
2000	14.360	82.176	57.082	198.472	11.793
2100	15.144	84.984	57.401	198.227	10.762
2200	15.957	87.874	57.689	197.980	9.824
2300	16.794	90.842	57.937	197.744	8.987
2400	17.650	93.884	58.150	197.484	8.187
2500	18.520	96.994	58.337	197.255	7.468
2600	19.400	100.164	58.491	197.015	6.805
2700	20.284	103.394	58.614	196.778	6.192
2800	21.176	106.674	58.709	196.550	5.624
2900	22.076	110.004	58.776	196.340	5.095
3000	22.984	113.374	58.814	196.140	4.602
3100	23.896	116.784	58.824	195.948	4.142
3200	24.812	120.234	58.814	195.764	3.711
3300	25.732	123.724	58.776	195.584	3.316
3400	26.656	127.244	58.709	195.404	2.956
3500	27.584	130.794	58.614	195.224	2.567
3600	28.516	134.374	58.491	195.044	2.229
3700	29.452	137.984	58.337	194.864	1.910
3800	30.392	141.624	58.150	194.684	1.606
3900	31.336	145.294	57.937	194.504	1.316
4000	32.284	148.994	57.689	194.324	1.050
4100	33.236	152.724	57.401	194.144	0.792
4200	34.192	156.484	57.082	193.964	0.546
4300	35.152	160.274	56.724	193.784	0.316
4400	36.116	164.094	56.337	193.604	0.096
4500	37.084	167.944	55.923	193.424	0.000
4600	38.056	171.824	55.485	193.244	0.000
4700	39.032	175.734	55.025	193.064	0.000
4800	40.012	179.674	54.583	192.884	0.000
4900	41.000	183.644	54.150	192.704	0.000
5000	42.000	187.644	53.709	192.524	0.000
5100	43.000	191.674	53.251	192.344	0.000
5200	44.000	195.734	52.776	192.164	0.000
5300	45.000	199.824	52.276	191.984	0.000
5400	46.000	203.944	51.751	191.804	0.000
5500	47.000	208.094	51.194	191.624	0.000
5600	48.000	212.274	50.614	191.444	0.000
5700	49.000	216.484	50.000	191.264	0.000
5800	50.000	220.724	49.351	191.084	0.000
5900	51.000	225.000	48.676	190.904	0.000
6000	52.000	229.314	47.976	190.724	0.000

Sept. 30, 1961; Dec. 31, 1959

Electronic Levels and Molecular Constants

State	ϵ_i , cm ⁻¹	g_i	r_e , Å	B_e , cm ⁻¹	α_e , cm ⁻¹	ω_e , cm ⁻¹
x^1_g	0	1	1.2425	1.81984	0.01765	1854.71
$x^3\pi_u$	610	6	1.3119	1.65246	0.01661	1641.35
A^3_2	6243.5	3	1.3693	1.49852	0.01634	1470.45
b^1_u	8268.33	2	1.3184	1.61634	0.01686	1608.35
A^3_2	13365	3	1.23	1.87	0.018	1961.6
1_0	[15000]	2	[1.39]	[1.454]	[0.015]	[1510]
1_0	[18570]	1	[1.38]	[1.475]	[0.013]	[1510]
1_0	19916	6	1.266	1.7527	0.01608	1788.2
$5\pi_g$	[22260]	10	[1.46]	[1.324]	[0.012]	[1400]
$5\pi_g$	[30320]	5	[1.35]	[1.557]	[0.015]	[1550]
1_0	34262	2	1.2552	1.7334	0.018	1809.1
3_0	[34530]	6	[1.51]	[1.23]	[0.013]	[1160]
3_0	[34760]	1	[1.90]	[0.778]	[0.005]	[1025]
3_0	[38020]	6	[1.53]	[1.20]	[0.011]	[1290]
3_0	40590	6	1.535	1.1922	0.0242	1106.56
3_0	[40780]	6	[1.51]	[1.23]	[0.011]	[1380]
3_0	[42370]	6	[1.49]	[1.265]	[0.012]	[1340]
1_0	[42860]	2	[1.51]	[1.232]	[0.011]	[1380]
d^1_0	43240	1	1.2378	1.8334	0.0204	1829.57
3_0	[43360]	3	[1.44]	[1.355]	[0.011]	[1660]

Heat of Formation

Messler and Kraus (1) have reported the dissociation energy as 49300 ± 300 cm⁻¹ from the variation of the rotational structure cut-off with vibrational level in the d^1_0 state. This state dissociates into $C^3P + C^3P$, due to an avoided crossing (2), these dissociation products are those of the ground state. The uncertainty in the determination is generous and thus we adopt $D_0 = 140.95 \pm 0.9$ kcal/mol, using $\Delta H_f^\circ(C, g) = 169.576$ kcal/mol (3).

Brewer et al. (4) have reviewed several other earlier determinations which confirm $\Delta H_f^\circ = 185 \pm 5$ kcal/mol. The extensive mass spectrometric data of Drowart et al. (5) yield a 3rd law $\Delta H_f^\circ = 199.2 \pm 1.4$ kcal/mol in excellent agreement with the adopted value.

Heat Capacity and Entropy

The observed molecular constants and electronic levels were taken from Ballik and Ramsay (2). The estimated parameters are from the correlation calculations of Fougere and Nesbet (E) and Clementi (Z), the electronic levels are T_0 values. Not all predicted states were included since the contribution of levels above 40000 cm⁻¹ is negligible. The functions were calculated from the partition function $Q = Q_e \sum_i g_i \exp(-\epsilon_i/T)$, the values for Q_e and Q_v were calculated with first order anharmonic corrections. The functions are similar to those reported by Altman (8) and Clementi (7) but include several additional states.

References

1. G. Messler and L. Kraus, Z. Naturforsch., **22a**, 2023 (1967), **22a** 1744 (1967) and **22a**, 2015 (1967).
2. E. A. Ballik and D. A. Ramsay, Astrophys. Journ., **137**, 84 (1963).
3. JANAF Table dated Mar. 31, 1961.
4. L. Brewer, W. T. Hicks, and O. H. Krikorian, J. Chem. Phys., **36**, 182 (1962).
5. J. Drowart, R. P. Burns, G. DeMaría and M. G. Inghram, J. Chem. Phys., **31**, 1131 (1959).
6. P. F. Fougere and R. K. Nesbet, J. Chem. Phys., **44**, 285 (1966).
7. E. Clementi, Astrophys. Journ., **133**, 303 (1961).
8. R. Altman, J. Chem. Phys., **32**, 615 (1960).

Dimeric Carbon Uninegative Ion (C₂⁻)

GFW = 24.02285

Ground State Configuration [2]

 $\Delta H_f^\circ = 106 \pm 20$ kcal/mol $S_{298.15}^\circ = 46.96 \pm 0.05$ gibbs/mol $\Delta H_f^{298.15} = 106 \pm 20$ kcal/mol

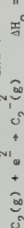
Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	$\frac{g_i}{2}$
0	[4]
18484	[2]

 $\omega_e = 1781.04$ cm⁻¹ $\sigma = 2$ $\omega_e x_e = 11.585$ cm⁻¹ $r_e = 1.2682$ Å $B_e = 1.74685$ cm⁻¹

Heat of Formation

The electron affinity of C₂ has been obtained by Honig (1) as 4 ± 0.8 eV from the difference in heats of sublimation of neutral C₂ and C₂⁻ and the work function of graphite. Thus, we have the reaction



Using $\Delta H_f^\circ(C_2, g) = 198.2$ kcal/mol (2), we obtain $\Delta H_f^\circ(C_2^-, g) = 106 \pm 20$ kcal/mol, which is adopted.

A value for the heat of formation may be obtained from a linear Birge-Sponer extrapolation of the ground state vibrational levels, which gives 185.8 kcal for the reaction



With auxiliary data (2) this yields $\Delta H_f^\circ(C_2^-, g) = 114.5$ kcal/mol, in good agreement with the adopted value.

Heat Capacity and Entropy

The molecular constants and electronic levels are from Herzberg and Lagerqvist (3). The values are not definitely ascribed to C₂⁻ by Herzberg and Lagerqvist, but there is a good deal of evidence to support this assignment. Recently Milligan and Jacox (4) have shown that matrix isolated bands previously attributed to C₂(g) are enhanced in the presence of a photoelectron source. The matrix spectra correspond to the gas system reported by Herzberg and Lagerqvist (3) and leave little doubt that the species is C₂⁻.

The estimated electronic level is assumed to be a ²Π state and is obtained from the isoelectronic CN(g) (2).

References

1. R. E. Honig, J. Chem. Phys. **22**, 126 (1954).
2. JANAF Thermochemical Tables, Dec. 31, 1969.
3. G. Herzberg and A. Lagerqvist, Can. J. Phys. **42**, 2363 (1968).
4. D. E. Milligan and M. E. Jacox, J. Chem. Phys. **51**, 1952 (1969).

T, °K	C _p ^o	S ^o - (C ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	6.989	46.961	.000	106.000	94.296	-69.121
300	6.990	47.004	46.961	105.994	94.224	-68.942
400	7.105	49.029	47.234	105.711	90.339	-68.359
500	7.292	50.633	47.761	105.295	86.541	-67.927
600	7.506	51.982	48.355	104.762	82.836	-67.530
700	7.747	53.197	49.009	104.153	79.236	-67.173
800	7.997	54.319	49.649	103.563	75.702	-66.841
900	8.055	55.136	50.119	102.850	72.256	-66.526
1000	8.189	55.992	50.664	102.193	68.860	-66.226
1100	8.303	56.778	51.184	101.475	65.593	-65.932
1200	8.396	57.513	51.683	100.704	62.364	-65.642
1300	8.471	58.183	52.155	99.892	59.197	-65.356
1400	8.571	58.813	52.609	99.036	56.000	-65.076
1500	8.648	59.407	53.042	98.147	52.804	-64.797
1600	8.724	59.968	53.458	97.204	49.611	-64.513
1700	8.793	60.504	53.846	96.215	46.411	-64.226
1800	8.873	61.016	54.206	95.185	43.211	-63.936
1900	8.960	61.486	54.608	94.136	40.011	-63.642
2000	9.044	61.948	54.964	93.068	36.811	-63.346
2100	9.130	62.391	55.307	91.977	33.611	-63.046
2200	9.216	62.816	55.630	90.870	30.411	-62.742
2300	9.303	63.228	55.934	89.746	27.211	-62.436
2400	9.398	63.628	56.271	88.604	24.011	-62.126
2500	9.489	64.013	56.573	87.446	20.811	-61.816
2600	9.580	64.387	56.867	86.274	17.611	-61.506
2700	9.670	64.750	57.147	85.090	14.411	-61.196
2800	9.758	65.104	57.413	83.894	11.211	-60.886
2900	9.844	65.448	57.700	82.688	8.011	-60.576
3000	9.928	65.783	57.964	81.472	4.811	-60.266
3100	10.009	66.110	58.222	80.246	1.611	-59.956
3200	10.086	66.430	58.473	79.010	-1.589	-59.646
3300	10.160	66.740	58.713	77.764	-4.789	-59.336
3400	10.230	67.045	58.959	76.508	-7.989	-59.026
3500	10.296	67.342	59.195	75.242	-11.189	-58.716
3600	10.359	67.633	59.425	73.966	-14.389	-58.406
3700	10.417	67.918	59.651	72.680	-17.589	-58.096
3800	10.471	68.198	59.871	71.384	-20.789	-57.786
3900	10.523	68.469	60.089	70.078	-23.989	-57.476
4000	10.569	68.736	60.302	68.762	-27.189	-57.166
4100	10.612	68.997	60.511	67.436	-30.389	-56.856
4200	10.652	69.254	60.716	66.090	-33.589	-56.546
4300	10.689	69.506	60.916	64.734	-36.789	-56.236
4400	10.720	69.753	61.115	63.368	-39.989	-55.926
4500	10.749	69.992	61.310	61.992	-43.189	-55.616
4600	10.775	70.228	61.501	60.606	-46.389	-55.306
4700	10.799	70.460	61.689	59.210	-49.589	-54.996
4800	10.820	70.689	61.871	57.804	-52.789	-54.686
4900	10.837	70.916	62.056	56.388	-55.989	-54.376
5000	10.852	71.130	62.236	54.962	-59.189	-54.066
5100	10.865	71.345	62.412	53.526	-62.389	-53.756
5200	10.876	71.557	62.586	52.070	-65.589	-53.446
5300	10.887	71.767	62.756	50.604	-68.789	-53.136
5400	10.892	71.967	62.926	49.128	-71.989	-52.826
5500	10.898	72.167	63.092	47.642	-75.189	-52.516
5600	10.901	72.364	63.256	46.146	-78.389	-52.206
5700	10.903	72.557	63.418	44.640	-81.589	-51.896
5800	10.904	72.746	63.576	43.124	-84.789	-51.586
5900	10.904	72.936	63.736	41.598	-87.989	-51.276
6000	10.902	73.116	63.889	40.062	-91.189	-50.966

June 30, 1968; Dec. 31, 1969

Beryllium Carbide (BeC₂)

(Ideal Gas) Mol. Wt. = 33.035

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	0.000	INFINITE	-	133.535	133.535	INFINITE
100	7.292	42.926	1.436	133.535	133.535	-137.143
200	8.694	48.481	0.925	134.715	125.509	-137.143
298	9.867	52.232	0.000	135.000	120.917	-68.630
300	9.881	52.293	0.018	135.003	120.830	-68.630
400	10.323	57.231	1.054	135.095	116.087	-68.630
500	11.150	61.691	2.127	135.039	111.539	-68.630
600	11.696	65.733	3.269	134.883	106.611	-31.819
700	12.174	69.351	4.463	134.655	101.917	-31.819
800	12.580	72.526	5.698	134.381	97.260	-26.569
900	12.915	75.277	6.977	134.065	92.636	-22.494
1000	13.197	77.620	8.285	133.719	88.051	-19.245
1100	13.427	79.631	9.615	133.341	83.502	-16.589
1200	13.618	81.349	10.968	132.933	78.990	-14.385
1300	13.776	82.806	12.338	132.493	74.512	-12.526
1400	13.903	84.050	13.722	132.029	70.071	-10.938
1500	14.001	85.109	15.119	131.538	65.662	-9.567
1600	14.115	86.000	16.526	128.266	61.363	-8.381
1700	14.196	86.741	17.941	127.840	57.195	-7.353
1800	14.266	87.365	19.364	127.407	53.052	-6.441
1900	14.326	87.898	20.794	126.970	48.934	-5.628
2000	14.376	88.352	22.229	126.527	44.838	-4.899
2100	14.423	88.731	23.669	126.080	40.767	-4.242
2200	14.463	89.038	25.114	125.625	36.711	-3.647
2300	14.499	89.274	26.562	125.166	32.685	-3.106
2400	14.530	89.450	28.013	124.699	28.673	-2.611
2500	14.556	89.571	29.468	124.228	24.679	-2.157
2600	14.583	89.645	30.925	123.749	20.708	-1.741
2700	14.605	89.676	32.384	123.266	16.752	-1.356
2800	14.625	89.670	33.846	122.774	12.806	-1.007
2900	14.644	89.635	35.309	122.274	8.871	-0.687
3000	14.660	89.571	36.774	121.766	4.946	-0.391
3100	14.675	89.485	38.241	121.251	1.021	-0.124
3200	14.689	89.378	39.709	120.729	-2.904	0.124
3300	14.701	89.250	41.179	120.200	-4.827	0.384
3400	14.713	89.100	42.650	119.664	-6.750	0.644
3500	14.723	88.929	44.121	119.121	-8.673	0.894
3600	14.733	88.731	45.594	118.571	-10.596	1.144
3700	14.742	88.504	47.068	118.016	-12.519	1.394
3800	14.750	88.250	48.543	117.457	-14.442	1.644
3900	14.758	87.978	50.018	116.894	-16.365	1.894
4000	14.765	87.681	51.494	116.326	-18.288	2.144
4100	14.771	87.365	52.971	115.753	-20.211	2.394
4200	14.778	87.038	54.448	115.176	-22.134	2.644
4300	14.783	86.690	55.927	114.594	-24.057	2.894
4400	14.789	86.320	57.405	114.007	-25.980	3.144
4500	14.794	85.932	58.884	113.416	-27.903	3.394
4600	14.798	85.526	60.364	112.821	-29.826	3.644
4700	14.803	85.100	61.844	112.222	-31.749	3.894
4800	14.807	84.655	63.324	111.619	-33.672	4.144
4900	14.811	84.196	64.805	111.012	-35.595	4.394
5000	14.814	83.721	66.285	110.400	-37.518	4.644
5100	14.818	83.231	67.768	109.783	-39.441	4.894
5200	14.821	82.726	69.254	109.161	-41.364	5.144
5300	14.824	82.206	70.732	108.534	-43.287	5.394
5400	14.827	81.671	72.215	107.902	-45.210	5.644
5500	14.830	81.126	73.698	107.265	-47.133	5.894
5600	14.833	80.569	75.181	106.623	-49.056	6.144
5700	14.835	80.000	76.664	105.976	-50.979	6.394
5800	14.837	79.415	78.148	105.323	-52.902	6.644
5900	14.840	78.816	79.632	104.664	-54.825	6.894
6000	14.842	78.306	81.116	104.000	-56.748	7.144

Dec. 31, 1960; Sept. 30, 1962; June 30, 1963; Dec. 31, 1963

BERYLLIUM CARBIDE (BeC₂)

(IDEAL GAS)

MOL. WT. = 33.035

Point Group [C_{∞v}]
 $\Delta H_f^0 = [134] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [52.2] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{298.15} = [135] \text{ kcal. mole}^{-1}$
 Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	σ
[1580] (1)	[1580] (1)
[423] (1)	[423] (1)
[1947] (1)	[1947] (1)

Bond Distances: Be-C = [1.407] Å C-C = [1.12] Å

Bond Angle: Be-C-C = [180°]

Rotational Constant: B₀ = [0.4809] cm.⁻¹

Heat of Formation

$\Delta H_f^{298.15}$ was estimated as a lower positive limit by National Bureau of Standards Report No. 6645, "Preliminary Report on the Thermodynamic Properties of Light-Element Compounds," January, 1960.

Heat Capacity and Entropy

The vibrational frequencies, bond angle, configuration and moment of inertia, $5.82 \times 10^{-39} \text{ g. cm.}^2$, were estimated by Chupka, Berkowitz, Giese, and Inghram, J. Phys. Chem. 62, 611 (1958). Bond distances were calculated assuming the C-C bond distance was the same as in acetylene.

Tetrachloroethylene (C₂Cl₄)

GFW = 165.8343

(Ideal Gas)

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	+0.00	+0.00	INFINITE	-	-	-	INFINITE
100	13.584	92.201	94.858	-	2.837	2.837	5.000
200	18.161	121.151	124.151	-	2.837	2.837	5.000
298	22.836	150.000	150.000	-	2.837	2.837	5.000
300	22.867	150.000	150.000	-	2.837	2.837	5.000
400	25.194	182.194	182.194	-	2.837	2.837	5.000
500	26.764	204.918	204.918	-	2.837	2.837	5.000
600	27.905	221.506	221.506	-	2.837	2.837	5.000
700	28.712	234.272	234.272	-	2.837	2.837	5.000
800	29.304	244.146	244.146	-	2.837	2.837	5.000
900	29.749	251.625	251.625	-	2.837	2.837	5.000
1000	30.069	257.777	257.777	-	2.837	2.837	5.000
1100	30.353	262.658	262.658	-	2.837	2.837	5.000
1200	30.562	266.408	266.408	-	2.837	2.837	5.000
1300	30.730	269.176	269.176	-	2.837	2.837	5.000
1400	30.866	271.064	271.064	-	2.837	2.837	5.000
1500	30.979	272.177	272.177	-	2.837	2.837	5.000
1600	31.072	272.600	272.600	-	2.837	2.837	5.000
1700	31.151	272.448	272.448	-	2.837	2.837	5.000
1800	31.217	271.848	271.848	-	2.837	2.837	5.000
1900	31.274	270.838	270.838	-	2.837	2.837	5.000
2000	31.323	269.433	269.433	-	2.837	2.837	5.000
2100	31.365	267.673	267.673	-	2.837	2.837	5.000
2200	31.402	265.500	265.500	-	2.837	2.837	5.000
2300	31.435	262.959	262.959	-	2.837	2.837	5.000
2400	31.463	260.088	260.088	-	2.837	2.837	5.000
2500	31.489	256.843	256.843	-	2.837	2.837	5.000
2600	31.511	253.188	253.188	-	2.837	2.837	5.000
2700	31.532	249.094	249.094	-	2.837	2.837	5.000
2800	31.550	244.525	244.525	-	2.837	2.837	5.000
2900	31.566	239.458	239.458	-	2.837	2.837	5.000
3000	31.581	233.863	233.863	-	2.837	2.837	5.000
3100	31.594	227.808	227.808	-	2.837	2.837	5.000
3200	31.606	221.342	221.342	-	2.837	2.837	5.000
3300	31.617	214.524	214.524	-	2.837	2.837	5.000
3400	31.628	207.318	207.318	-	2.837	2.837	5.000
3500	31.637	199.775	199.775	-	2.837	2.837	5.000
3600	31.645	191.857	191.857	-	2.837	2.837	5.000
3700	31.653	183.524	183.524	-	2.837	2.837	5.000
3800	31.661	174.748	174.748	-	2.837	2.837	5.000
3900	31.668	165.491	165.491	-	2.837	2.837	5.000
4000	31.674	155.802	155.802	-	2.837	2.837	5.000
4100	31.680	145.648	145.648	-	2.837	2.837	5.000
4200	31.685	135.094	135.094	-	2.837	2.837	5.000
4300	31.691	124.122	124.122	-	2.837	2.837	5.000
4400	31.696	112.714	112.714	-	2.837	2.837	5.000
4500	31.700	100.850	100.850	-	2.837	2.837	5.000
4600	31.705	88.512	88.512	-	2.837	2.837	5.000
4700	31.709	75.665	75.665	-	2.837	2.837	5.000
4800	31.714	62.281	62.281	-	2.837	2.837	5.000
4900	31.718	48.435	48.435	-	2.837	2.837	5.000
5000	31.722	34.100	34.100	-	2.837	2.837	5.000
5100	31.726	19.250	19.250	-	2.837	2.837	5.000
5200	31.729	4.000	4.000	-	2.837	2.837	5.000
5300	31.733	-11.250	-11.250	-	2.837	2.837	5.000
5400	31.737	-22.500	-22.500	-	2.837	2.837	5.000
5500	31.741	-33.750	-33.750	-	2.837	2.837	5.000
5600	31.745	-45.000	-45.000	-	2.837	2.837	5.000
5700	31.749	-56.250	-56.250	-	2.837	2.837	5.000
5800	31.753	-67.500	-67.500	-	2.837	2.837	5.000
5900	31.757	-78.750	-78.750	-	2.837	2.837	5.000
6000	31.762	-90.000	-90.000	-	2.837	2.837	5.000

Sept. 30, 1967

C₂Cl₄

(IDEAL GAS)

GFW = 165.8343

Point Group D_{2h}

ΔHf° = -2.84 ± 0.7 kcal/mol

ΔHf° = -2.97 ± 0.7 kcal/mol

S°_{298.15} = 82.052 gibbs/mol

Electronic Levels and Quantum Weights

e _i , cm ⁻¹	g _i	e _i , cm ⁻¹	g _i
0	1	6357	1
[37700] [1]	70097 [1]		
[50350] [1]	72410 [1]		
[59000] [1]			

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	ω _i , cm ⁻¹	ω _i , cm ⁻¹
1571 (1)	1000 (1)	918 (1)
447 (1)	347 (1)	176 (1)
235 (1)	324 (1)	777 (1)
110 (1)	512 (1)	288 (1)

Bond Distances: C1 - C = 1.724 Å C - C = 1.327 Å
 Bond Angle: C1 - C - C1 = 113.3°
 Product of the Moments of Inertia: I_AI_BI_C = 3.43114 × 10⁻¹¹² g cm⁶ σ = 4

Heat of Formation

The heat of combustion (ΔE₂₉₈) of C₂Cl₄(g) has been determined by the "Quartz Wool" method by L. Smith, L. Bjellerup, S. Krook and H. Westermark, Acta Chem. Scand. Z, 65 (1953). The free chlorine produced from combustion was reduced to hydrogen chloride by a quartz spiral moistened with a solution of arsenious acid in the combustion bomb. Based on the reported results, the enthalpy change at 298°K for the reaction C₂Cl₄(g) + 2H₂O(g) = 2CO₂(g) + 4HCl(600H₂O) is evaluated as -198.40 kcal/mol, using recent auxiliary data from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965 and V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965, and Cp for C₂Cl₄(g) from V. Y. Kurbatov, J. Gen. Chem. USSR(Eng. Transl.) 16, 372 (1946). Employing ΔH₂₉₈ = -94.054, -39.823 and -68.315 kcal/mol for CO₂(g), HCl(600H₂O) and H₂O(g), respectively, we calculate the heat of formation for C₂Cl₄(g) as -12.367 kcal/mol. Incorporating this value with the value ΔH₂₉₈ = 9.4 kcal/mol obtained from E. Efring, Ph.D. Thesis, University of Lund, 1938, we derive ΔH₂₉₈ = -2.97±0.7 kcal/mol for C₂Cl₄(g).

Heat Capacity and Entropy

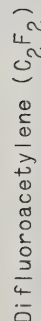
The molecular structure of C₂Cl₄(g) was investigated by the sector-visual method of electron diffraction by C. H. Ramachandra and R. L. Livingston, Current Sci. 27, 330 (1958). The reported bond distances and angle are in agreement with those measured by I. L. Karle and J. Karle, J. Chem. Phys. 20, 63 (1952), using the sector-microphotometer method, and W. N. Lipscomb, Ph.D. Thesis, California Institute of Technology, 1946. The molecular structure has also been determined by L. O. Brockway, J. Y. Beach and L. Pauling, J. Am. Chem. Soc. 57, 2693 (1935), H. de Laszlo, Nature 135, 474 (1935), and R. W. Dornte, J. Chem. Phys. 3, 566 (1933), by use of electron diffraction. The values reported by Ramachandra and Livingston, loc. cit., are adopted.

The vibrational spectra of tetrachloroethylene have been studied by numerous investigators. The vibrational frequencies assigned by D. E. Mann, M. Acquista and E. K. Plyler, J. Res. Natl. Bur. Std. 52, 67 (1954), are adopted here. These authors also reviewed the results of earlier investigations in detail.

The electronic levels and quantum weights are obtained from G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, 1966.

The three principal moments of inertia are: I_A = 4.88344 × 10⁻³⁸, I_B = 6.28884 × 10⁻³⁸ and I_C = 1.11723 × 10⁻³⁷ g cm².

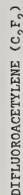
C₂Cl₄



(Ideal Gas) GFW = 62.0191

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.00	-0.00	INFINITE	-2.964	4.450	4.450	INFINITE
100	8.228	46.483	64.902	-2.242	4.649	4.112	-8.988
200	11.556	53.280	59.449	-1.242	4.793	3.534	-3.862
298	13.508	58.305	56.305	.000	5.000	2.971	-2.105
300	13.520	58.380	.025	5.003	2.958	2.958	-2.082
400	15.117	62.525	38.855	1.467	5.183	1.332	-1.582
500	16.242	66.025	59.951	3.037	5.308	1.332	-1.582
600	17.111	69.066	61.222	4.706	5.389	.528	-1.192
700	17.765	71.757	62.539	6.453	5.435	.089	-0.898
800	18.210	74.167	63.844	8.254	5.456	-1.104	-0.302
900	18.506	76.339	65.141	10.098	5.451	-2.787	1.400
1000	19.046	78.339	66.339	12.000	5.432	-	.709
1100	19.311	80.167	67.514	13.919	5.405	-4.351	-1.798
1200	19.523	81.857	68.639	15.861	5.366	-4.381	-1.206
1300	19.696	83.426	69.717	17.922	5.325	-5.196	-0.873
1400	19.838	84.881	70.742	19.999	5.284	-6.011	-0.992
1500	19.958	86.264	71.739	21.749	5.274	-	1.041
1600	20.058	87.556	72.697	23.790	5.220	-7.519	1.082
1700	20.143	88.774	73.598	25.800	5.164	-9.419	1.119
1800	20.215	89.928	74.473	27.814	5.102	-11.279	1.138
1900	20.276	91.015	75.326	29.843	5.035	-13.100	1.149
2000	20.339	92.063	76.127	31.873	4.972	-14.516	1.300
2100	20.379	93.057	76.910	33.909	4.904	-15.469	1.358
2200	20.420	94.006	77.656	35.949	4.829	-16.237	1.375
2300	20.456	94.915	78.396	37.993	4.754	-17.029	1.382
2400	20.486	95.786	79.103	40.040	4.680	-17.845	1.389
2500	20.516	96.623	79.747	42.090	4.590	-18.684	1.395
2600	20.542	97.428	80.450	44.143	4.502	-19.546	1.401
2700	20.564	98.204	81.093	46.194	4.412	-20.434	1.405
2800	20.585	98.952	81.718	48.256	4.321	-21.351	1.410
2900	20.603	99.665	82.325	50.334	4.229	-22.295	1.414
3000	20.620	100.373	82.915	52.434	4.125	-23.264	1.418
3100	20.635	101.050	83.489	54.539	4.017	-24.257	1.422
3200	20.649	101.705	84.048	56.653	3.904	-25.283	1.426
3300	20.662	102.341	84.593	58.769	3.795	-26.340	1.429
3400	20.673	102.958	85.124	60.885	3.685	-27.427	1.432
3500	20.684	103.557	85.642	62.974	3.557	-28.543	1.435
3600	20.694	104.140	86.148	64.772	3.432	-29.689	1.438
3700	20.703	104.707	86.642	66.862	3.302	-30.864	1.440
3800	20.711	105.259	87.124	69.133	3.169	-32.068	1.443
3900	20.718	105.798	87.586	71.400	3.035	-33.300	1.446
4000	20.726	106.322	88.058	73.057	2.898	-34.559	1.449
4100	20.732	106.834	88.510	75.120	2.739	-35.846	1.452
4200	20.738	107.334	88.952	77.203	2.566	-37.161	1.455
4300	20.744	107.822	89.385	79.277	2.429	-38.504	1.458
4400	20.749	108.299	89.810	81.352	2.285	-40.000	1.461
4500	20.755	108.765	90.220	83.427	2.097	-41.544	1.464
4600	20.759	109.221	90.634	85.503	1.924	-43.134	1.467
4700	20.764	109.668	91.034	87.579	1.746	-44.764	1.470
4800	20.768	110.105	91.427	89.655	1.561	-46.434	1.473
4900	20.772	110.533	91.812	91.733	1.372	-48.144	1.476
5000	20.775	110.953	92.191	93.810	1.175	-49.894	1.479
5100	20.779	111.364	92.563	95.887	.975	-51.684	1.482
5200	20.782	111.768	92.928	97.964	.770	-53.514	1.485
5300	20.785	112.164	93.287	100.040	.555	-55.384	1.488
5400	20.788	112.554	93.641	102.116	.339	-57.294	1.491
5500	20.791	112.938	93.989	104.232	.115	-59.244	1.494
5600	20.793	113.308	94.330	106.281	.115	-61.234	1.497
5700	20.796	113.676	94.666	108.360	.353	-63.264	1.500
5800	20.798	114.038	94.997	110.440	.595	-65.334	1.503
5900	20.800	114.396	95.323	112.520	.844	-67.444	1.506
6000	20.803	114.743	95.643	114.600	1.099	-69.594	1.509

Dec. 31, 1960; Dec. 31, 1966; Dec. 31, 1967



(IDEAL GAS)

GFW = 62.0191

Point Group [D_{∞h}]

ΔH_f⁰ = {4.65 ± 5} kcal/mol

S_{298.15} = {58.3 ± 1.5} gibbs/mol

ΔH_f⁰ = {4.65 ± 5} kcal/mol

Vibrational Frequencies and Degeneracies

$\frac{S}{\text{cm}^{-1}}$	$\frac{S}{\text{cm}^{-1}}$	$\frac{S}{\text{cm}^{-1}}$
[1050] (1)	[450] (2)	[300] (2)
[1900] (1)	[300] (2)	
1149 (1)		

Bond Distance: C-F = {1.28} Å

Bond Angle: F-C-F = {180°}

Rotational Constant: B₀ = {0.1179} cm⁻¹

C-C = {1.20} Å

σ = 2

Heat of Formation

M. Farber, M. A. Greenbaum, M. A. Frisch, H. C. Ko, G. Grenier and E. Graper, Rocket Power Inc., 3rd Quarterly Report, AFPL-TR-67-147, Contract F04611-67-C-0010, May 1967, have obtained equilibrium-weight-change data over the C-CF₄ system. Our reanalysis of these data assumes that the equilibrium constants for CF₄, CF₃ and CF₂ are those in the JANAF Tables, and that C₂F₂ was the only other C-F species present at equilibrium. This gives maximum possible concentrations of C₂F₂ and places a lower limit on the heat of formation. The ΔH_f⁰ (C₂F₂, g) values so obtained range from +10 kcal/mol from data at 2023°K to -10 kcal/mol from data at 2373°K; we adopt a weighted mean of +55 kcal/mol. This value still predicts complete dimerization of CF at 1 atmosphere pressure below about 2200°K, but only CF would exist under experimental conditions such as the study by Farber.

Farber et al. also investigated the mass spectrum of the vapor over the C-CF₄ system and did not detect any ion ascribable to C₂F₂. This is additional support for the value adopted.

The C-C bond dissociation energy in C₂F₂ is 113 kcal/mol, using the JANAF CF(g) table (Dec. 31st, 1967). This value is 115 kcal weaker than the bond dissociation energy of acetylene. In order to explain such a large decrease, a crossing of the repulsive approach of two ²H CF molecules with an attractive approach of two ²F CF molecules may be postulated. This follows the reasoning used by J. P. Simons, Nature 205, 1308 (1965), to explain the bond dissociation energy of C₂F₄.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that for C₂H₂(g). The C-F and C-C bond distances are estimated from those in HC = CF reported by J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661, 1956. The asymmetric stretching frequency, ν₃ = 1149 cm⁻¹, was observed by J. Heicklen and V. Knight, J. Phys. Chem. 69, 2484 (1965). The other vibrational frequencies were estimated by comparison with those for C₂H₂(g) and C₂H₄(g) reported by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, 1945, G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961), and J. K. Brown and J. K. Tyler, Proc. Chem. Soc. 1961, 13 (1961). The moment of inertia is 2.3735 × 10⁻³⁸ g cm².



Point Group C_{3v}

$$\Delta H_f^\circ = -117.5 \pm 0.7 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 71.32 \pm 0.1 \text{ gbbbs/mol}$$

$$\Delta H_f^\circ = -118.4 \pm 0.7 \text{ kcal/mol}$$

Ground State Quantum Weight = 1

Trifluoroacetoneitrile (CF₃CN)

GFW = 95.0242

(Ideal Gas)

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔH°	ΔG°	Log Kp
0	+0.00	INFINITE	-	3.799	-	-117.494	INFINITE
100	10.459	56.021	85.281	-2.926	-118.038	-	252.611
200	18.924	64.627	72.920	-1.659	-113.000	-	123.480
298	18.703	71.324	-	-0.000	-114.400	-	80.900
300	18.765	71.460	71.324	-0.035	-110.316	-	80.365
400	21.692	77.250	72.097	2.061	-118.301	-	58.802
500	23.774	82.313	73.645	4.334	-116.297	-	45.871
600	25.285	86.783	75.469	6.748	-114.203	-	37.256
700	26.465	90.774	77.376	9.165	-112.103	-	29.100
800	27.400	94.380	79.262	11.586	-110.000	-	22.921
900	28.078	97.636	81.180	14.066	-107.892	-	17.781
1000	28.618	100.624	82.941	16.683	-105.784	-	12.621
1100	29.087	103.375	84.675	20.570	-103.672	-	7.452
1200	29.450	105.822	86.341	24.487	-101.563	-	2.282
1300	29.724	108.000	87.958	28.434	-99.458	-	-2.888
1400	29.995	110.006	89.527	32.405	-97.356	-	-7.916
1500	30.201	112.582	90.945	36.455	-95.255	-	-12.944
1600	30.375	114.537	92.359	40.584	-93.156	-	-17.972
1700	30.522	116.383	93.767	44.798	-91.058	-	-22.999
1800	30.648	118.050	95.169	49.094	-88.963	-	-28.026
1900	30.757	119.701	96.567	53.468	-86.871	-	-33.053
2000	30.851	121.371	97.502	57.829	-84.779	-	-38.080
2100	30.934	122.879	98.675	62.228	-82.687	-	-43.107
2200	31.006	124.319	99.808	66.668	-80.595	-	-48.134
2300	31.067	125.697	101.007	71.149	-78.503	-	-53.161
2400	31.126	127.023	101.865	75.670	-76.411	-	-58.188
2500	31.176	128.294	102.693	80.234	-74.319	-	-63.215
2600	31.221	129.518	103.609	84.844	-72.227	-	-68.242
2700	31.261	130.697	104.607	89.498	-70.135	-	-73.269
2800	31.297	131.833	105.687	94.200	-68.043	-	-78.296
2900	31.329	132.933	106.810	98.952	-65.951	-	-83.323
3000	31.359	133.996	107.699	103.750	-63.859	-	-88.350
3100	31.386	135.025	108.564	108.600	-61.767	-	-93.377
3200	31.410	136.022	109.406	113.513	-59.675	-	-98.404
3300	31.431	136.987	110.227	118.488	-57.583	-	-103.431
3400	31.453	137.927	111.028	123.520	-55.491	-	-108.458
3500	31.472	138.839	111.810	128.602	-53.399	-	-113.485
3600	31.489	139.726	112.573	133.730	-51.307	-	-118.512
3700	31.505	140.599	113.318	138.900	-49.215	-	-123.539
3800	31.519	141.450	114.048	144.110	-47.123	-	-128.566
3900	31.533	142.289	114.760	149.360	-45.031	-	-133.593
4000	31.546	143.047	115.457	154.650	-42.939	-	-138.620
4100	31.558	143.826	116.140	159.980	-40.847	-	-143.647
4200	31.569	144.566	116.808	165.350	-38.755	-	-148.674
4300	31.579	145.276	117.460	170.760	-36.663	-	-153.701
4400	31.589	145.956	118.104	176.210	-34.571	-	-158.728
4500	31.598	146.766	118.733	181.700	-32.479	-	-163.755
4600	31.606	147.460	119.350	187.230	-30.387	-	-168.782
4700	31.614	148.140	119.956	192.800	-28.295	-	-173.809
4800	31.621	148.859	120.548	198.410	-26.203	-	-178.836
4900	31.628	149.559	121.133	204.060	-24.111	-	-183.863
5000	31.635	150.097	121.706	209.750	-22.019	-	-188.890
5100	31.641	150.723	122.269	215.480	-19.927	-	-193.917
5200	31.646	151.338	122.822	221.250	-17.835	-	-198.944
5300	31.651	151.943	123.369	227.060	-15.743	-	-203.971
5400	31.657	152.532	123.900	232.910	-13.651	-	-208.998
5500	31.662	153.113	124.426	238.800	-11.559	-	-214.025
5600	31.667	153.684	124.944	244.730	-9.467	-	-219.052
5700	31.671	154.244	125.453	250.700	-7.375	-	-224.079
5800	31.676	154.794	125.953	256.710	-5.283	-	-229.106
5900	31.679	155.337	126.447	262.760	-3.191	-	-234.133
6000	31.683	155.869	126.933	268.850	-1.099	-	-239.160

Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
2271 (1)	1215 (2)
1228 (1)	825 (2)
801 (1)	464 (2)
521 (1)	192 (2)

Bond Distances: C-F = 1.335 Å C-C = 1.461 Å CN = 1.153 Å

Bond Angle: F-C-F = 107.5° F-C-C = 111.38°

Product of the Moments of Inertia: $I_A I_B I_C = 1.18645 \times 10^{-113} \text{ g cm}^6$

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, C₂F₄, and CF₃X (X = H, Cl, Br, I, CN). Details of the input data and adjustment are given in (1). Input included a calorimetric link to NF₃(g) plus an equilibrium link to C₂F₆(g) and C₂N₂(g). The calorimetric study (2) gave ΔH° = -824.4 ± 0.6 kcal/mol at 298.15 K for the reaction 3CF₃CN(g) + 5NF₃(g) + 4N₂(g). Equilibrium data (3) in the range 865-925 K give ΔH° (3rd law) = 10.59 ± 0.20 kcal/mol at 298.15 K for the reaction C₂F₆(g) + C₂N₂(g) + 2CF₃CN(g). The entropy difference, ΔS° (2nd law) = 1.58 cal/mol, is 0.0 ± 1.5 gbbbs/mol. Deviations between the selected ΔH° and the two observations are 1.37 and 0.15 kcal/mol, respectively, both considerably less than the overall uncertainties including those in auxiliary values of ΔH°. Subsequent to the adjustment, Cornutt and Sinko (4) reported ΔH° = -187.6 ± 0.9 kcal/mol from a calorimetric study of CF₃CN(g) + 1.25 O₂(g) + 1.5 H₂O(g) + 2 CO₂(g) + 0.5 N₂(g) + 3 HF(120 H₂O). Their result of ΔH° = -118.4 ± 1.2 kcal/mol is confirmation of the selected value.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Danford and Livingston (5) and from microwave data by Sheridan and Gordy (6) and Thomas et al. (7). These studies are in substantial agreement except for a difference of about 0.04 Å in the C-C bond distance. We adopt the results of Thomas et al. (7) since they are based on data for several isotopic species. Principal moments of inertia are $I_A = 14.676 \times 10^{-39}$ and $I_B = I_C = 28.482 \times 10^{-39} \text{ g cm}^2$. Vibrational frequencies are taken from the assignments of Edgell and Potter (8). All values except ν_9 are from infrared spectra of the vapor phase. Raman spectra of the liquid provide ν_9 and confirm the infrared data. Similar assignments have been given by Janz and Wait (9) based on spectra of Wait and Janz (10).

Pace and Bobka (11) used low temperature calorimetric data to derive the entropy of the ideal gas at the normal boiling point of 205.47 K. The experimental value of 65.01 ± 0.2 gbbbs/mol is in good agreement with 65.03 gbbbs/mol obtained from this table. The largest uncertainty in Cp° and S° probably arises from neglect of anharmonicity and rotational distortion. Uncertainty in the entropy is estimated to vary from 0.1 to 0.5 gbbbs/mol over the range 300 to 1000°K. Discussions of the neglect of anharmonicity are given on the tables for CClF₃(g) and CF₄(g).

References

1. A. N. Sverud, Quarterly Technical Report AFRL-TR-69-187, Aug., 1969.
2. L. C. Walker, The Dow Chemical Co., personal communication, June, 1969.
3. D. J. Perrettie, The Dow Chemical Co., personal communication, June, 1969.
4. J. L. Cornutt and G. C. Sinko, presented at the 24th Annual Calorimetry Conference, Portsmouth, New Hampshire, October, 1969.
5. M. D. Danford and R. L. Livingston, J. Amer. Chem. Soc. **77**, 2944 (1955).
6. J. Sheridan and W. Gordy, J. Chem. Phys. **20**, 591 (1952).
7. L. F. Thomas, J. S. Haeks and J. Sheridan, Z. Elektrochem. **61**, 935 (1957).
8. W. F. Edgell and R. M. Potter, J. Chem. Phys. **24**, 80 (1955).
9. G. J. Janz and S. C. Wait, J. Chem. Phys. **26**, 1766 (1957).
10. S. C. Wait and G. J. Janz, J. Chem. Phys. **25**, 1554 (1957).
11. E. L. Pace and R. J. Bobka, J. Chem. Phys. **35**, 454 (1961).

Tetrafluoroethylene (C₂F₄)

(Ideal Gas) GFW = 100.0159

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log K ^e
0	∞	∞	∞	∞	∞	∞	∞
100	10.562	55.830	66.157	3.903	156.579	156.579	INFINITE
200	15.583	64.734	73.329	1.719	137.127	137.127	137.722
300	19.287	71.678	78.046	-0.036	117.400	117.400	165.890
400	21.965	77.731	82.860	2.105	97.409	97.409	199.272
500	23.989	82.860	86.909	4.407	77.409	77.409	230.561
600	25.531	87.377	90.807	6.887	57.409	57.409	259.861
700	26.611	90.807	93.759	9.442	37.409	37.409	284.261
800	27.310	93.759	95.827	12.016	17.409	17.409	303.661
900	27.658	95.827	97.046	14.687	-3.409	-3.409	318.061
1000	27.774	97.046	97.510	17.409	-23.409	-23.409	328.461
1100	27.774	97.510	97.216	20.166	-43.409	-43.409	334.861
1200	27.658	97.216	96.166	22.969	-63.409	-63.409	338.261
1300	27.310	96.166	94.442	25.774	-83.409	-83.409	339.661
1400	26.858	94.442	92.166	28.577	-103.409	-103.409	339.061
1500	26.292	92.166	89.442	31.377	-123.409	-123.409	336.461
1600	25.611	89.442	86.166	34.166	-143.409	-143.409	331.861
1700	24.810	86.166	82.442	36.944	-163.409	-163.409	325.261
1800	23.896	82.442	78.216	39.710	-183.409	-183.409	316.661
1900	22.874	78.216	73.556	42.472	-203.409	-203.409	306.061
2000	21.750	73.556	68.442	45.222	-223.409	-223.409	293.461
2100	20.522	68.442	62.887	47.957	-243.409	-243.409	278.861
2200	19.199	62.887	56.887	50.677	-263.409	-263.409	262.261
2300	17.784	56.887	50.442	53.377	-283.409	-283.409	243.661
2400	16.287	50.442	43.556	56.044	-303.409	-303.409	223.061
2500	14.722	43.556	36.222	58.677	-323.409	-323.409	200.461
2600	13.100	36.222	28.442	61.277	-343.409	-343.409	175.861
2700	11.433	28.442	20.222	63.844	-363.409	-363.409	149.261
2800	9.722	20.222	11.556	66.377	-383.409	-383.409	120.661
2900	8.000	11.556	2.442	68.877	-403.409	-403.409	90.061
3000	6.277	2.442	-6.887	71.344	-423.409	-423.409	58.461
3100	4.556	-6.887	-15.774	73.777	-443.409	-443.409	25.861
3200	2.833	-15.774	-24.774	76.177	-463.409	-463.409	-7.861
3300	1.111	-24.774	-33.887	78.544	-483.409	-483.409	-39.261
3400	-0.611	-33.887	-43.111	80.877	-503.409	-503.409	-99.661
3500	-2.333	-43.111	-52.442	83.177	-523.409	-523.409	-159.061
3600	-4.056	-52.442	-61.774	85.444	-543.409	-543.409	-218.461
3700	-5.777	-61.774	-71.111	87.677	-563.409	-563.409	-277.861
3800	-7.500	-71.111	-80.442	89.877	-583.409	-583.409	-337.261
3900	-9.222	-80.442	-90.222	92.044	-603.409	-603.409	-396.661
4000	-10.944	-90.222	-100.000	94.177	-623.409	-623.409	-456.061
4100	-12.667	-100.000	-109.774	96.277	-643.409	-643.409	-515.461
4200	-14.389	-109.774	-119.556	98.344	-663.409	-663.409	-574.861
4300	-16.111	-119.556	-129.333	100.377	-683.409	-683.409	-634.261
4400	-17.833	-129.333	-139.111	102.377	-703.409	-703.409	-693.661
4500	-19.556	-139.111	-148.887	104.344	-723.409	-723.409	-753.061
4600	-21.278	-148.887	-158.667	106.277	-743.409	-743.409	-812.461
4700	-22.999	-158.667	-168.444	108.177	-763.409	-763.409	-871.861
4800	-24.722	-168.444	-178.222	110.044	-783.409	-783.409	-931.261
4900	-26.444	-178.222	-187.999	111.877	-803.409	-803.409	-990.661
5000	-28.167	-187.999	-197.774	113.677	-823.409	-823.409	-1050.061
5100	-29.889	-197.774	-207.556	115.444	-843.409	-843.409	-1109.461
5200	-31.611	-207.556	-217.333	117.177	-863.409	-863.409	-1168.861
5300	-33.333	-217.333	-227.111	118.877	-883.409	-883.409	-1228.261
5400	-35.056	-227.111	-236.887	120.544	-903.409	-903.409	-1287.661
5500	-36.778	-236.887	-246.667	122.277	-923.409	-923.409	-1347.061
5600	-38.500	-246.667	-256.444	124.000	-943.409	-943.409	-1406.461
5700	-40.222	-256.444	-266.222	125.677	-963.409	-963.409	-1465.861
5800	-41.944	-266.222	-276.000	127.344	-983.409	-983.409	-1525.261
5900	-43.667	-276.000	-285.774	129.000	-1003.409	-1003.409	-1584.661
6000	-45.389	-285.774	-295.556	130.677	-1023.409	-1023.409	-1644.061

June 30, 1962; June 30, 1963; Mar. 31, 1964; Sept. 30, 1964; June 30, 1965

TETRAFLUOROETHYLENE (C₂F₄)

(IDEAL GAS) GFW = 100.0159

Point Group D_{2h}ΔH₀^a = -156.6 ± 0.7 kcal/molS_{298.15} = 71.678 ± 0.1 gibbs/molΔH_{298.15} = -157.4 ± 0.7 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω ₁ , cm ⁻¹	ω ₂ , cm ⁻¹	ω ₃ , cm ⁻¹	ω ₄ , cm ⁻¹
1072 (1)	1340 (1)	1337 (1)	
778 (1)	551 (1)	218 (1)	
394 (1)	406 (1)	1186 (1)	
190 (1)	508 (1)	558 (1)	

Bond Distance: C-F = 1.313 Å C-C = 1.313 Å

Bond Angle: F-C-F = 114°

Product of the Moments of Inertia: I_AI_BI_C = 1.5877 × 10⁻¹¹³ g³ cm⁶

Heat of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF₃, CF₃X (X = H, Cl, Br, I, CF₃) and C₂F₄. Details of the input data and the adjustment are given in (1). In this case, the selected ΔH^a corresponds to the weighted average of three calorimetric studies (2, 3) which may be reduced to the following:

Reference	Reaction	ΔH _{298.15} kcal/mol	ΔH _{298.15} kcal/mol
(2)	C ₂ F ₄ (g) + CF ₄ (g) + C(graphite)	-65.4 ± 0.5	-157.6 ± 0.6
(2)	C ₂ F ₄ (g) + 2H ₂ (g) + 4HF(50 H ₂ O) + 2C(graphite)	-150.9 ± 1.2	-156.2 ± 1.3
(3)	C ₂ F ₄ (g) + 4Na(c) + 4NaF(c) + 2C(graphite)	-392.9 ± 1.3	-157.2 ± 1.4

Amorphous carbon was formed in all three calorimetric reactions and separate combustions were made to refer the observed product to the standard state of graphite. Other calorimetric studies (4, 5, 6) are omitted because of apparent uncertainties in the reductions to the standard-state reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction data by Karle (7), Broun (8) and Young (9). The resulting structures differ in minor respects, particularly in the exact location of the two carbons. Values from Karle (7) are adopted since they are intermediate between the others. Values from Young (9) and Broun (8) correspond to changes of ± 2.4 in the product of the moments of inertia. Principal moments of inertia for the adopted structure are I_A = 15.30 × 10⁻³⁹, I_B = 25.46 × 10⁻³⁹ and I_C = 40.76 × 10⁻³⁹ g cm². Vibrational fundamentals are those selected by Shimanouchi (10) from the data of Mann (11), Honfils (12) and Nielsen (13).

Furukawa (14) reported low-temperature calorimetric data from which the ideal gas entropy may be derived as 64.54 ± 0.09 gibbs/mol at 197.53°K. The calculated entropy from this table is also 64.54 eu. The range in values of I_AI_BI_C corresponds to an entropy change of ± 0.022 eu.

References

1. A. N. Syverud, Quarterly Tech. Report T-0009-20-69 under AFRL Contract Nr. F04611-67-C-0009, Dow Chemical Co., July, 1969.
2. C. Neugebauer and J. L. Margrave, J. Phys. Chem. **69**, 1318 (1965).
3. V. P. Kolesov, I. D. Zenkov and S. M. Skuratov, Russ. J. Phys. Chem. (English translation) **36**, 45 (1962).
4. H. C. Dues, Ind. Eng. Chem. **47**, 1445 (1955).
5. F. W. Kirkbride and F. G. Davidson, Nature **174**, 79 (1954).
6. H. von Wartenberg and J. Schiefer, Z. Anorg. Allg. Chem. **278**, 326 (1955).
7. I. L. Karle and J. Karle, J. Chem. Phys. **18**, 963 (1950).
8. T. P. Broun and R. L. Livingston, J. Am. Chem. Soc. **74**, 6084 (1952).
9. J. A. Young, Dissertation Abstracts **16**, 460 (1956).
10. T. Shimanouchi, U. S. Nat. Bur. Stand. NSRDS-NBS **6**, 25 (1967).
11. D. E. Mann, N. Acquista and E. K. Plyler, J. Res. Nat. Bur. Stand. **18**, 1415 (1950).
12. A. Honfils and J. Duchene, J. Chem. Phys. **18**, 1415 (1950).
13. J. R. Nielsen, H. H. Claassen and D. C. Smith, J. Chem. Phys. **18**, 812 (1950).
14. G. T. Furukawa, R. McCoskey and M. L. Reilly, J. Res. Nat. Bur. Stand. **51**, 69 (1953).

CCH Radical (C₂H)
(Ideal Gas)

GFW = 25.0303

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° ^o kcal/mol	ΔG°	Log Kp
0	6.000	∞	∞	-2.248	113.268	113.268	INFINITE
100	6.989	41.186	56.517	-1.553	113.555	110.995	241.931
200	7.978	42.452	57.412	-1.000	113.642	111.642	117.416
298	8.968	43.553	49.554	.000	114.000	104.568	76.739
300	8.985	49.608	49.554	.016	114.002	104.630	76.223
400	9.555	52.276	49.912	.946	114.092	101.691	55.452
500	10.234	54.495	50.613	1.941	114.100	98.339	42.984
600	10.716	56.404	51.423	2.989	114.042	95.190	34.673
700	11.141	58.089	52.257	4.082	113.938	92.056	28.741
800	11.523	59.602	53.082	5.216	113.797	88.941	24.297
900	11.867	60.979	53.884	6.386	113.637	85.841	20.645
1000	12.176	62.246	54.658	7.588	113.468	82.761	18.087
1100	12.453	63.420	55.402	8.820	113.291	79.698	15.634
1200	12.701	64.514	56.116	10.078	113.110	76.654	13.941
1300	12.925	65.540	56.802	11.359	112.921	73.622	12.377
1400	13.129	66.505	57.461	12.662	112.735	70.610	11.023
1500	13.317	67.417	58.094	13.985	112.547	67.608	9.850
1600	13.492	68.282	58.704	15.325	112.358	64.615	8.826
1700	13.656	69.105	59.292	16.683	112.174	61.637	7.924
1800	13.813	69.890	59.859	18.056	111.991	58.670	7.123
1900	13.964	70.641	60.407	19.445	111.813	55.714	6.409
2000	14.109	71.361	60.937	20.849	111.639	52.765	5.766
2100	14.250	72.053	61.450	22.267	111.471	49.828	5.186
2200	14.386	72.719	61.947	23.698	111.305	46.892	4.658
2300	14.519	73.362	62.430	25.147	111.147	43.971	4.178
2400	14.648	73.982	62.898	26.602	110.992	41.054	3.739
2500	14.773	74.583	63.353	28.073	110.843	38.140	3.334
2600	14.893	75.165	63.797	29.557	110.699	35.235	2.962
2700	15.008	75.729	64.228	31.052	110.560	32.331	2.617
2800	15.119	76.277	64.649	32.558	110.428	29.439	2.298
2900	15.224	76.809	65.059	34.075	110.298	26.552	2.001
3000	15.324	77.327	65.459	35.603	110.174	23.664	1.724
3100	15.418	77.831	65.850	37.140	110.055	20.784	1.465
3200	15.506	78.322	66.232	38.686	109.938	17.906	1.223
3300	15.589	78.800	66.606	40.241	109.823	15.029	.995
3400	15.665	79.267	66.971	41.804	109.713	12.160	.782
3500	15.736	79.722	67.329	43.374	109.602	9.289	.580
3600	15.801	80.166	67.680	44.951	109.495	6.425	.390
3700	15.861	80.600	68.023	46.534	109.386	3.566	.211
3800	15.915	81.023	68.360	48.123	109.280	.712	.041
3900	15.963	81.438	68.690	49.716	109.172	-2.145	.120
4000	16.007	81.842	69.013	51.315	109.065	-4.995	.273
4100	16.046	82.238	69.331	52.918	108.958	-7.859	.419
4200	16.080	82.625	69.643	54.520	108.843	-10.733	.556
4300	16.110	83.004	69.949	56.134	108.728	-13.624	.688
4400	16.136	83.374	70.250	57.748	108.612	-16.563	.814
4500	16.158	83.737	70.546	59.361	108.492	-19.527	.934
4600	16.177	84.093	70.837	60.978	108.368	-22.043	1.048
4700	16.192	84.481	71.122	62.596	108.242	-24.595	1.159
4800	16.203	84.782	71.404	64.216	108.109	-27.224	1.262
4900	16.212	85.116	71.680	65.837	107.973	-30.552	1.363
5000	16.219	85.444	71.952	67.454	107.832	-33.360	1.459
5100	16.223	85.765	72.220	69.080	107.684	-36.210	1.552
5200	16.224	86.080	72.483	70.703	107.532	-39.027	1.640
5300	16.224	86.389	72.743	72.325	107.375	-41.839	1.725
5400	16.221	86.692	72.998	73.947	107.211	-44.651	1.807
5500	16.217	86.990	73.250	75.569	107.039	-47.464	1.886
5600	16.212	87.282	73.498	77.191	106.863	-50.273	1.942
5700	16.205	87.569	73.742	78.811	106.679	-53.083	2.005
5800	16.196	87.851	73.983	80.432	106.488	-55.886	2.106
5900	16.187	88.127	74.220	82.051	106.291	-58.670	2.173
6000	16.177	88.399	74.454	83.669	106.087	-61.475	2.239

Dec. 31, 1966; Mar. 31, 1967

(IDEAL GAS)

CCH RADICAL (C₂H)

GFW = 25.0303



Point Group [C_{∞v}]

ΔH_f^o = [113.3 ± 7] kcal/mol

S_{298.15}^o = [49.55 ± 1.3] gibbs/mol

ΔH_f^o = [114 ± 7] kcal/mol

Electronic Levels and Quantum Weights

E ₁ , cm ⁻¹	E ₂
0	(2)
[9000]	(4)

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[1920] (1)
[640] (2)
[3220] (1)

Bond Distances: C-C = [1.207]Å

C-H = [1.061]Å

Bond Angle: C-C-H = [180°]

σ = 1

Rotational Constant: B₀ = [1.475]cm⁻¹

Heat of Formation.

The heat of formation of C₂H(g) is not well established; however, we can place reliable upper and lower limits on the value.

T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Academic Press, New York, 1958, gives an upper limit for the C-H bond dissociation energy in acetylene, D(HCC-H) <121 kcal. This was obtained from the fact that ultraviolet light of 121 kcal/mol energy causes acetylene to form diacetylene and hydrogen; assuming that this process occurs through the CCH radical, the light energy is equated with D(HCC-H). This value of D(HCC-H) gives an upper limit for ΔH_f^o(CCH,g) <123 kcal/mol.

A lower limit for D(HCC-H) is obtained from a consideration of the C-H bond dissociation energies in ethylene and ethane, D(C₂H₅-H) = 105 kcal and D(C₂H₄-H) = 98 kcal. The heats of formation of the C₂H₅ and C₂H₄ radicals and their parent compounds are taken from S. W. Benson, J. Chem. Educ. 42, 502 (1965). The vibrational frequency of the C-H stretch increases steadily from ethane to ethylene and acetylene. Similarly we expect the bond strength to increase, and so D(HCC-H) >103 kcal; this yields ΔH_f^o(CCH,g) >105 kcal/mol.

F. H. Coates and R. C. Anderson, J. Am. Chem. Soc. 79, 1340 (1957), obtained several values for ΔH_f^o(CCH,g) from mass-spectroscopic measurements; their values range from 110 kcal/mol to 153 kcal/mol, but they chose to adopt 112 ± 3 kcal/mol.

Our adopted value of ΔH_f^o(CCH,g), 114 ± 7 kcal/mol, is 2 kcal smaller than that estimated by W. Tseng.

S. H. Bauer and M. Comperthwaite, J. Chem. Phys. 35, 1768 (1962).

Heat Capacity and Entropy.

The molecule is assumed to be linear; the bond lengths are assumed to be the same as in acetylene and were taken from L. E. Sutton, "Interatomic Distances Supplement," Special Publication No. 18, The Chemical Society, London, 1955.

The vibrational frequencies are those estimated by M. N. Flooster and T. B. Reed, J. Chem. Phys. 31, 66 (1959). It should be noted that the values of the free energy function given by Flooster and Reed are incorrect due to the neglect of the electronic contributions.

The electronic levels, X²Σ⁺ and A²Π⁺, were estimated by analogy with those of CN(g) which is isoelectronic; this assumption holds very well in the parent molecules HCC and HCN (D. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., New York, 1966). The molecule C₂H₂⁺, which is also isoelectronic with CCH, is predicted to have a ²Π ground state by Herzberg, loc. cit.



Chloroacetylene (C₂HCl)

GFW = 60.48327

Point Group C_{2v} $\Delta H_f^\circ = [50.9 \pm 10] \text{ kcal/mol}$  $S_{298.15}^\circ = 57.811 \text{ gibbs/mol}$ $\Delta H_f^\circ = [51.1 \pm 10] \text{ kcal/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	2.617	50.896	50.896	INFINITE
100	7.858	46.738	67.777	2.104	50.854	108.616	-
200	10.774	53.065	58.935	1.174	50.963	48.506	-
298	12.692	57.811	57.811	∞	51.100	47.270	-
300	13.015	57.892	57.812	∞	51.102	47.246	-
400	14.394	61.840	58.341	1.400	51.224	45.942	-
500	15.130	65.156	59.381	2.887	51.297	44.612	-
600	15.971	68.007	60.587	4.452	51.322	43.271	-
700	16.811	70.428	61.929	6.105	51.346	41.929	-
800	17.651	72.728	63.057	7.753	51.268	40.594	-
900	17.188	74.772	64.248	9.472	51.212	39.261	-
1000	17.746	76.653	65.1394	11.229	51.151	37.936	-
1100	18.061	78.329	66.493	13.019	51.088	36.617	-
1200	18.299	79.853	67.523	14.840	51.026	35.307	-
1300	18.595	81.191	68.555	16.686	50.961	33.999	-
1400	18.850	82.776	69.522	18.556	50.870	32.709	-
1500	18.992	84.080	70.449	20.446	50.766	31.407	-
1600	19.161	85.311	71.340	22.354	50.721	30.113	-
1700	19.422	87.585	73.197	24.275	50.574	28.829	-
1800	19.559	88.639	73.816	26.165	50.501	27.587	-
1900	19.663	89.645	74.562	30.126	50.427	24.996	-
2000	19.697	90.485	75.322	32.097	50.355	23.736	-
2100	19.759	91.064	76.036	34.077	50.278	22.460	-
2200	19.814	92.412	76.731	36.065	50.202	21.202	-
2300	19.861	93.260	77.402	38.060	50.123	19.942	-
2400	20.042	94.077	78.053	40.061	50.043	18.683	-
2500	20.097	94.865	78.685	42.066	49.960	17.432	-
2600	20.162	96.358	79.894	44.097	49.787	16.180	-
2700	20.213	97.087	80.474	46.119	49.695	14.936	-
2800	20.271	97.753	81.039	48.114	49.600	13.694	-
2900	20.306	98.419	81.589	50.113	49.504	12.452	-
3000	20.367	99.064	82.125	52.117	49.402	11.217	-
3100	20.418	100.299	83.156	54.240	49.295	9.983	-
3200	20.441	101.066	84.143	56.278	49.186	8.749	-
3300	20.482	102.572	85.084	60.319	49.071	7.526	-
3400	20.517	103.623	85.985	64.431	48.953	6.297	-
3500	20.533	104.430	86.421	68.481	48.829	5.074	-
3600	20.552	105.109	87.268	72.607	48.702	3.851	-
3700	20.575	105.582	87.679	76.773	48.568	2.632	-
3800	20.599	106.044	88.062	80.831	48.431	1.444	-
3900	20.620	106.497	88.477	84.891	48.289	0.291	-
4000	20.638	106.826	89.088	88.924	48.143	0.13	-
4100	20.657	107.179	89.256	92.925	47.997	-	-
4200	20.672	107.374	89.246	97.013	47.851	-	-
4300	20.685	107.799	89.075	101.136	47.667	-	-
4400	20.699	107.799	89.075	105.258	47.432	-	-
4500	20.706	107.799	89.075	109.373	47.146	-	-
4600	20.711	107.799	89.075	113.484	46.811	-	-
4700	20.716	107.799	89.075	117.595	46.466	-	-
4800	20.720	107.799	89.075	121.706	46.111	-	-
4900	20.724	107.799	89.075	125.817	45.756	-	-
5000	20.728	107.799	89.075	129.928	45.401	-	-
5100	20.732	107.799	89.075	134.039	45.046	-	-
5200	20.736	107.799	89.075	138.150	44.691	-	-
5300	20.740	107.799	89.075	142.261	44.336	-	-
5400	20.744	107.799	89.075	146.372	43.981	-	-
5500	20.748	107.799	89.075	150.483	43.626	-	-
5600	20.752	107.799	89.075	154.594	43.271	-	-
5700	20.756	107.799	89.075	158.705	42.916	-	-
5800	20.760	107.799	89.075	162.816	42.561	-	-
5900	20.764	107.799	89.075	166.927	42.206	-	-
6000	20.768	107.799	89.075	171.038	41.851	-	-

Dec. 31, 1968



Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}
3340 (1)	804 (2)
2110 (1)	326 (2)
756 (1)	

Bond Distances: C-C = 1.204 Å C-H = 1.055 Å C-Cl = 1.637 Å

Bond Angles: Cl-C-C = 180° C-C-H = 180° σ = 1

Rotational Constant: B₀ = 0.188641 cm⁻¹

Heat of Formation

The value of $\Delta H_f^\circ = 51.1 \text{ kcal/mol}$ is calculated from the estimated $\Delta H_{298}^\circ = -53 \pm 10 \text{ kcal/mol}$ for $\text{HCCl}(\text{g}) + \text{Cl}_2(\text{g}) + \text{CHCl}_2\text{Cl}(\text{g})$, using $\Delta H_f^\circ(\text{HCCl}(\text{g})) = -1.86 \text{ kcal/mol}$ (1). The value of ΔH_{298}° is assumed to be the same as that for the reaction $\text{HCCl}(\text{g}) + \text{Cl}_2(\text{g}) + \text{CHCl}_2\text{Cl}(\text{g})$, using $\Delta H_f^\circ(\text{C}_2\text{H}_2, \text{g}) = 54.19 \text{ kcal/mol}$ (2) and $\Delta H_f^\circ(\text{CHCl}_2\text{Cl}, \text{g}) = 1.2 \text{ kcal/mol}$ (2).

Heat Capacity and Entropy

The linear molecular structure and bond distances were determined from the microwave spectrometrical studies by Tyler and Sheridan (3). Their results are in good agreement with those of Westenberg, Goldstein and Wilson (4). The principal moment of inertia is $1.48381 \times 10^{-38} \text{ g cm}^2$.

The vibrational frequencies were observed in the infrared spectra by Hunt and Wilson (5), and Richardson and Goldstein (6).

References

- (1) U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
- (2) This is an average value of 0.9 and 1.47 kcal/mol for cis- and trans- $\text{CHCl}(\text{g})$, respectively which are obtained from reference (1).
- (3) J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963).
- (4) A. A. Westenberg, J. H. Goldstein and E. B. Wilson, Jr., J. Chem. Phys. 27, 1319 (1949).
- (5) G. R. Hunt and M. K. Wilson, J. Chem. Phys. 34, 1301 (1961).
- (6) W. S. Richardson and J. H. Goldstein, J. Chem. Phys. 18, 1314 (1950).

Monofluoroacetylene (C_2HF)

(Ideal Gas)

GFW = 44.02867

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0	+0.00	+0.00	INFINITE	-	29.834	29.834	INFINITE
100	7.591	44.639	64.942	- 2.030	29.786	28.618	- 65.544
200	10.404	50.753	56.412	- 1.132	29.877	27.420	- 29.964
298	12.505	55.329	55.000	-	30.000	26.188	- 19.197
300	12.536	55.407	55.130	-0.23	30.002	26.164	- 19.061
400	13.207	59.215	55.840	1.350	30.105	24.869	- 13.598
500	14.552	62.425	56.844	2.791	30.154	23.553	- 10.295
600	15.370	65.199	58.011	4.313	30.155	22.232	- 8.098
700	16.159	67.845	59.216	5.900	30.115	20.915	- 5.530
800	16.915	70.381	60.456	7.558	30.040	19.600	- 3.000
900	17.605	72.826	61.568	9.291	29.974	18.301	- 4.444
1000	17.894	73.648	62.686	10.962	29.891	17.059	- 3.717
1100	17.937	75.332	63.760	12.724	29.803	15.724	- 3.124
1200	18.139	76.997	64.791	14.528	29.715	14.450	- 2.632
1300	18.339	78.632	65.732	16.207	29.620	13.232	- 2.200
1400	18.539	79.732	66.727	17.772	29.520	12.068	- 1.860
1500	18.845	81.025	67.637	20.082	29.438	10.868	- 1.554
1600	19.028	82.248	68.513	21.976	29.366	9.646	- 1.286
1700	19.168	83.006	69.355	23.687	29.256	8.414	- 1.051
1800	19.285	83.556	70.152	25.250	29.120	7.174	- 0.840
1900	19.387	84.056	70.909	26.752	28.975	5.935	- 0.656
2000	19.470	84.557	71.705	29.704	28.986	4.678	- 0.489
2100	19.570	87.514	72.435	31.666	28.897	3.256	- 0.339
2200	19.760	88.431	73.181	33.637	28.804	2.033	- 0.202
2300	19.941	89.151	73.885	35.610	28.711	1.061	- 0.135
2400	20.111	90.151	74.685	37.605	28.618	- 0.368	- 0.015
2500	20.279	90.971	75.131	39.600	28.523	- 1.598	- 0.140
2600	20.338	91.756	75.756	41.601	28.428	- 2.779	- 0.235
2700	20.392	92.313	76.362	43.607	28.325	- 4.001	- 0.324
2800	20.441	92.785	76.945	45.618	28.219	- 5.264	- 0.403
2900	20.485	93.155	77.502	47.635	28.119	- 6.564	- 0.475
3000	20.526	94.638	78.086	49.656	28.011	- 7.575	- 0.552
3100	20.563	95.301	78.630	51.680	27.902	- 8.758	- 0.617
3200	20.597	95.945	79.161	53.708	27.789	- 9.938	- 0.679
3300	20.629	96.570	79.689	55.720	27.675	- 11.100	- 0.736
3400	20.659	97.186	80.210	57.720	27.552	- 12.250	- 0.790
3500	20.684	97.768	80.670	59.611	27.426	- 13.563	- 0.841
3600	20.699	98.343	81.162	61.651	27.299	- 14.629	- 0.888
3700	20.732	98.902	81.634	63.593	27.165	- 15.700	- 0.933
3800	20.763	99.479	82.093	65.540	27.027	- 16.770	- 0.976
3900	20.791	99.979	82.527	67.487	26.887	- 17.840	- 1.012
4000	20.817	100.497	82.990	70.032	26.743	- 19.251	- 1.052
4100	20.804	101.004	83.423	72.082	26.592	- 20.405	- 1.088
4200	20.824	101.498	83.847	74.133	26.436	- 21.543	- 1.121
4300	20.853	101.951	84.293	76.186	26.268	- 22.655	- 1.143
4400	20.879	102.376	84.761	78.240	26.097	- 23.749	- 1.163
4500	20.866	102.916	85.072	80.297	25.937	- 24.963	- 1.212
4600	20.879	103.368	85.465	82.354	25.760	- 26.087	- 1.239
4700	20.890	103.810	85.850	84.413	25.579	- 27.211	- 1.265
4800	20.901	104.244	86.229	86.471	25.397	- 28.349	- 1.290
4900	20.911	104.666	86.586	88.526	25.210	- 29.487	- 1.316
5000	20.921	105.085	86.966	90.594	25.019	- 30.551	- 1.336
5100	20.930	105.494	87.326	92.657	24.792	- 31.680	- 1.358
5200	20.939	105.895	87.679	94.721	24.561	- 32.780	- 1.376
5300	20.948	106.286	88.026	96.784	24.328	- 33.859	- 1.392
5400	20.955	106.676	88.366	98.850	24.094	- 34.978	- 1.415
5500	20.962	107.053	88.708	100.916	23.910	- 36.066	- 1.433
5600	20.969	107.425	89.035	102.982	23.675	- 37.156	- 1.450
5700	20.976	107.791	89.361	105.050	23.432	- 38.245	- 1.466
5800	20.983	108.151	89.682	107.116	23.187	- 39.334	- 1.482
5900	20.988	108.501	89.992	109.186	22.937	- 40.383	- 1.492
6000	20.994	108.852	90.310	111.255	22.666	- 41.475	- 1.511

Dec. 31, 1967

C_2HF

MONOFLUOROACETYLENE (C_2HF)

(IDEAL GAS)

GFW = 44.02867

Point Group $C_{\infty v}$

$\Delta H_f^\circ = [30 \pm 15] \text{ kcal/mol}$

$\Delta H_f^\circ_{298.15} = [30 \pm 15] \text{ kcal/mol}$

$S^\circ_{298.15} = 55.33 \pm 0.01 \text{ gibbs/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm}^{-1}$

3360 (1)

2250 (1)

1060 (1)

580 (2)

367 (2)

C-C = 1.138 Å

C-H = 1.053 Å

C-C-H = 180°

$\sigma = 1$

Bond Distances: C-F = 1.279 Å

Bond Angles: F-C-C = 180°

Rotational Constant: $B_0 = 0.323571 \text{ cm}^{-1}$

Heat of Formation

The heat of formation is estimated by assuming that the C-C bond strength is the average of those in C_2F_4 (113 kcal) and C_2H_2 (229 kcal). Combining the average value (171 kcal) with the heats of formation of CF and CH from the JANAF Tables, yields $\Delta H_f^\circ_{298} (C_2HF, g) = 30 \pm 15 \text{ kcal/mol}$.

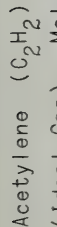
Heat Capacity and Entropy

G. R. Hunt and M. K. Wilson, J. Chem. Phys. 24, 1301 (1961), and J. K. Brown and J. K. Tyler, Proc. Chem. Soc. (London) 1961, 13 (1961), have reported the infrared spectrum and have assigned the fundamental frequencies. The frequencies used in the present table are median values of the two sets and are generally within 5 cm^{-1} of each set.

The molecule has been shown to be linear by J. K. Tyler and J. Sheridan, Trans. Faraday Soc. 59, 2661 (1963), who reported the rotational constant B_0 .

The electronic ground state is assumed to be $^1\Sigma$ by analogy with C_2H_2 .

C_2HF



(Ideal Gas) Mol. Wt. = 26.038

ACETYLENE (C₂H₂) (IDEAL GAS)

MOL. WT. = 26.038

$\Delta H_f^\circ = 54.33 \pm 0.19$ kcal. mole⁻¹
 $\Delta H_f^\circ = 54.19 \pm 0.19$ kcal. mole⁻¹
Point group D_{∞h}
 $S_{298.15}^\circ = 48.004$ cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω , cm. ⁻¹
3373.7 (1)
1973.8 (1)
3281.9 (1)
611.6 (2)
729.3 (2)

Rotational Constant B₀ = 1.17684 ± 0.00016 cm.⁻¹ σ = 2

Ground State Multiplicity = 1

Spectroscopic constants used in calculating corrections to rigid rotator-harmonic oscillator approximation (cm.⁻¹):

X ₁₁ = -24.08	X ₂₂ = -7.92	X ₃₄ = -9.06	D ₀ = 2.19 X 10 ⁻⁶
X ₁₂ = -16.84	X ₂₃ = -1.38	X ₃₅ = -5.73	ε ₄₄ = 1.1
X ₁₃ = -99.01	X ₂₄ = -6.15	X ₄₄ = 5.38	ε ₅₅ = 2.49
X ₁₄ = -16.46	X ₂₅ = -0.85	X ₄₅ = -12.65	
X ₁₅ = -11.75	X ₃₃ = -25.69	X ₅₅ = -2.27	

Values of α_i not available.

Heat of Formation

Taken from D. D. Wagman, J. E. Kilpatrick, K. S. Pitzer, and P. D. Rossini, J. Research Natl. Bureau Standards 55, 467 (1945).

Heat Capacity and Entropy

J. S. Gordon (private communication, February, 1961) has used the constants listed above to calculate C_p from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954). The constants are from E. E. Bell and H. H. Nielsen, J. Chem. Phys. 18, 1382 (1950) and H. C. Allen, E. D. Tidwell, and E. K. Plyler, J. Research Natl. Bureau Standards 57, 213 (1956). Heat capacities below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

March 31, 1961



Ethylene (C₂H₄)

(Ideal Gas)

Mol. Wt. = 28.05418

T, °K.	C _p	S°	-(F°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.952	40.00	INFINITE	2.514	14.578	INFINITE
200	8.451	48.721	53.267	1.710	14.434	-31.544
300	8.851	55.196	52.396	1.000	13.275	-16.638
400	9.167	60.468	52.028	0.619	12.595	-11.018
500	9.433	64.821	51.722	0.423	12.031	-8.444
600	9.659	68.474	51.474	0.314	11.577	-7.652
700	9.848	71.574	51.268	0.246	11.214	-7.114
800	10.000	74.321	51.090	0.200	10.918	-6.718
900	10.125	76.821	50.932	0.168	10.674	-6.423
1000	10.230	79.092	50.792	0.143	10.466	-6.213
1100	10.318	81.166	50.666	0.123	10.288	-6.034
1200	10.390	83.081	50.551	0.106	10.134	-5.889
1300	10.448	84.859	50.448	0.092	10.000	-5.766
1400	10.496	86.521	50.352	0.080	9.884	-5.662
1500	10.535	88.081	50.268	0.070	9.784	-5.575
1600	10.567	89.552	50.194	0.062	9.696	-5.497
1700	10.592	90.940	50.130	0.056	9.618	-5.423
1800	10.611	92.275	50.074	0.051	9.548	-5.360
1900	10.626	93.568	50.026	0.046	9.484	-5.306
2000	10.638	94.821	50.000	0.042	9.424	-5.261
2100	10.646	96.040	49.979	0.039	9.368	-5.223
2200	10.651	97.225	49.960	0.036	9.314	-5.183
2300	10.654	98.374	49.946	0.034	9.262	-5.146
2400	10.656	99.492	49.934	0.032	9.212	-5.112
2500	10.657	100.581	49.924	0.031	9.164	-5.081
2600	10.658	101.646	49.916	0.030	9.118	-5.052
2700	10.658	102.688	49.910	0.029	9.074	-5.025
2800	10.658	103.707	49.906	0.028	9.032	-5.000
2900	10.658	104.702	49.903	0.027	8.992	-4.975
3000	10.658	105.674	49.901	0.026	8.954	-4.950
3100	10.658	106.624	49.899	0.025	8.918	-4.925
3200	10.658	107.552	49.897	0.024	8.884	-4.900
3300	10.658	108.459	49.895	0.023	8.850	-4.875
3400	10.658	109.346	49.893	0.022	8.818	-4.850
3500	10.658	110.212	49.891	0.021	8.786	-4.825
3600	10.658	111.059	49.889	0.020	8.754	-4.800
3700	10.658	111.886	49.887	0.019	8.722	-4.775
3800	10.658	112.694	49.885	0.018	8.690	-4.750
3900	10.658	113.482	49.883	0.017	8.658	-4.725
4000	10.658	114.250	49.881	0.016	8.626	-4.700
4100	10.658	115.000	49.879	0.015	8.594	-4.675
4200	10.658	115.732	49.877	0.014	8.562	-4.650
4300	10.658	116.446	49.875	0.013	8.530	-4.625
4400	10.658	117.142	49.873	0.012	8.498	-4.600
4500	10.658	117.821	49.871	0.011	8.466	-4.575
4600	10.658	118.482	49.869	0.010	8.434	-4.550
4700	10.658	119.126	49.867	0.009	8.402	-4.525
4800	10.658	119.754	49.865	0.008	8.370	-4.500
4900	10.658	120.366	49.863	0.007	8.338	-4.475
5000	10.658	120.962	49.861	0.006	8.306	-4.450
5100	10.658	121.542	49.859	0.005	8.274	-4.425
5200	10.658	122.107	49.857	0.004	8.242	-4.400
5300	10.658	122.657	49.855	0.003	8.210	-4.375
5400	10.658	123.192	49.853	0.002	8.178	-4.350
5500	10.658	123.712	49.851	0.001	8.146	-4.325
5600	10.658	124.218	49.849	0.000	8.114	-4.300
5700	10.658	124.710	49.847	0.000	8.082	-4.275
5800	10.658	125.188	49.845	0.000	8.050	-4.250
5900	10.658	125.652	49.843	0.000	8.018	-4.225
6000	10.658	126.102	49.841	0.000	7.986	-4.200

Dec. 31, 1960; Sept. 30, 1965

ETHYLENE (C₂H₄)

(IDEAL GAS)

MOL. WT. = 28.05418

Point Group D_{2h}ΔH_f⁰ = 14.58 ± 0.07 kcal. mole⁻¹ΔH_f⁰ 298.15 = 12.54 ± 0.07 kcal. mole⁻¹S_{298.15} = 52.396 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
3026.4 (1)	3102.5 (1)	3105.5 (1)	3105.5 (1)
1622.9 (1)	1222.0 (1)	826.0 (1)	826.0 (1)
1342.2 (1)	949.3 (1)	2988.7 (1)	2988.7 (1)
1023.0 (1)	943.0 (1)	1443.5 (1)	1443.5 (1)

Bond Distance: H-C = 1.086 Å C-C = 1.337 Å

Bond Angle: H-C-H = 117° 22' H-C-C = 121° 19'

Product of the Moments of Inertia: I_AI_BI_C = 5.4466 × 10⁻¹¹⁷ g.³ cm.⁶σ⁻ = 4

Heat of Formation.

The heat of combustion of ethylene was measured by F. D. Rossini and J. W. Knowlton, *J. Res. Natl. Bur. Std.* **19**, 249 (1937). From the value, ΔH_f⁰ 298.15 = -337.28 ± 0.07 kcal. mole⁻¹ for the reaction C₂H₄(g) + 3 O₂(g) = 2 CO₂(g) + 2 H₂O(l), the heat of formation (ΔH_f⁰ 298.15) for C₂H₄(g) was derived to be 12.54 ± 0.07 kcal. mole⁻¹. The values of ΔH_f⁰ 298.15 for CO₂(g) and H₂O(l) used for calculation were obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and Irving Jaffe, "Selected Values of Chemical Thermodynamic Properties", Circular of the National Bureau of Standards 500, 1952.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from H. C. Allen, Jr. and E. K. Plyler, *J. Am. Chem. Soc.* **80**, 2673 (1958). The vibrational frequencies were taken from W. L. Smith and I. M. Mills, *J. Chem. Phys.* **40**, 2095 (1964). Eight of the twelve frequencies were reported by R. L. Arnett and B. L. Crawford, *J. Chem. Phys.* **19**, 118 (1950); B. L. Crawford, J. E. Lancaster and R. Inakeep, *J. Chem. Phys.* **21**, 676 (1953); B. P. Stoicheff, *J. Chem. Phys.* **21**, 755 (1953); T. Feldman, J. Romanko and H. L. Welsh, *Can. J. Phys.* **34**, 737 (1956); and H. C. Allen and E. K. Plyler, loc. cit. G. Herzberg, "Infrared and Raman Spectra", D. Van Nostrand Company, Inc., New York, 1945, also reported the vibrational frequencies for ethylene as 3019.3 (1), 1623.3 (1), 1342.4 (1), 825.0 (1), 3272.3 (1), 1050 (1), 949.2 (1), 943 (1), 3105.5 (1), 995 (1), 2989.5 (1) and 1443.5 (1) which are very close to the values adopted. The infrared and Raman spectra of ethylene before 1945 have been summarized by G. Herzberg, loc. cit. The molecular structure of ethylene was also determined by L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957). Their results, r_{C-H} = 1.085 Å, r_{C-C} = 1.334 Å and ∠H-C-H = 116° are in excellent agreement with the values adopted. The three principal moments of inertia are I_A = 0.5762 × 10⁻³⁹, I_B = 2.7999 × 10⁻³⁹ and I_C = 3.3761 × 10⁻³⁹ g.² cm.²



T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	7.956	48.444	46.457	-	-	9.587	-	INFINITE
200	8.772	59.006	58.006	-	-	10.694	-	18.670
298	11.449	50.056	50.056	-	-	11.576	-	6.640
300						12.580	-	2.519
300	11.510	58.127	58.056	∞21	12.599	3.107	2.263	
400	14.913	61.904	59.548	1.362	13.514	.201	.110	
500	18.023	65.575	59.589	2.993	14.264	3.719	1.625	
600	20.629	69.099	62.082	4.930	15.851	7.373	2.485	
700	22.793	72.446	64.297	7.104	16.930	11.119	3.471	
800	24.611	75.612	66.376	9.477	15.686	14.922	4.076	
900	26.155	78.602	68.250	12.017	15.951	18.764	4.556	
1000	27.477	81.428	69.977	14.701	16.129	22.631	4.946	
1100	28.615	84.102	71.507	17.507	16.240	26.512	5.267	
1200	29.597	86.635	72.919	20.418	16.293	30.404	5.537	
1300	30.447	89.038	74.222	23.422	16.304	34.294	5.765	
1400	31.184	91.322	75.501	26.504	16.273	38.189	5.961	
1500	31.826	93.496	76.776	29.655	16.218	42.078	6.131	
1600	32.386	95.568	78.027	32.847	16.141	45.957	6.277	
1700	32.876	97.547	79.264	36.130	16.040	49.837	6.407	
1800	33.306	99.438	80.493	39.440	15.927	53.708	6.521	
1900	33.686	101.249	81.728	42.780	15.801	57.576	6.622	
2000	34.022	102.986	82.968	46.175	15.665	61.433	6.713	
2100	34.319	104.653	84.198	49.593	15.522	65.288	6.794	
2200	34.585	106.256	85.438	53.038	15.379	69.128	6.867	
2300	34.822	107.799	86.679	56.509	15.228	72.969	6.933	
2400	35.034	109.285	87.924	60.002	15.080	76.804	6.994	
2500	35.226	110.719	89.173	63.515	14.933	80.622	7.048	
2600	35.398	112.104	90.437	67.046	14.786	84.446	7.098	
2700	35.554	113.444	91.707	70.596	14.641	88.256	7.143	
2800	35.695	114.739	92.984	74.157	14.498	92.063	7.186	
2900	35.824	115.994	94.269	77.733	14.360	95.872	7.225	
3000	35.941	117.210	95.553	81.321	14.226	99.667	7.260	
3100	36.048	118.390	96.837	84.921	14.093	103.464	7.294	
3200	36.146	119.537	98.121	88.530	13.968	107.251	7.325	
3300	36.237	120.650	99.405	92.150	13.850	111.037	7.353	
3400	36.319	121.733	100.689	95.777	13.736	114.820	7.380	
3500	36.396	122.787	101.972	99.413	13.631	118.597	7.405	
3600	36.466	123.813	103.256	103.056	13.531	122.375	7.429	
3700	36.532	124.814	104.539	106.706	13.442	126.148	7.451	
3800	36.592	125.789	105.822	110.363	13.356	129.925	7.472	
3900	36.649	126.740	107.105	114.025	13.282	133.696	7.492	
4000	36.701	127.668	108.387	117.692	13.214	137.466	7.510	
4100	36.750	128.575	109.670	121.365	13.155	141.226	7.528	
4200	36.795	129.461	110.952	125.042	13.106	144.998	7.545	
4300	36.838	130.328	112.234	128.724	13.067	148.755	7.560	
4400	36.878	131.175	113.515	132.410	13.034	152.516	7.575	
4500	36.915	132.004	114.796	136.099	13.013	156.272	7.589	
4600	36.950	132.816	116.077	139.793	12.999	160.043	7.603	
4700	36.983	133.611	117.358	143.489	12.996	163.806	7.617	
4800	37.014	134.390	118.639	147.180	13.001	167.570	7.629	
4900	37.043	135.153	119.920	150.862	13.015	171.333	7.641	
5000	37.071	135.902	121.201	154.548	13.039	175.089	7.653	
5100	37.097	136.636	122.482	158.236	13.075	178.851	7.664	
5200	37.121	137.357	123.763	161.924	13.117	182.611	7.675	
5300	37.144	138.064	125.045	165.610	13.160	186.369	7.686	
5400	37.166	138.759	126.326	169.298	13.232	190.145	7.695	
5500	37.187	139.441	127.607	172.986	13.305	193.916	7.705	
5600	37.207	140.111	128.887	176.674	13.387	197.680	7.714	
5700	37.226	140.770	129.568	180.362	13.480	201.445	7.723	
5800	37.243	141.417	130.249	184.050	13.583	205.210	7.733	
5900	37.260	142.054	130.936	187.738	13.694	208.975	7.742	
6000	37.277	142.681	131.623	191.426	13.815	212.760	7.749	

Dec. 31, 1960; Sept. 30, 1965

Point Group C_{2v}
ΔH_f^o 0 = -9.59 ± 0.15 kcal. mole⁻¹
ΔH_f^o 298.15 = -12.56 ± 0.15 kcal. mole⁻¹
Ground State Quantum Weight = {1}

Vibrational Frequencies and Degeneracies
(ω), cm.⁻¹ (ω), cm.⁻¹

Bond Distances: C-H = 1.0802 Å C-O = 1.4363 Å C-C = 1.4728 Å
Bond Angles: H-C-H = 116° 51' H₂-C-C = 159° 5'
H-C-O = 142° 45.6'

Product of the Moments of Inertia: I_AI_BI_C = 7.42336 X 10⁻¹¹⁶ g.³ cm.⁶

σ⁻ = 2

Heat of Formation.

The heat of combustion of ethylene oxide (g) was determined by A. S. Fell and G. Filcher, *Trans. Faraday Soc.*, 51, 71 (1955) and R. S. Crag and H. Hunt, *J. Phys. Chem.*, 46, 1162 (1942), as -312.15 ± 0.14 and -312.55 ± 0.20 kcal. mole⁻¹, respectively. The corresponding value of ΔH_f^o 298.15 (C₂H₄O, g) was evaluated to be -12.56 ± 0.15 and -12.19 ± 0.22 kcal. mole⁻¹. The former value is adopted.

Heat Capacity and Entropy.

The vibrational frequencies were taken from R. C. Lord and B. Nollin, *J. Chem. Phys.*, 24, 658 (1956). The infrared and Raman spectra of ethylene oxide have also been examined by J. W. Linnett, *J. Chem. Phys.*, 6, 692 (1938) and H. W. Thompson and M. T. Cave, *Trans. Faraday Soc.*, 47, 946 (1951). The vibrational frequencies assigned were slightly different from the ones reported by R. C. Lord and B. Nollin, loc. cit. As a result of analogies between ethylene oxide and ethylene imine, small changes of R. C. Lord and B. Nollin's assignment have been made by W. J. Potts, *Spectrochim. Acta*, 21, 511 (1965). The bond distances and angles were obtained from G. L. Cunningham, A. W. Boyd and W. D. Ginn, *J. Chem. Phys.*, 17, 211 (1949). The investigation of the structure of ethylene oxide by electron diffraction was reported by F. C. Ackermann and J. E. Mayer, *J. Chem. Phys.*, 21, 377 (1956) and M. Igarashi, *Bull. Chem. Soc. Japan*, 26, 330 (1953). The three principal moments of inertia are: I_A = 3.9052 X 10⁻³⁹, I_B = 3.2788 X 10⁻³⁹ and I_C = 5.9499 X 10⁻³⁹ g.² cm.²

The calculated heat capacities (307.2 - 371.2°K.) are in good agreement with the experimentally measured ones reported by G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, 9, 618 (1940).

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _P
0						
100	17.100	14.000	14.000	.000	- 13.415	9.833
200	17.200	14.106	14.000	.032	- 14.196	9.769
300	20.690	19.630	14.728	1.961	- 14.003	7.197
400	22.720	24.508	16.208	4.150	- 15.288	5.612
500	23.830	28.756	17.953	6.482	- 15.138	4.503
600	24.600	32.421	19.759	8.906	- 14.964	3.720
700	25.180	35.615	21.571	11.396	- 14.776	3.139
800	25.660	38.610	23.322	13.936	- 14.568	2.693
900	26.070	41.535	25.009	16.525	- 14.395	2.342
1000	26.430	44.037	26.627	19.151	- 14.189	2.057
1100	26.770	46.352	28.179	21.811	- 13.977	1.825
1200	27.090	48.507	29.657	24.504	- 13.750	1.630
1300	27.390	50.525	31.077	27.228	- 13.508	1.466
1400	27.680	52.425	32.437	29.982	- 13.248	1.327
1500	27.940	54.221	33.743	32.764	- 12.970	1.208
1600	28.240	55.924	34.998	35.574	- 12.764	.763
1700	28.510	57.546	36.206	38.411	- 82.077	1.433
1800	28.760	59.094	37.370	41.276	- 81.370	3.027
1900	28.990	60.577	38.494	44.167	- 80.643	7.446
2000						.614

December 31, 1960.

DILITHIUM DICARBIDE (Li₂C₂) (solid)

Mol. Wt. = 37.902

ΔH_f⁰ 298.15 = -14.2 ± 2 kcal mole⁻¹

S_{298.15}⁰ = 14 ± 1 cal. deg.⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

Monomagnesium Dicarbide (MgC_2)
(Solid) Mol. Wt. = 48.33

INTERIM TABLE

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔH_f°	ΔF_f°	Log K _p
0						
100	13.440	13.000	.000	21.500	20.270	-14.857
200	13.490	13.063	.025	21.006	20.265	-14.742
300	13.530	13.125	.081	21.360	19.966	-10.908
400	13.560	13.187	.166	21.677	19.578	-8.537
500	13.590	13.250	.283	21.954	19.133	-6.949
600	13.620	13.313	.439	22.190	18.653	-5.653
700	13.650	13.375	.635	22.386	18.154	-4.959
800	13.680	13.438	.871	22.542	17.643	-4.284
900	13.710	13.500	1.148	22.658	17.119	-3.782
1000	13.740	13.563	1.465	22.734	16.588	-3.352
1100	13.770	13.625	1.822	22.770	16.048	-2.982
1200	13.800	13.688	2.219	22.766	15.499	-2.679
1300	13.830	13.750	2.656	22.722	14.944	-2.431
1400	13.860	13.813	3.133	22.638	14.375	-2.231
1500	13.890	13.875	3.650	22.514	13.794	-2.071
1600	13.920	13.938	4.207	22.350	13.203	-1.941
1700	13.950	13.999	4.804	22.146	12.603	-1.841
1800	13.980	14.063	5.441	21.902	12.003	-1.761
1900	14.010	14.125	6.118	21.618	11.403	-1.691
2000	14.040	14.188	6.835	21.294	10.803	-1.631
2100	14.070	14.250	7.592	20.930	10.203	-1.581
2200	14.100	14.313	8.389	20.526	9.603	-1.541
2300	14.130	14.375	9.226	20.082	9.003	-1.511
2400	14.160	14.438	10.103	19.598	8.403	-1.481
2500	14.190	14.500	11.020	19.074	7.803	-1.451

MONOMAGNESIUM DICARBIDE (MgC_2) (Solid)

Mol. Wt. = 48.33

ΔH_f° 298.15 = 21 ± 5 kcal. mole⁻¹

$S_{298.15}^\circ$ = 13 ± 2 cal. deg.⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

(IDEAL GAS)

OPW = 38.029

CNC RADICAL (C₂N)Point Group D_{∞h} $\Delta H_f^\circ = [131.9] \text{ kcal/mol}$ $\Delta H_f^\circ = [133 \pm 30] \text{ kcal/mol}$ $S_{298.15}^\circ = [55 \pm 2] \text{ gibbs/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1
0	2
26.41	2
30338.53	4
34602.33	2

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	$(1200) (1)$	$(900) (1)$

Bond Distances: C-N = 1.245 Å

Bond Angles: C-N-C = 180°

Rotational Constant: B₀ = 0.4555 cm⁻¹

σ = 2

Heat of Formation

A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 353 (1966), state that the observed bond length in CNC(g) indicates double-bonded CN links. The value of the C = N dissociation energy is derived as 147 kcal from the heat of combustion of n-butyl-isobutylidene amine determined by G. E. Coates and L. E. Sutton, J. Chem. Soc. 1187, (1948). However, due to possible extra binding energy from the unpaired electron, we assume here a slightly higher value of 160 kcal. This yields a $\Delta H_f^\circ(\text{CNC}, g) = 133 \text{ kcal/mol}$. It is also possible to calculate another value by assuming that the ratio of the heat of atomization (ΔH_a) of Si₂N to that of C₂N(g) is equal to the ratio of the dissociation energies of SiN(g) and CN(g); by this method $\Delta H_f^\circ(\text{CNC}, g) = 144 \text{ kcal/mol}$.

Heat Capacity and Entropy

Merer and Travis, loc. cit., have observed the ultraviolet absorption spectrum of the CNC radical. They have assigned the configuration, bond distance, and the electronic levels. In addition, they have derived w_p , the remaining frequencies are estimated by comparison with the w_p of Si₂N(g), which has been assigned by W. Weltner and D. J. McLeod, J. Chem. Phys. **40**, 1305 (1964), and J. Chem. Phys. **45**, 3096 (1966).

Mar. 31, 1967

C₂N

Cyanogen (C₂N₂)

(Ideal Gas) Mol. Wt. = 52.038

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	Log K _p
0	0.000	INFINITE	3.019	73.428	INFINITE
100	6.760	68.408	2.275	72.782	-158.676
200	11.890	52.663	3.890	73.859	-78.650
298	13.363	37.711	4.000	73.870	-52.128
300	13.390	37.795	4.025	73.874	-51.794
400	14.771	61.878	5.260	74.107	-38.321
500	15.615	65.269	5.332	74.287	-30.213
600	16.305	68.178	5.455	74.415	-24.797
700	16.899	70.737	5.583	74.589	-20.923
800	17.415	73.028	5.706	74.554	-18.015
900	17.858	75.106	5.821	74.586	-15.751
1000	18.237	77.007	5.926	74.604	-13.939
1100	18.559	78.761	6.023	74.610	-12.457
1200	18.830	80.405	6.112	74.608	-11.277
1300	19.066	81.905	6.198	74.598	-10.372
1400	19.264	83.325	6.279	74.578	-9.681
1500	19.434	84.660	6.356	74.556	-9.105
1600	19.579	85.919	6.429	74.531	-8.636
1700	19.700	87.100	6.498	74.506	-8.262
1800	19.815	88.240	6.563	74.482	-7.985
1900	19.910	89.314	6.625	74.444	-7.792
2000	19.993	90.337	6.682	74.412	-7.626
2100	20.066	91.314	6.734	74.379	-7.486
2200	20.128	92.245	6.781	74.346	-7.362
2300	20.181	93.135	6.825	74.306	-7.252
2400	20.239	94.000	6.863	74.267	-7.156
2500	20.285	94.833	6.895	74.227	-7.072
2600	20.326	95.629	6.920	74.183	-7.000
2700	20.362	96.388	6.945	74.135	-6.938
2800	20.396	97.110	6.965	74.084	-6.885
2900	20.426	97.795	6.983	74.047	-6.837
3000	20.454	98.448	6.998	73.997	-6.793
3100	20.479	99.072	7.012	73.947	-6.753
3200	20.502	99.668	7.025	73.896	-6.716
3300	20.522	100.230	7.036	73.846	-6.682
3400	20.542	100.763	7.045	73.797	-6.650
3500	20.559	101.270	7.052	73.748	-6.619
3600	20.575	101.758	7.058	73.699	-6.589
3700	20.590	102.228	7.063	73.650	-6.560
3800	20.604	102.680	7.067	73.601	-6.532
3900	20.617	103.117	7.070	73.552	-6.505
4000	20.629	103.537	7.074	73.503	-6.479
4100	20.640	103.940	7.077	73.454	-6.454
4200	20.650	104.328	7.079	73.405	-6.429
4300	20.660	104.695	7.081	73.356	-6.404
4400	20.669	105.042	7.082	73.307	-6.380
4500	20.678	105.372	7.083	73.258	-6.356
4600	20.685	105.686	7.084	73.209	-6.332
4700	20.693	105.986	7.085	73.160	-6.309
4800	20.700	106.272	7.085	73.111	-6.286
4900	20.707	106.544	7.085	73.062	-6.263
5000	20.713	106.802	7.085	73.013	-6.240
5100	20.719	107.048	7.085	72.964	-6.217
5200	20.725	107.281	7.085	72.915	-6.194
5300	20.730	107.500	7.085	72.866	-6.171
5400	20.734	107.706	7.085	72.817	-6.148
5500	20.739	107.900	7.085	72.768	-6.125
5600	20.744	108.081	7.085	72.719	-6.102
5700	20.748	108.249	7.085	72.670	-6.079
5800	20.752	108.405	7.085	72.621	-6.056
5900	20.756	108.549	7.085	72.572	-6.033
6000	20.759	108.683	7.085	72.523	-6.010

March 31, 1961

C₂N₂

MOL. WT. = 52.038

(IDEAL GAS)

CYANOGEN (C₂N₂)

ΔH_f° 298.15 = 73.87 ± 0.43 kcal. mole⁻¹
 ΔG_f° 298.15 = 57.71 cal. deg.⁻¹ mole⁻¹

ΔH_f° 0 = 73.428 kcal. mole⁻¹
 Point Group D_{∞h}

Vibrational Levels and Multiplicities

(<i>v</i> , <i>m</i>)-1
2328.5 (1)
850.6 (1)
214.9 (1)
507.2 (2)
240 (2)

Rotational constant B₀ = 0.15752 ± 0.00015 cm.⁻¹ CN distance = 1.157 Å CC distance = 1.380 Å σ = 2

Moment of Inertia = 1.776 (g) × 10⁻³⁸ g. cm.²

Heat of Formation

J. W. Knowlton and E. J. Frosen, J. Research Natl. Bur. Standards 45, 489 (1951), report ΔH_f° 298.15 = -281.94 ± 0.43 kcal. for the reaction C₂N₂(g) + 2 O₂(g) → 2 CO₂(g) + N₂(g). When corrected for a change in the atomic weight of carbon, this becomes ΔH_f° 298.15 = -261.95 ± 0.43 kcal., whence ΔH_f° 298.15 for C₂N₂(g) is found to be 73.87 ± 0.43 kcal. mole⁻¹.

Heat Capacity and Entropy

A Langseth and C. K. Møller, Acta Chem. Scand. 4, 725 (1950), determined the vibrational frequencies by Raman spectroscopy. C. K. Møller and B. P. Stoicheff, Can. J. Phys. 32, 625 (1954), determined B₀ by Raman spectroscopy and calculated the bond lengths listed above. These agree with lengths found from electron-diffraction measurements by Langseth and Møller, loc. cit., (CN distance = 1.15 Å, CC distance = 1.38 Å) and L. Pauling, H. D. Springall, and K. J. Palmer, J. Am. Chem. Soc. 61, 927 (1939) (CN distance = 1.15 ± 0.02 Å, CC distance = 1.37 ± 0.02 Å). From measurements reported by R. A. Ruehrwein and W. F. Glaue, J. Am. Chem. Soc. 61, 2940 (1939), S_{298.15} is calculated by the third law to be 57.63 cal. deg.⁻¹ mole⁻¹, in satisfactory agreement with the value calculated here.

C₂N₂

Sodium Cyanide, Dimeric ((NaCN)₂)

(Ideal Gas)

Mol. Wt. = 98.0153

SODIUM CYANIDE, DIMERIC ((NaCN)₂)

(IDEAL GAS)



MOL. WT. = 98.0153

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔG _f ⁰	Log K _p
	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹ deg. ⁻¹		kcal. mole ⁻¹			
0	+0.00	INFINITE	-	5.340	1.982		INFINITE
100	16.175	59.048	104.034	-	2.294	3.207	7.009
200	23.539	73.050	85.231	-	2.436	4.479	4.479
298	25.737	82.932	82.932	+0.00	2.100	5.036	3.682
300	25.762	83.091	82.932	+0.048	2.097	5.054	3.682
400	26.716	90.647	83.926	2.676	3.346	5.948	3.250
500	27.339	96.678	85.918	5.380	3.465	6.586	2.879
600	27.867	101.710	88.142	8.141	3.614	7.196	2.621
700	28.366	106.000	90.000	10.900	3.786	7.786	2.427
800	28.776	109.696	92.595	13.406	3.987	8.336	2.277
900	29.115	113.268	94.706	16.706	4.203	8.869	2.154
1000	29.482	116.357	96.719	19.638	4.437	9.375	2.049
1100	29.763	119.181	98.635	22.601	4.700	9.861	1.959
1200	29.982	121.784	100.479	25.624	5.000	10.324	1.882
1300	30.206	124.191	102.191	28.600	5.357	10.769	1.812
1400	30.381	126.436	103.843	31.629	5.765	11.197	1.746
1500	30.530	128.537	105.420	34.675	6.230	11.611	1.681
1600	30.659	130.512	106.927	37.735	6.750	12.011	1.617
1700	30.776	132.369	108.369	40.800	7.320	12.397	1.553
1800	30.866	134.119	109.753	43.888	7.950	12.769	1.489
1900	30.930	135.806	111.081	46.979	8.640	13.127	1.425
2000	31.024	137.396	112.357	50.078	9.390	13.473	1.361
2100	31.088	138.911	113.586	53.184	10.200	13.807	1.297
2200	31.126	140.359	114.774	56.312	11.070	14.129	1.233
2300	31.146	141.744	115.913	59.460	12.000	14.439	1.169
2400	31.151	143.073	117.017	62.634	13.000	14.737	1.105
2500	31.282	144.349	118.085	65.861	14.070	15.023	1.041
2600	31.318	145.577	119.119	69.150	15.210	15.297	0.977
2700	31.340	146.760	120.130	72.500	16.420	15.559	0.913
2800	31.380	147.900	121.093	75.900	17.700	15.809	0.849
2900	31.406	149.002	122.026	79.350	19.050	16.047	0.785
3000	31.431	150.067	122.933	82.842	20.470	16.273	0.721
3100	31.453	151.098	123.844	86.386	21.960	16.487	0.657
3200	31.471	152.097	124.762	90.000	23.520	16.689	0.593
3300	31.491	153.066	125.689	93.730	25.150	16.879	0.529
3400	31.508	154.006	126.637	97.560	26.850	17.057	0.465
3500	31.524	154.919	127.612	101.490	28.620	17.223	0.401
3600	31.538	155.807	128.644	105.520	30.460	17.377	0.337
3700	31.550	156.672	129.732	109.650	32.370	17.519	0.273
3800	31.563	157.513	129.875	113.880	34.350	17.650	0.209
3900	31.575	158.333	130.205	118.210	36.400	17.770	0.145
4000	31.585	159.133	130.918	122.640	38.520	17.879	0.081
4100	31.595	159.913	131.616	127.170	40.710	17.977	0.017
4200	31.603	160.674	132.287	131.800	42.970	18.064	-0.047
4300	31.613	161.418	132.932	136.530	45.300	18.140	-0.111
4400	31.621	162.145	133.622	141.360	47.700	18.205	-0.175
4500	31.628	162.856	134.264	146.290	50.170	18.260	-0.239
4600	31.635	163.551	134.893	151.320	52.710	18.305	-0.303
4700	31.642	164.230	135.548	156.450	55.320	18.340	-0.367
4800	31.648	164.888	136.215	161.680	58.000	18.365	-0.431
4900	31.654	165.550	136.909	167.010	60.750	18.380	-0.495
5000	31.659	166.190	137.293	172.440	63.570	18.385	-0.559
5100	31.664	166.817	137.865	177.970	66.460	18.379	-0.623
5200	31.674	167.435	138.498	183.600	69.420	18.362	-0.687
5300	31.678	168.035	139.181	189.330	72.450	18.335	-0.751
5400	31.682	168.627	139.924	195.160	75.550	18.297	-0.815
5500	31.682	169.208	140.729	201.090	78.720	18.248	-0.879
5600	31.686	169.779	141.595	207.120	81.960	18.188	-0.943
5700	31.690	170.340	142.520	213.250	85.270	18.117	-1.007
5800	31.694	170.891	143.500	219.480	88.650	18.035	-1.071
5900	31.697	171.433	144.530	225.810	92.100	17.942	-1.135
6000	31.700	171.966	145.610	232.240	95.620	17.838	-1.199

Mar. 31, 1966

Point Group [D_{2h}]ΔH_f⁰ = [-2.0 ± 3] kcal. mole⁻¹S°_{298.15} = [82.93] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ΔH_f⁰ 298.15 = [-2.1 ± 3] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
[235](1)	[250](1)	[2176](1)
[175](1)	[290](1)	[2176](1)
[250](1)	[239](1)	[2176](1)
[170](1)	[239](1)	[2176](1)

Bond Distance: N-C = [1.16] Å C-Na = [2.19] Å

Bond Angle: C-Na-C = [105]° Na-C-Na = [75]° N-C-Na = [142.5]°

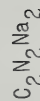
Product of the Moments of Inertia: I_AI_BI_C = [4.48269 X 10⁻¹¹³] g.³ cm.⁶

Heat of Formation.

The mass spectra of vapors from samples of NaCN have been observed by R. F. Porter, J. Chem. Phys. **35**, 318 (1961), at temperatures around 1000°K. The results indicate that the compound evaporates as NaCN(g) and Na₂(CN)₂(g). A comparison of relative ion currents produced by electron bombardment of NaCN vapors effusing from single - and double-oven-type Knudsen cells, yielded information on the partial pressures of monomer and dimer. Based on the partial pressures for NaCN(g) and (NaCN)₂(g) reported at temperatures, 803-1049°K., the vapor pressures of (NaCN)₂(g) over NaCN(l), 1078.2-1026.2°K., were calculated from the total vapor pressure measurements reported by C. K. Ingold, J. Chem. Soc. 123, 885 (1923). By the second and third law methods, the values of ΔH_f⁰ 298.15 (1 → dimer) were evaluated to be 38.89 and 38.21 kcal. mole⁻¹, respectively. Using the third law value, the heat of formation for (NaCN)₂(g) was evaluated.

Heat Capacity and Entropy.

The molecular structure, bond distances and C-Na-C bond angle were estimated by R. F. Porter, loc. cit. The vibrational frequencies were estimated by comparison with those for NaCl(g). The last six frequencies were the bending and asymmetric stretching frequencies for NaCN(g). The three principal moments of inertia are: I_A = 1.3570 X 10⁻³⁸, I_B = 5.1030 X 10⁻³⁸ and I_C = 6.4660 X 10⁻³⁸ g. cm.²



CCO Radical (C₂O)
(Ideal Gas) GFW = 40.0217

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log K _p
0	∞.000	∞.000	INFINITE	- 2.503	67.538	67.538	INFINITE
100	7.456	46.046	64.034	- 1.799	67.868	65.375	- 142.877
200	9.209	51.783	56.587	- .861	68.202	62.755	- 69.575
298	10.292	55.677	50.616	∞.000	68.500	60.016	- 43.993
300	10.309	55.741	50.633	∞.019	68.505	59.963	- 43.683
400	11.024	58.819	56.092	1.091	68.729	57.079	- 31.187
500	11.722	61.364	56.899	2.233	68.867	54.150	- 23.669
600	12.293	63.569	57.859	3.432	68.933	51.198	- 18.649
700	12.762	65.470	58.819	4.672	68.968	48.287	- 14.372
800	13.156	67.189	59.731	5.966	68.911	45.487	- 10.280
900	13.477	68.745	60.657	7.288	68.852	42.735	- 6.809
1000	13.727	70.170	61.559	8.640	68.779	39.993	- 3.460
1100	13.993	71.483	62.375	10.018	68.691	37.247	- 0.243
1200	14.275	72.685	63.105	11.340	68.597	34.500	- 2.983
1300	14.571	73.790	63.750	12.615	68.500	31.753	- 5.725
1400	14.880	74.808	64.326	13.842	68.399	29.007	- 8.467
1500	15.201	75.743	64.832	15.018	68.282	26.260	- 11.209
1600	15.534	76.597	65.268	16.143	68.150	23.513	- 13.951
1700	15.879	77.370	65.632	17.218	68.007	20.766	- 16.693
1800	16.235	78.061	65.926	18.243	67.855	18.019	- 19.435
1900	16.599	78.673	66.149	19.218	67.698	15.272	- 22.177
2000	16.970	79.206	66.300	20.143	67.538	12.525	- 24.919
2100	17.346	79.663	66.380	21.018	67.375	9.778	- 27.661
2200	17.727	80.048	66.390	21.843	67.209	7.031	- 30.403
2300	18.112	80.357	66.332	22.618	67.040	4.284	- 33.145
2400	18.500	80.593	66.197	23.343	66.868	1.537	- 35.887
2500	18.890	80.763	66.000	24.018	66.695	- 1.210	- 38.629
2600	19.281	80.868	65.747	24.643	66.522	- 3.963	- 41.371
2700	19.673	80.908	65.432	25.218	66.350	- 6.716	- 44.113
2800	20.066	80.873	65.067	25.743	66.179	- 9.469	- 46.855
2900	20.460	80.773	64.657	26.218	66.007	- 12.221	- 49.597
3000	20.854	80.608	64.212	26.643	65.835	- 14.974	- 52.339
3100	21.248	80.379	63.737	27.018	65.663	- 17.726	- 55.081
3200	21.642	80.086	63.232	27.343	65.490	- 20.478	- 57.823
3300	22.036	79.730	62.707	27.618	65.318	- 23.230	- 60.565
3400	22.430	79.317	62.162	27.843	65.146	- 25.982	- 63.307
3500	22.824	78.846	61.607	28.018	64.974	- 28.734	- 66.049
3600	23.218	78.317	61.032	28.143	64.802	- 31.486	- 68.791
3700	23.612	77.730	60.437	28.218	64.630	- 34.238	- 71.533
3800	24.006	77.086	59.812	28.243	64.458	- 36.990	- 74.275
3900	24.400	76.383	59.167	28.218	64.286	- 39.742	- 77.017
4000	24.794	75.630	58.500	28.143	64.114	- 42.494	- 79.759
4100	25.188	74.827	57.812	28.018	63.942	- 45.246	- 82.501
4200	25.582	73.969	57.100	27.843	63.770	- 47.998	- 85.243
4300	25.976	73.056	56.362	27.618	63.598	- 50.750	- 87.985
4400	26.370	72.086	55.600	27.343	63.426	- 53.502	- 90.727
4500	26.764	71.057	54.812	27.018	63.254	- 56.254	- 93.469
4600	27.158	69.969	54.000	26.643	63.082	- 59.006	- 96.211
4700	27.552	68.821	53.167	26.218	62.910	- 61.758	- 98.953
4800	27.946	67.614	52.212	25.743	62.738	- 64.510	- 101.695
4900	28.340	66.347	51.147	25.218	62.566	- 67.262	- 104.437
5000	28.734	65.020	50.000	24.643	62.394	- 70.014	- 107.179
5100	29.128	63.643	48.773	24.018	62.222	- 72.766	- 110.000
5200	29.522	62.216	47.500	23.343	62.050	- 75.518	- 112.821
5300	29.916	60.739	46.187	22.618	61.878	- 78.270	- 115.643
5400	30.310	59.212	44.832	21.843	61.706	- 81.022	- 118.465
5500	30.704	57.635	43.437	21.018	61.534	- 83.774	- 121.287
5600	31.098	56.008	42.000	20.143	61.362	- 86.526	- 124.109
5700	31.492	54.331	40.525	19.218	61.190	- 89.278	- 126.931
5800	31.886	52.604	39.000	18.243	61.018	- 92.030	- 129.753
5900	32.280	50.827	37.432	17.218	60.846	- 94.782	- 132.575
6000	32.674	49.000	35.812	16.143	60.674	- 97.534	- 135.397

June 30, 1968; Sept. 30, 1966

CCO RADICAL (C₂O)

(IDEAL GAS)

GFW = 40.0217

Point Group C_{∞v}ΔH_f⁰ = 67.5 ± 15 kcal/molΔH_f⁰ = 68.5 ± 15 kcal/molS_{298.15}⁰ = 55.7 gibbs/mol

Electronic Levels and Quantum Weights

ε, cm ⁻¹	g _i
0	3
[4050]	[2]
[6450]	[1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
1074 (1)
381 (2)
1978 (1)

C-O = [1.279] Å

Bond Distance: C-C = [1.160] Å

Bond Angle: C-C-O = [180]°

Rotational Constant: B₀ = [0.408475] cm⁻¹

σ = 1

Heat of Formation

The adopted heat of formation, ΔH_f⁰ = 68.5 kcal/mol, was calculated from the heat of reaction ΔH_f⁰ = 65.5 kcal/mol for C₂O(g) + CO(g) = C₂O₂(g) using all JANAF functions (dated Sept. 30, 1965). The value of ΔH_f⁰ was obtained from the third law calculation of the equilibrium constant (K_p = 3.3 x 10⁻⁶ atm at 1060°K) which was determined in the studies of decomposition rate of C₂O₂(g) by H. B. Palmer and W. D. Cross, Carbon 3, 475 (1966).

M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. 43, 3745 (1965), have observed the photo-dissociation of C₂O near 5000 Å, which corresponds to a minimum of 57 kcal/mol for C₂O(g) → C(g) + CO(g). This yields ΔH_f⁰(C₂O, g) ≤ 87 kcal/mol, which was not adopted because the irradiation was not monochromatic and thus possibly contained all wavelengths below 5000 Å.

Heat Capacity and Entropy

Jacox et al., loc. cit., have observed three vibrational fundamentals in the infrared spectrum by matrix isolation, and suggested a linear structure with Σ ground state for the CCO radical (g). They also estimated the bond distances C-C = 1.160 Å and C-O = 1.279 Å based on the structural analogy between the carbon suboxide and the CCO radical. The principal moment of inertia is 8.825 x 10⁻³⁵ g cm². K. D. Bayes, J. Am. Chem. Soc. 85, 1730 (1963), has predicted that the Λ and Σ states lie respectively 0.5 and 0.8 eV above the ground state. These two electronic states have been included in the tabulation.



$$\Delta H_f^\circ = 145.6 \pm 7 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 147 \pm 7 \text{ kcal/mol}$$

Point Group C_{∞v}

$$S^\circ_{298.15} = 56.55 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

ϵ_1 , cm ⁻¹	$\frac{g_1}{g_0}$
0	1
[13000]	[6]
20085	2

Vibrational Frequencies and Degeneracies

ω_1 , cm ⁻¹
853 (1)
300 (2)
1742 (1)

$$C-Si = [1.75] \text{ \AA}$$

$$g = 1$$

$$\text{Bond Distances: } C-C-Si = [1.28] \text{ \AA}$$

$$\text{Bond Angle: } C-C-Si = 180^\circ$$

$$\text{Rotational Constant: } B_0 = [0.012] \text{ cm}^{-1}$$

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor equilibria over the systems SiC-graphite¹, SiC-silicon², and boron-carbon-silicon³. Third law analysis of the partial pressures of C₂Si and Si lead to the concordant values 146.7, 149.0 and 146.0 kcal/mol. Although the drifts all suggest that the entropy of C₂Si may be about 3.5 eu less than tabulated, this is of doubtful significance because the uncertainty bands are so large. The low condensation coefficient suggested by Drowart⁴ may also be involved. Rates of free evaporation reported by Voronin⁵ lead to apparent pressures which are smaller by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of $\Delta H_f^\circ_{298} = 147 \pm 7$ kcal/mol includes allowance for the unlikely possibility that the entropy may be in error by up to 3.5 eu.

Source	Method	Reaction	Range, T°K	No. of Points	$\Delta H_f^\circ_{298}$ (kcal/mol)	Drift (eu)
Drowart (1958)	Mass Spec.	A	2149-2316	7	31±9	36.98
Drowart (1960)	" "	B	1835-2160	4	108±10	194.8
Verhaegen (1964)	" "	A	2166-2344	5	30±16	36.31
A) 2 C(graph) + Si(g) = C ₂ Si(g)						146.7
B) 2SiC(s) = Si(l) + C ₂ Si(g)						149.0
						146.0

Heat Capacity and Entropy.

The known molecular constants are from the assignments of Welter and McLeod⁵. These authors observed the infrared spectrum, emission spectrum and visible absorption spectrum of C₂Si in matrix isolation. The matrix data allowed more certain assignment of the A-X band system of the gas as observed by Klemm⁶ and McKellar⁷. Welter concluded that this system probably involves transitions between a ¹Σ⁺ ground state and a ¹Π excited state. The two stretching frequencies were observed in the matrix infrared spectrum, whereas the bending mode, 300 cm⁻¹, was derived solely from the analysis of the A-X band system. The analysis presumed a linear unsymmetrical structure for the molecule.

A ³Π excited state is assumed to lie 7000 cm⁻¹ below the ¹Π state, which presumably arises from the same molecular orbital configuration. The effect of the estimated level is to increase the entropy by about 0.2 and 1.8 eu at 3000 and 6000°K. Bond distances are estimated by comparison with those in Si₂, C₂ and C₃. The moment of inertia is 13.91 x 10⁻⁵⁹ g cm².

References.

1. J. Drowart, G. DeMaris and M. G. Ingham, *J. Chem. Phys.*, **29**, 1015 (1958).
2. J. Drowart and G. DeMaris, pp. 16-23 in *Silicon Carbide*, Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, New York, 1960.
3. G. Verhaegen, F. E. Stafford and J. Drowart, *J. Chem. Phys.*, **40**, 1622 (1964).
4. N. I. Voronin, N. L. Mekarova and B. P. Yudin, *Isolad.*, v Obl. Khim. Siliikatov i Okislav, Akad. Nauk SSSR, Sb. Statei 1955.
5. W. J. Welter, Jr., and D. McLeod, *Int. J. Chem. Phys.*, **41**, 235 (1964).
6. B. Klemm, *Astrophys. J.*, **123**, 62 (1956).
7. A. McKellar, *J. Roy. Astron. Soc. Canada*, **41**, 147 (1947).



Point Group D_{∞h}S_{298.15} = 56.7 ± 3 gibbs/mol

Ground State Quantum Weight = [1]

ΔHf⁰ = 194 ± 4 kcal/molΔHf⁰_{298.15} = 196 ± 4 kcal/molCarbon, Triatomic (C₃)

(Ideal Gas)

C₃

GFW = 36.03345

T, K	Cp ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H ^b - H ^c ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	1.000	∞	INFINITE	193.945	193.945	INFINITE	
100	10.146	46.107	65.054	194.819	194.819	415.638	
200	9.527	57.984	57.515	195.575	195.575	402.595	
298	9.020	58.677	56.677	196.006	196.006	400.317	132.116
300	9.015	56.733	56.677	196.005	196.005	180.220	131.290
400	8.962	59.310	57.029	196.162	196.162	174.928	95.576
500	8.917	61.330	57.694	196.111	196.111	169.692	74.142
600	8.890	63.029	58.485	195.905	195.905	166.340	59.865
700	8.829	65.518	59.208	195.600	195.600	159.103	49.674
800	10.153	65.952	59.957	195.223	195.223	153.915	42.048
900	10.448	67.065	60.680	194.792	194.792	148.774	36.127
1000	10.711	68.179	61.375	194.332	194.332	143.685	31.402
1100	10.943	69.241	62.041	193.846	193.846	138.642	27.586
1200	11.149	70.173	62.679	193.363	193.363	133.648	24.361
1300	11.332	71.072	63.291	192.820	192.820	128.693	21.635
1400	11.495	71.918	63.881	192.294	192.294	123.784	19.324
1500	11.642	72.716	64.440	191.759	191.759	118.909	17.325
1600	11.775	73.472	64.981	191.200	191.200	114.066	15.581
1700	11.895	74.190	65.502	190.661	190.661	109.261	14.046
1800	12.006	74.873	66.004	190.130	190.130	104.487	12.686
1900	12.108	75.525	66.488	189.599	189.599	99.745	11.473
2000	12.202	76.148	66.955	189.060	189.060	95.030	10.364
2100	12.290	76.746	67.407	188.523	188.523	90.345	9.402
2200	12.371	77.319	67.845	187.984	187.984	85.677	8.511
2300	12.448	77.871	68.269	187.449	187.449	81.044	7.701
2400	12.520	78.402	68.680	186.912	186.912	76.428	6.960
2500	12.588	78.915	69.079	186.379	186.379	71.833	6.280
2600	12.652	79.410	69.467	185.844	185.844	67.262	5.658
2700	12.712	79.884	69.844	185.311	185.311	62.708	5.076
2800	12.770	80.352	70.211	184.784	184.784	58.160	4.541
2900	12.825	80.801	70.569	184.257	184.257	53.659	4.045
3000	12.877	81.236	70.917	183.722	183.722	49.174	3.582
3100	12.927	81.659	71.257	183.184	183.184	44.700	3.151
3200	12.975	82.072	71.591	182.645	182.645	40.241	2.748
3300	13.020	82.470	71.912	182.104	182.104	35.791	2.370
3400	13.064	82.860	72.228	181.564	181.564	31.371	2.016
3500	13.106	83.239	72.538	181.074	181.074	26.953	1.683
3600	13.146	83.609	72.840	180.546	180.546	22.557	1.369
3700	13.184	83.972	73.136	179.994	179.994	18.178	1.076
3800	13.222	84.322	73.426	179.484	179.484	13.817	0.795
3900	13.258	84.666	73.709	178.951	178.951	9.466	0.530
4000	13.293	85.002	73.988	178.418	178.418	5.126	0.280
4100	13.326	85.330	74.260	177.883	177.883	0.795	0.02
4200	13.358	85.657	74.527	177.346	177.346	-3.510	-0.18
4300	13.390	85.977	74.790	176.805	176.805	-7.813	-0.397
4400	13.420	86.275	75.048	176.265	176.265	-12.103	-0.601
4500	13.450	86.577	75.300	175.721	175.721	-16.382	-0.796
4600	13.478	86.873	75.549	175.174	175.174	-20.641	-0.981
4700	13.505	87.167	75.793	174.624	174.624	-24.891	-1.157
4800	13.532	87.447	76.033	174.075	174.075	-29.125	-1.326
4900	13.558	87.727	76.268	173.521	173.521	-33.355	-1.488
5000	13.583	88.001	76.500	172.964	172.964	-37.570	-1.642
5100	13.608	88.270	76.729	172.401	172.401	-41.769	-1.791
5200	13.632	88.534	76.954	171.834	171.834	-45.954	-1.935
5300	13.654	88.794	77.174	171.269	171.269	-50.156	-2.084
5400	13.677	89.050	77.392	170.697	170.697	-54.335	-2.199
5500	13.698	89.301	77.606	170.119	170.119	-58.486	-2.324
5600	13.719	89.548	77.817	169.540	169.540	-62.601	-2.445
5700	13.739	89.794	78.024	168.964	168.964	-66.691	-2.562
5800	13.760	90.030	78.230	168.442	168.442	-70.921	-2.672
5900	13.780	90.266	78.432	167.877	167.877	-75.030	-2.779
6000	13.799	90.497	78.631	167.172	167.172	-79.154	-2.883

Dec. 31, 1960, Dec. 31, 1969

The contribution of the doubly degenerate bending frequency was approximated by direct summation of the following levels (cm⁻¹): 0, 63.5, 132.7, 207.4, 286.5, 370.5, 458.2, and 650 x n where n = 1 to 76. The contribution to each function due to these levels was doubled to account for the degeneracy.

Bond Distance: C-C = 1.277 Å

Bond Angle: C-C-C = 180°

Rotational Constant: B₀ = 0.4305 cm⁻¹

σ = 2

Heat of Formation

Drowart et al. (1) have measured mass spectrometrically the ion intensity ratio C₃⁺/C⁺ as a function of temperature from 1800 to 2700°K. We derive from a 2nd law analysis of their data ΔH₂₇₀₀⁰ = 185.2 ± 3.3 kcal, and S₂₀₀₀⁰ = 74.9 ± 2.8 eu by calculation of the absolute pressure from the vapor pressure of monatomic carbon and a relative ionization cross-section ratio of 2.3. The entropy uncertainty includes 1.3 eu for uncertainty in the absolute pressure. Several earlier mass-spectrometric determinations (2, 3, 4) are in reasonable agreement. The absolute magnitude of the pressure is also confirmed by the work of Thorm and Winslow (5) who measured the total pressure of all species over graphite as 1.2 to 4.8 x 10⁻⁷ atm. at 2400°K.

Subtracting the JANAF values for C and C₂ we obtain C₃ = 5.4 x 10⁻⁸ to 2.2 x 10⁻⁷ atm., which compares with Drowart's value of 3.3 x 10⁻⁸ to 1.3 x 10⁻⁷ atm. The 2nd law heat of formation is reported (3) to be ΔH₂₄₀₀⁰ = 184.4 but the range is only 80°K. It does, however, confirm the magnitude of the mass-spectrometric values for both heat and entropy. We have adopted a heat of formation within the uncertainty limits of Drowart's measurements which with the adopted functions yields pressures in the 2000-3000°K range consistent with the measurements. We were not able to generate functions which agree exactly with the 2nd law entropies, since even direct summation over only the observed levels of the bending frequency gives an entropy which is already too large.

Heat Capacity and Entropy

The stretching frequencies are from Merer (6), Weltner et al. (7) and Weltner and McLeod (8). The bending frequency and its harmonics are from Gausset et al. (9) and Merer (6). The rotational constant and bond distance are from Gausset et al. (9).

As indicated briefly above, the calculated entropy of C₃ gas is higher than the experimental value even when a summation is performed only over the observed first six levels of the bending frequency. Treatment of the vibration as a harmonic oscillator or as an anharmonic oscillator gives values considerably higher. Straus and Thiele (10) have also calculated functions based on a quartic potential function which still yields values several units higher than the experiments. In order to reduce the entropy to the approximate range of the measurements we have made the assumption that the potential function is of an unusual form above the sixth vibrational level. We assume that the large amplitude of the bending vibration causes a drastic change in the function, possibly due to the increasing repulsion between end carbons, as the amplitude increases. Thus, we assume a very steeply rising potential above the sixth vibrational level. We have chosen to represent this part of the potential by a harmonic oscillator of 650 cm⁻¹. The choice of 650 cm⁻¹ is arbitrary, but is not unreasonable for a bending vibration, and yields functions which approximate the experimental data.

In order to explain the observed spectrum of C₃O₂, a molecule with a bending frequency of 63 cm⁻¹, Smith and Barrett (11) have proposed that potential maxima occur in the bending potential away from linearity. Thus, the adoption of an unusual potential function for C₃ bending may be justifiable. We do not claim that our functions are necessarily correct but only that they include all known facts and satisfy the experimental equilibrium observations. Further investigation of the carbon vapor pressure and of the higher vibrational levels of C₃ is desirable.

References

1. J. Drowart, R. P. Burns, G. Delaria, and M. G. Inghram, *J. Chem. Phys.* **31**, 1131 (1959).
2. W. A. Chupka and M. G. Inghram, *J. Phys. Chem.* **59**, 100 (1955).
3. W. A. Chupka and M. G. Inghram, *J. Chem. Phys.* **21**, 371 and 1313, (1953).
4. R. E. Honig, *J. Chem. Phys.* **22**, 126 (1954).
5. R. J. Thorm and G. H. Winslow, *J. Chem. Phys.* **26**, 186 (1957).
6. A. J. Merer, *Can. J. Phys.* **45**, 4103 (1967).
7. W. Weltner, P. N. Walsh and C. L. Angell, *J. Chem. Phys.* **40**, 1299 (1964).
8. W. Weltner and D. McLeod, *J. Chem. Phys.* **40**, 1305 (1964).
9. L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *Astrophys. J.* **142**, 45 (1965).
10. H. L. Straus and E. Thiele, *J. Chem. Phys.* **46**, 2473 (1967).
11. W. H. Smith and J. J. Barrett, *J. Chem. Phys.* **51**, 1475 (1969).

(Crystal) Mol. Wt. = 143.95945

TETRALUMINUM TRICARBIDE (Al₄C₃)

(CRYSTAL)

MOL. WT. = 143.95945

T, °K. C_p cal. mole⁻¹ deg.⁻¹ S° - (H° - H°₂₉₈)/T H° - H°₂₉₈ kcal. mole⁻¹ ΔH_f⁰ ΔF_f⁰ Log K_p

0	-0.00	INFINITE	3.936	-	50.354	-	50.354	INFINITE
100	7.099	2.808	40.088	3.728	-	50.612	-	109.641
200	19.622	11.759	23.579	2.364	-	51.250	-	54.102
298	27.912	21.264	21.264	0.000	-	51.550	-	48.602
300	28.035	21.437	21.265	0.052	-	51.554	-	48.585
400	33.104	30.269	22.434	3.134	-	51.598	-	47.581
500	36.064	37.997	24.792	6.603	-	51.594	-	46.579
600	38.050	44.757	27.568	10.313	-	51.642	-	45.575
700	39.479	50.734	30.459	14.192	-	51.786	-	44.553
800	40.704	55.878	33.133	18.126	-	52.000	-	43.519
900	41.411	60.907	35.413	22.206	-	52.372	-	42.419
1000	42.099	65.307	38.834	26.473	-	52.801	-	40.552
1100	42.669	69.346	41.426	30.712	-	52.831	-	38.322
1200	43.150	73.080	43.911	35.004	-	53.047	-	36.077
1300	43.543	76.541	46.183	39.348	-	53.282	-	33.864
1400	43.922	79.793	48.568	43.714	-	53.535	-	31.664
1500	44.239	82.834	50.752	48.123	-	53.535	-	29.497
1600	44.521	85.698	52.848	52.561	-	53.407	-	27.028
1700	44.704	88.395	54.860	57.026	-	53.464	-	24.735
1800	44.876	90.952	56.791	61.519	-	53.505	-	22.582
1900	45.021	93.410	58.659	66.026	-	53.547	-	20.191
2000	45.406	95.734	60.455	70.557	-	53.571	-	17.909
2100	45.562	97.953	62.188	75.105	-	53.584	-	15.626
2200	45.710	100.076	63.863	79.669	-	53.593	-	13.345
2300	45.852	102.100	65.493	84.250	-	53.598	-	11.064
2400	45.982	104.055	67.089	88.839	-	53.584	-	8.773
2500	46.106	105.945	68.567	93.443	-	53.568	-	6.490
2600	46.222	107.755	70.040	98.060	-	53.548	-	4.211
2700	46.330	109.502	71.469	102.687	-	53.521	-	1.936
2800	46.430	111.189	72.849	107.328	-	53.489	-	-0.341
2900	46.522	112.819	74.208	111.973	-	53.452	-	-2.640
3000	46.606	114.398	75.522	116.630	-	53.400	-	-4.948

Dec. 31, 1960; June 30, 1963; Sept. 30, 1965

$\Delta H_f^0 = -50.35 \pm 1.6$ kcal. mole⁻¹
 ΔH_f^0 298.15 = -51.55 \pm 1.6 kcal. mole⁻¹
 ΔH_m^0 = Unknown

$S_{298.15} = 21.26 \pm 0.3$ cal. deg.⁻¹ mole⁻¹
 $T_m = [2500]^\circ K.$

Heat of Formation.

The ΔH_f^0 298.15 = -51.55 \pm 1.6 kcal. mole⁻¹ is the average value of ΔH_f^0 298.15 = -49.7 \pm 1.2 kcal. mole⁻¹ by R. C. King and G. T. Armstrong, National Bureau of Standards Report No. 8504 (1964) and that of ΔH_f^0 298.15 = -53.4 \pm 2.0 kcal. mole⁻¹ by A. D. Meh, United States Bureau of Mines, Report No. 6415 (1964). Both measured the heat of reaction $Al_4C_3(c) + 6O_2(g) \rightarrow 2Al_2O_3(c, w) + 3CO_2(g)$ and used their ΔH_f^0 298.15 and the ΔH_f^0 298.15 of $Al_2O_3(c)$ and $CO_2(g)$ to calculate the ΔH_f^0 298.15 of $Al_4C_3(c)$. The ΔH_f^0 298.15 measured by King and Armstrong was -1033.3 \pm 1.1 kcal. mole⁻¹, the ΔH_f^0 298.15 measured by Meh was -1029.6 \pm 1.9 kcal. mole.

Heat Capacity and Entropy.

The low temperature heat capacities, 18-390°K., were measured by W. G. Saba and G. T. Furukawa, National Bureau of Standards Report 7587, July 1, 1962. The high temperature heat capacities, 275-1173°K., were measured by A. C. Victor, W. R. Thurber, and T. B. Douglas, National Bureau of Standards Report 7437, January 1, 1962. These two sets of heat capacity data were joined smoothly and extrapolated to 2000°K. by W. G. Saba and G. T. Furukawa, loc. cit. The values of C_p above 2000°K. were estimated by extrapolation graphically. $S_{298.15}^0$ was reported by W. G. Saba and G. T. Furukawa, loc. cit., using $S_{298.15}^0(\text{extrap.}) = 0.013$ cal. deg.⁻¹ mole⁻¹.

Melting Temperature.

T_m was estimated by O. Ruff and E. Jellinek, Z. anorg. u. allgem. Chem. 37, 312 (1916).

Dimagnesium Tricarbide (Mg_2C_3)

(Solid) Mol. Wt. = 84.67

INTERIM TABLE

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K_p
0							
100	22.410	24.700	24.000	.000	19.000	17.729	12.995
200	22.500	24.139	24.000	.042	19.008	17.721	12.909
300	25.660	31.105	24.929	2.470	19.478	17.223	9.410
400	27.260	37.019	26.772	5.124	19.901	16.606	7.258
500	28.250	42.084	28.912	7.903	20.224	15.916	5.797
600	29.490	46.395	31.286	10.784	20.468	15.184	4.731
700	29.890	50.195	33.786	13.687	20.528	14.425	3.931
800	29.940	53.695	35.885	16.659	20.518	13.662	3.317
900	30.340	57.071	37.397	19.673	16.171	13.257	2.887
1000	30.700	59.979	39.320	22.726	16.056	12.972	2.577
1100	31.130	62.663	41.802	25.912	15.850	12.649	2.313
1200	31.450	65.145	44.000	29.120	15.582	12.282	2.092
1300	31.650	67.495	46.580	32.081	15.262	11.874	1.910
1400	31.850	69.689	48.182	35.261	14.886	11.434	1.751
1500	32.280	71.760	49.716	38.471	14.465	10.966	1.616
1600	32.520	73.409	50.409	41.679	14.004	10.479	1.504
1700	32.680	74.800	51.066	44.829	13.504	9.974	1.416
1800	32.770	76.074	51.686	47.969	12.972	9.456	1.345
1900	32.800	77.271	52.279	51.074	12.406	8.921	1.287
2000	32.820	78.404	52.847	54.157	11.804	8.371	1.241
2100	32.830	79.480	53.397	57.213	11.174	7.806	1.204
2200	32.840	80.500	53.927	60.249	10.513	7.227	1.174
2300	32.850	81.470	54.437	63.269	9.821	6.634	1.149
2400	32.860	82.390	54.927	66.269	9.100	6.029	1.126
2500	32.870	83.260	55.397	69.249	8.359	5.414	1.104

DI-MAGNESIUM TRICARBIDE (Mg_2C_3)

(Solid)

Mol. Wt. = 84.67

ΔH°_f 298.15 = 19 ± 8 kcal. mole⁻¹

$S^\circ_{298.15}$ = 24 ± 3 cal. deg.⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

(Ideal Gas)

GFW = 68.03225

(IDEAL GAS)

CARBON SUBOXIDE (C₃O₂)

GFW = 68.03225

T, °K	Cp°	$\frac{dh_{\text{sub}}}{dT} - (C_p - H^{\circ}_{\text{sub}})/T$	$H^{\circ} - H^{\circ}_{\text{sub}}$	kcal/mol ΔH°	ΔG°	Log Kp
0	16.452	11.111	3.589	23.138	23.138	INFINITE
100	16.454	51.596	2.688	23.933	23.933	52.277
200	16.456	60.096	67.345	22.685	25.008	27.328
298	16.459	65.959	1.430	22.380	25.008	19.219
300	16.452	66.058	0.30	22.375	26.284	19.119
400	16.454	66.062	1.430	22.375	26.284	19.119
500	16.456	66.064	3.598	21.984	26.958	12.957
600	20.436	78.725	5.587	21.844	30.372	11.063
700	21.368	81.948	7.679	21.805	31.766	9.527
800	22.147	84.853	9.856	21.803	32.224	8.076
900	22.819	87.591	12.104	21.803	32.675	6.845
1000	23.337	89.931	14.411	21.808	33.075	5.788
1100	23.787	92.177	16.768	21.919	37.495	7.450
1200	24.164	94.264	19.166	21.977	38.906	7.086
1300	24.480	96.111	21.596	22.048	40.315	6.778
1400	24.745	97.750	24.061	22.135	41.711	6.521
1500	24.973	99.168	26.569	22.235	43.100	6.307
1600	25.167	101.468	29.054	22.349	44.587	6.079
1700	25.332	102.969	31.529	22.478	45.893	5.900
1800	25.476	104.451	34.000	22.620	47.216	5.749
1900	25.600	105.916	36.468	22.776	48.559	5.614
2000	25.708	107.368	38.928	22.946	50.025	5.466
2100	25.804	108.805	41.389	23.130	51.389	5.348
2200	25.887	110.227	43.840	23.329	52.759	5.241
2300	25.962	111.635	46.288	23.534	54.133	5.142
2400	26.028	113.029	48.728	23.754	55.516	5.050
2500	26.086	114.409	51.166	23.989	56.922	4.967
2600	26.139	115.773	53.609	24.241	58.365	4.889
2700	26.186	117.121	56.054	24.507	59.841	4.817
2800	26.229	118.454	58.504	24.786	61.349	4.749
2900	26.268	119.774	60.959	25.078	62.889	4.685
3000	26.303	121.080	63.420	25.383	64.460	4.626
3100	26.335	122.371	65.886	25.699	66.062	4.570
3200	26.364	123.646	68.356	26.027	67.696	4.517
3300	26.390	124.906	70.830	26.367	69.363	4.468
3400	26.413	126.152	73.299	26.719	71.062	4.424
3500	26.433	127.384	75.764	27.083	72.791	4.376
3600	26.452	128.601	78.224	27.458	74.550	4.333
3700	26.467	129.804	80.679	27.844	76.341	4.292
3800	26.479	130.994	83.129	28.241	78.164	4.253
3900	26.489	132.171	85.574	28.648	80.020	4.216
4000	26.496	133.336	88.014	29.066	81.910	4.180
4100	26.500	134.489	90.449	29.494	83.833	4.146
4200	26.504	135.631	92.879	29.932	85.790	4.113
4300	26.506	136.762	95.304	30.380	87.781	4.082
4400	26.508	137.884	97.724	30.838	89.806	4.052
4500	26.508	138.996	100.139	31.306	91.866	4.022
4600	26.508	140.100	102.549	31.784	93.960	3.994
4700	26.508	141.194	104.954	32.272	96.088	3.967
4800	26.508	142.279	107.354	32.770	98.250	3.940
4900	26.508	143.354	109.749	33.278	100.446	3.914
5000	26.508	144.420	112.139	33.796	102.676	3.889
5100	26.508	145.477	114.524	34.324	104.940	3.866
5200	26.508	146.524	116.904	34.862	107.238	3.843
5300	26.508	147.561	119.279	35.410	109.570	3.820
5400	26.508	148.589	121.649	35.968	111.936	3.797
5500	26.508	149.608	124.014	36.536	114.336	3.776
5600	26.508	150.618	126.374	37.114	116.770	3.756
5700	26.508	151.619	128.729	37.702	119.238	3.736
5800	26.508	152.611	131.079	38.300	121.740	3.716
5900	26.508	153.594	133.424	38.908	124.276	3.696
6000	26.508	154.568	135.764	39.526	126.846	3.677

Dec. 31, 1960; Sept. 30, 1965; June 30, 1968

Point Group D_{2h}S_{298.15} = 65.959 ± 0.2 gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
2200 (1)	2258 (1)	550 (2)
830 (1)	1573 (1)	63 (2)
	577 (2)	

Bond Distances: C-C = 1.28 Å C-O = 1.16 Å

Bond Angles: C-C-C = 180° O-C-C = 180°

Rotational Constant: B₀ = 0.073206 cm⁻¹

σ = 2

Heat of Formation

Kybett et al. (1) have determined the heat of combustion of the liquid form under its own pressure using the sample from the heat capacity determinations (2).

The average of four determinations gave $\Delta H^{\circ}_{298}(l) = -28.03 \pm 0.24$ kcal/mol; the authors report -29.03 due to an arithmetic error. The sample was 99.98 mole percent pure. McDougall et al. (2) measured $\Delta H^{\circ}_{298}(g) = 6.421 \pm 0.012$ kcal/mol from which we calculate $\Delta H^{\circ}_{298}(g) = 5.65 \pm 0.2$ kcal/mol. Thus the heat of formation of the gas is found to be -22.38 ± 0.44 kcal/mol.

Heat Capacity and Entropy

There has been considerable controversy as to the configuration of this molecule and the assignment of its vibrational frequencies. However, the evidence seems fairly conclusive for the linearity of the molecule from the work of Lafferty et al. (3) and Miller et al. (4). The rotational constant adopted here is that found by Lafferty et al. (3) and the vibrational frequencies are those reported by Miller et al. (4), except for ν_7 which is taken from Miller et al. (5) and Borgers (7). The low frequency ν_u mode is confirmed by the work of McDougall et al. (2), who measured the low temperature entropy of C₃O₂(c) and (4) and also the heat of vaporization. From a comparison of the entropy calculated statistically and that measured, they conclude $\nu_7 = 63.2$ cm⁻¹. The values adopted are confirmed by third law analysis of the vapor pressure data of McDougall et al. (5) which indicate a heat of vaporization in fair agreement with their calorimetric value. The drift in the third law analysis indicates that the entropy of the solid is too low or that of the gas is too high by 1 eu. Alternatively as systematic error in the pressure measurements could have caused this deviation.

The bond distances are taken from the electron diffraction experiments of Livingston et al. (6) and are in good accord with the adopted rotational constant.

References

1. B. D. Kybett, G. K. Johnson, C. K. Barker and J. L. Margrave, J. Phys. Chem. **69**, 3603 (1965).
2. L. A. McDougall and J. E. Kilpatrick, J. Chem. Phys. **42**, 2311 (1965).
3. W. J. Lafferty, A. G. Vaki and E. K. Plyler, J. Chem. Phys. **40**, 224 (1964).
4. F. A. Miller and W. G. Fateley, Spectrochim. Acta **20**, 753 (1964).
5. F. A. Miller, D. H. Lemmon and R. E. Witkowski, Spectrochim. Acta **21**, 1709-16 (1965).
6. R. L. Livingston and C. N. Rao, J. Am. Chem. Soc. **81**, 285 (1959).
7. T. R. Borgers, Ph.D. Thesis, University of California, Berkeley, 1961.

T, °K	C _p ^a	S ^b	(C ^c -H ^c 300)/T	H ^c -H ^c 300	ΔH ^d	ΔG ^e	Log K ^f
0	+0.00	INFINITE	2.579	230.429	230.429	INFINITE	INFINITE
100	7.138	64.675	63.449	1.861	231.071	226.667	-495.428
200	9.311	50.253	58.567	1.063	231.577	242.702	-242.702
298	11.892	54.543	54.543	+0.00	232.004	217.339	-159.328
300	12.031	54.618	54.544	-0.22	232.004	217.267	-156.279
400	13.780	58.333	55.038	1.318	232.418	212.305	-115.998
500	15.057	61.552	56.026	2.763	232.467	207.279	-90.601
600	16.045	64.368	57.188	4.320	232.532	202.259	-73.662
700	16.831	66.523	58.401	7.265	231.463	172.215	-51.485
800	17.456	68.119	59.581	10.531	230.587	162.181	-39.851
900	17.973	71.500	60.796	9.454	232.157	187.131	-45.842
1000	18.367	73.216	61.944	11.272	231.676	192.136	-39.406
1100	18.725	74.995	63.050	13.129	231.741	177.102	-35.199
1200	19.003	76.627	64.114	15.015	231.463	172.215	-31.485
1300	19.248	78.139	65.137	16.911	230.809	167.280	-28.199
1400	19.468	79.530	66.119	18.861	230.609	162.305	-25.248
1500	19.668	80.936	67.061	20.872	230.664	157.350	-22.948
1600	19.824	82.204	67.868	22.672	230.280	152.632	-20.649
1700	19.941	83.404	68.681	24.756	229.972	147.768	-18.999
1800	20.032	84.531	69.412	26.744	229.514	136.159	-15.999
1900	20.076	85.591	70.092	28.744	228.846	124.619	-13.304
2000	20.104	86.650	71.275	30.751	228.683	133.370	-14.578
2100	20.169	87.633	72.031	32.764	228.668	128.603	-13.304
2200	20.227	88.573	72.761	34.784	228.338	123.838	-12.032
2300	20.278	89.473	73.473	36.804	227.762	119.378	-10.587
2400	20.328	90.337	74.159	38.820	227.452	114.378	-9.147
2500	20.364	91.167	74.818	40.844	227.262	109.664	-7.987
2600	20.400	91.967	75.462	42.912	226.904	104.968	-8.923
2700	20.432	92.737	76.046	45.024	226.546	100.260	-9.117
2800	20.468	93.499	76.587	47.164	226.188	95.559	-9.653
2900	20.498	94.249	77.087	49.084	225.830	90.949	-6.999
3000	20.512	94.994	77.662	51.096	225.468	86.313	-6.268
3100	20.533	95.567	78.223	53.168	225.076	81.665	-5.759
3200	20.553	96.219	78.769	55.203	224.699	77.065	-5.263
3300	20.571	96.852	79.301	57.237	224.332	72.460	-4.800
3400	20.589	97.469	79.826	59.270	223.976	67.850	-4.361
3500	20.603	98.064	80.327	61.377	223.537	63.266	-3.991
3600	20.617	98.644	81.023	63.438	223.162	58.693	-3.563
3700	20.630	99.209	81.507	65.500	222.780	54.134	-3.198
3800	20.642	99.761	81.980	67.553	222.382	49.572	-2.832
3900	20.653	100.300	82.449	69.597	221.976	45.010	-2.466
4000	20.663	100.819	82.895	71.684	221.550	40.523	-2.218
4100	20.673	101.329	83.339	73.761	221.089	35.994	-1.919
4200	20.682	101.828	83.773	75.869	220.661	31.495	-1.639
4300	20.690	102.314	84.199	77.977	220.260	27.050	-1.375
4400	20.705	102.785	84.625	80.037	219.881	22.650	-1.122
4500	20.705	103.255	85.025	82.037	219.531	18.104	-0.875
4600	20.712	103.710	85.426	84.108	219.468	13.551	-0.648
4700	20.718	104.156	85.820	86.179	219.431	9.094	-0.423
4800	20.730	104.591	86.206	88.206	219.420	4.700	-0.205
4900	20.738	105.016	86.586	90.234	219.429	0.280	-0.001
5000	20.735	105.438	86.959	92.397	217.013	=	4.218
5100	20.740	105.849	87.325	94.471	216.523	=	36.528
5200	20.745	106.252	87.685	96.545	216.099	=	38.974
5300	20.753	106.645	88.039	98.616	215.656	=	41.462
5400	20.761	107.029	88.386	100.679	215.256	=	43.933
5500	20.757	107.416	88.730	102.770	214.898	=	46.406
5600	20.761	107.799	89.067	104.846	213.974	=	48.808
5700	20.765	108.157	89.399	106.923	213.474	=	51.241
5800	20.768	108.518	89.725	108.999	212.895	=	53.695
5900	20.774	108.869	90.046	111.066	212.356	=	56.179
6000	20.774	109.223	90.364	113.156	211.786	=	58.686

Dec. 31, 1960; Dec. 31, 1959



Tetramethylsilane (Si(CH₃)₄)
(Ideal Gas) Mol. Wt. = 88.230

INTERIM TABLE

T, °K.	cal. mole ⁻¹ deg. ⁻¹		kcal. mole ⁻¹		Log K _p
	C _p ^o	S ^o	H ^o - H ₂₉₈ ^o	ΔF _T ^o	
0					
100					
298	33.120	86.300	86.300	0.000	25.989
300	33.240	86.505	86.301	0.061	25.660
400	40.060	96.896	186.596	8.722	13.258
500	46.310	106.617	300.520	18.048	5.233
600	51.690	115.548	430.956	27.955	0.077
700	56.370	123.675	577.642	38.363	3.936
800	60.470	131.077	741.414	49.210	6.968
900	64.060	137.811	921.182	60.458	9.868
1000	67.200	143.933	109.920	72.015	11.922
1100	70.040	152.477	112.595	83.661	12.345
1200	72.440	158.678	116.170	91.010	13.616
1300	74.620	164.566	119.666	96.367	14.991
1400	76.460	170.157	123.107	101.596	15.567
1500	78.080	175.466	126.395	107.651	16.606

December 31, 1960.

Tetramethylsilane (Si(CH₃)₄) (Ideal Gas)

Mol. Wt. = 88.230
ΔH_f^o 298.15 = (-68.5) kcal. mole⁻¹
S_{298.15}^o = 86.300 cal. deg.⁻¹ mole⁻¹
Point Group T_d

Heat of Formation. ΔH_f^o 298.15 was estimated.

Heat Capacity and Entropy. C_p and S_{298.15} were taken from G. Janz, Y. Miawa, and F. Behnke, private communication, March 16, 1960.

Tetracarbon Dinitride (C₄N₂)

(Ideal Gas) Mol. Wt. = 76.06

C₄N₂

MOL. WT. = 76.06

(IDEAL GAS)

TETRACARBON DINITRIDE (C₄N₂)

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	Log K _p
100	11.900	51.900	126.341	126.341	10.711
200	17.205	61.766	126.937	126.937	10.711
298	20.558	69.314	127.500	127.500	10.711
300	20.576	69.441	127.509	127.509	10.711
400	24.162	80.892	128.363	128.363	10.711
500	25.370	89.397	129.016	129.016	10.711
600	26.391	95.655	129.478	129.478	10.711
700	27.156	100.907	129.798	129.798	10.711
800	27.686	105.533	129.998	129.998	10.711
900	28.017	109.692	130.106	130.106	10.711
1000	28.187	113.237	130.141	130.141	10.711
1100	29.141	101.969	128.981	128.981	10.711
1200	29.562	104.524	129.364	129.364	10.711
1300	29.755	106.907	129.608	129.608	10.711
1400	29.861	109.152	129.743	129.743	10.711
1500	30.542	111.237	129.786	129.786	10.711
1600	30.773	113.215	129.820	129.820	10.711
1700	30.972	115.087	129.848	129.848	10.711
1800	31.145	116.861	129.870	129.870	10.711
1900	31.295	118.539	129.886	129.886	10.711
2000	31.426	120.119	129.897	129.897	10.711
2100	31.541	121.695	129.902	129.902	10.711
2200	31.642	123.165	129.902	129.902	10.711
2300	31.732	124.574	129.897	129.897	10.711
2400	31.811	125.926	129.886	129.886	10.711
2500	31.884	127.226	129.870	129.870	10.711
2600	31.948	128.478	129.848	129.848	10.711
2700	32.006	129.685	129.820	129.820	10.711
2800	32.058	130.849	129.786	129.786	10.711
2900	32.106	131.974	129.743	129.743	10.711
3000	32.148	133.064	129.692	129.692	10.711
3100	32.187	134.119	129.634	129.634	10.711
3200	32.222	135.142	129.569	129.569	10.711
3300	32.255	136.134	129.498	129.498	10.711
3400	32.287	137.094	129.421	129.421	10.711
3500	32.312	138.033	129.338	129.338	10.711
3600	32.337	138.944	129.249	129.249	10.711
3700	32.361	139.830	129.154	129.154	10.711
3800	32.382	140.693	129.054	129.054	10.711
3900	32.403	141.535	128.948	128.948	10.711
4000	32.421	142.356	128.836	128.836	10.711
4100	32.438	143.156	128.718	128.718	10.711
4200	32.453	143.938	128.594	128.594	10.711
4300	32.470	144.702	128.464	128.464	10.711
4400	32.484	145.446	128.328	128.328	10.711
4500	32.497	146.179	128.186	128.186	10.711
4600	32.509	146.893	128.038	128.038	10.711
4700	32.521	147.592	127.884	127.884	10.711
4800	32.532	148.277	127.724	127.724	10.711
4900	32.542	148.948	127.558	127.558	10.711
5000	32.552	149.606	127.386	127.386	10.711
5100	32.561	150.250	127.208	127.208	10.711
5200	32.569	150.883	127.024	127.024	10.711
5300	32.577	151.503	126.834	126.834	10.711
5400	32.585	152.112	126.638	126.638	10.711
5500	32.592	152.710	126.436	126.436	10.711
5600	32.599	153.297	126.228	126.228	10.711
5700	32.606	153.875	126.014	126.014	10.711
5800	32.612	154.442	125.794	125.794	10.711
5900	32.618	154.999	125.568	125.568	10.711
6000	32.624	155.546	125.336	125.336	10.711

March 31, 1961

$\Delta H_f^\circ = 126.3 \pm 0.2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 127.5 \pm 0.2 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = 69.31 \pm 0.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Point Group D_{2h}

Vibrational Levels and Multiplicities

$\omega_{cm.}^{-1}$	$\omega_{cm.}^{-1}$	$\omega_{cm.}^{-1}$
2230 (1)	2241 (1)	265 (2)
2119 (1)	1154 (1)	472 (2)
692 (1)	504 (2)	107 (2)

Bond Distances CN 1.14 Å C-C 1.37 Å C≡C 1.19 Å

Moment of Inertia I = 61.65 X 10⁻³⁹ g. cm.² σ = 2

Heat of Formation

O. T. Armstrong and S. Marantz, J. Phys. Chem. 64, 1776 (1960), measured the heat of combustion of the liquid for which they obtain a ΔH_f° 298.15 of 120.6 kcal. mole⁻¹ using 94.05 kcal. mole⁻¹ for ΔH_f° 298.15 of CO₂(g). They calculate the ΔH_f° 298.15 of C₄N₂(g) with a ΔH_{vap} taken from A. J. Saggio, J. Org. Chem. 22, 1171 (1957).

Heat Capacities and Entropies

Bond lengths determined by P. A. Miller and R. B. Hamman Jr., J. Chem. Phys. 21, 110 (1953) from X-ray diffraction measurements on the solid. The vibrational frequencies were observed in the infra red and Raman by F. A. Miller, R. B. Hamman Jr., and L. R. Cousins, J. Chem. Phys. 23, 2127 (1955).

C₄N₂

Carbon, Pentatomic (C₅)

GFW = 60.05575

Point Group [D_{3h}]S_{298.15} = 57.8 ± 4 gibbs/molGround State Configuration [1²]ΔHf₀⁰ = 232.4 ± 6 kcal/molΔHf_{298.15}⁰ = 234 ± 6 kcal/mol

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	ω_i , cm ⁻¹
[1320] (1)	[550] (2)
[770] (1)	[550] (2)
[2210] (1)	[550] (2)
[1430] (1)	

Bond Distance: C-C = [1.28] Å

Bond Angle: C-C-C = [180°]

Rotational Constant = B₀ = [0.085682] cm⁻¹

σ = 2

Heat of Formation

The heat of formation is obtained from the mass-spectrometric results of Drowart et al. (1) who obtained ΔHf_{298.15}⁰ = 230 ± 5 kcal/mol. This was obtained from a 2nd law analysis of the ion intensity ratio C₅⁺/C⁺ over a temperature range of 2200-2700°K. The absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross-section ratio of 6.3, yields a 2nd law entropy at 2400°K of 103.7 ± 2 eu. The uncertainty in the ionization cross-section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of ±3.5 eu. The heats of formation at temperatures other than 2400°K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C₅ are all estimated. We have chosen a set of functions which is consistent with the mass-spectrometric observations of Drowart et al. (1). The thermodynamic functions of C₅ were first estimated by Pitzer and Clementi (2) but the basis for this estimate has completely changed. Originally they were calculated by analogy with C₃, C₃O₂ and CO₂, but the discovery of very low bending frequencies in C₃ and C₃O₂ complicated the picture by raising the calculated entropies significantly. Sandborn (3) has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C₄ and C₅. These vibrational frequencies yield high entropies outside the limits of the second law determination. Since these frequencies are estimates, based on a basically triatomic correlation we have chosen to adopt three doubly degenerate bending frequencies of 550 cm⁻¹ in place of the 130 cm⁻¹, 330 cm⁻¹ and 520 cm⁻¹ frequencies estimated by Sandborn. The basis for this change is to make the functions conform to the only available measured data. Use of the present tables will yield values for the vapor pressure of C₄ in excellent agreement with the measurements in the 2000-3000°K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn (3) and the bond length is estimated equal to that in C₃.

References

1. J. Drowart, R. P. Burns, G. DeMaria, M. G. Inghram, J. Chem. Phys. **31**, 1131 (1959).
2. K. S. Pitzer and E. Clementi, J. Am. Chem. Soc. **81**, 4477 (1959).
3. R. H. Sandborn, J. Chem. Phys. **43**, 4219 (1965).

Cp⁰ - (G⁰-H⁰)/TS⁰ - (G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Cp⁰S⁰-(G⁰-H⁰)/TH⁰-H²⁹⁸ΔH⁰ΔG⁰

Log Kp

T, °K

Dec. 31, 1960; Dec. 31, 1969

Calcium, Alpha (Ca, α)

GFW = 40.08

Ca

$\Delta H_f^\circ = 0$ kcal/mol

$\Delta H_f^\circ_{298.15} = 0$ kcal/mol

$\Delta H_t^\circ = 0.220 \pm 0.05$ kcal/mol

$\Delta H_e^\circ_{298.15} = 42.85 \pm 0.3$ kcal/mol

$S^\circ_{298.15} = 9.93 \pm 0.06$ gibbs/mol

$T_t = 721 \pm 2^\circ\text{K}$

Heat of Formation
Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity data of Griffel et al. (1), 1.8° to 4.2°K, Roberts (2), 1.5° to 20°K, and Clusius and Vaughan (3), 10° to 200°K, were fit with polynomial expressions. Up to 20°K the three sets fit the adopted curve within ± 6 with a maximum deviation of 14%. This is considered excellent agreement since the heat capacity is only 0.35 gibbs/mol at 20°K. From 20° to 200°K the data of Clusius were within $\pm 1\%$ of the adopted polynomial. The data of Gunther (4), 22° to 62°K, generally deviated from the adopted curve by 10%. The polynomial fit of the data of Clusius was arranged to be linear in temperature at high temperatures and was extrapolated to 298°K. The data of Eastman et al. (5), 67° to 293°K, were consistently high by 5.8 to 9% over the whole range. The extrapolation of the heat capacity to 6.28 gibbs/mol at 298°K is further justified by comparison with the heat capacity of magnesium, which is almost identical to that of calcium over the whole range, if its temperature scale is multiplied by 0.75.

The heat capacity between 298° and 721°K was obtained by forcing a polynomial of the type $H = aT^2 + bT + c + d/T$ through 298° with a slope of 6.28 and also through a value of $H_{721} = 2736$ cal, and making a good fit of the adopted low temperature enthalpies. The choice of $H_{721} = 2736$ cal was made, since Zalesinski and Zulinsky (6), Jauch (7), and Eastman et al. (8) were in essential agreement in the beta-phase at this temperature. The enthalpy of transition was subtracted to give the adopted value. The individual measurements of Jauch (7) were not available, but the value at 720°K could be read from a small plot with reasonable accuracy; Eastman et al. (8) gave only an equation for their data. There is no question that reliable measurements of the heat capacity and enthalpy are needed in the range 200° to 700°K.

Transition Data

The temperature of transition was that reported by Peterson and Fattore (9) and confirmed by Chiotti et al. (10). Earlier reports on impure specimens ranged from 718° to 737°K and were not considered. The heat of transition was measured by Chiotti et al. (10) using an adiabatic high temperature calorimeter, and is in agreement with that reported by Kubaschewski (11) of 0.24 ± 0.04 kcal from enthalpy data.

Sublimation Data

See Ca(g) for details.

References:

1. M. Griffel, R. W. Vest and J. F. Smith, J. Chem. Phys. **27**, 1267 (1957).
2. L. M. Roberts, Proc. Phys. Soc. (London), **70B**, 738 (1957).
3. K. Clusius and J. V. Vaughan, J. Amer. Chem. Soc. **52**, 4686 (1930).
4. P. Gunther, Ann. Physik **51**, 828 (1916).
5. E. D. Eastman and W. H. Rodebush, J. Amer. Chem. Soc. **40**, 489 (1918).
6. E. Zalesinski and R. Zulinsky, Bull. Intern. Acad. Polon. **1928A**, 479 (1928).
7. R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946. Quoted in Ref. 11.
8. E. D. Eastman, A. M. Williams and T. F. Young, J. Amer. Chem. Soc. **46**, 1178 (1924).
9. D. T. Peterson and V. G. Fattore, J. Phys. Chem. **65**, 2062 (1961).
10. P. Chiotti, G. J. Gartner, E. R. Stevens, and Y. Saito, J. Chem. Eng. Data **11**, 571 (1966).
11. O. Kubaschewski, Z. Elektrochem. **54**, 275 (1950).

Calcium, Beta (Ca, β)

(Crystal)

GFV = 40.08

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	5.594	10.151	10.151	.000	.117	.052	.038
300	5.604	10.185	10.151	.010	.116	.051	.037
400	6.134	11.870	10.377	.597	.065	.038	.021
500	6.664	13.596	10.621	1.237	.059	.034	.015
600	7.194	14.958	11.361	1.930	.101	.026	.009
700	7.724	16.706	11.684	2.676	.194	.006	.002
800	8.254	18.772	12.329	3.475	.000	.000	.000
900	8.784	17.775	12.968	4.327	.000	.000	.000
1000	9.314	18.788	13.496	5.232	.000	.000	.000
1100	9.844	19.461	14.014	6.190	.000	.000	.000
1200	10.374	20.520	14.520	7.200	.132	.028	.000
1300	10.904	21.371	15.014	8.264	1.437	.299	.050
1400	11.434	22.199	15.498	9.381	1.041	.418	.065
1500	11.964	23.006	15.971	10.551	.591	.507	.074
1600	12.494	23.795	16.436	11.774	.080	.564	.077
1700	13.024	24.568	16.892	13.050	.468	.588	.076
1800	13.554	25.327	17.339	14.379	.35.817	1.259	.153
1900	14.084	26.075	17.779	15.761	34.934	3.294	.379
2000	14.614	26.810	18.213	17.196	33.999	5.282	.577

CALCIUM, BETA (Ca)

(CRYSTAL)

GFV = 40.08

 ΔH°_0 = unknown $\Delta H^\circ_{298.15} = 10.15$ gibbs/mol $T_t = 721 \pm 2^\circ\text{K}$ $T_m = 1112 \pm 2^\circ\text{K}$ $\Delta H^\circ_t = 0.220 \pm 0.05$ kcal/mol $\Delta H^\circ_m = 2.04 \pm 0.10$ kcal/mol

Heat of Formation

Obtained from that of α -Ca by adding ΔH°_t and the difference in $H^\circ_{721} - H^\circ_{298}$ for α - and β -Ca.

Heat Capacity and Entropy

The enthalpy at 721°K was fixed as described on the α -Ca table. The data of Jauch (2), and Zalesinski and Zulinski (2), and Eastman et al. (3) were then fitted by an equation of the form $H = a + bT + cT^2$ where $a = -1315$, $b = 4.014$ and $c = 0.00285$. The values of Jauch, read from a small graph, fit within 1% generally and within 2% maximum deviation; those of Zalesinski and Zulinski fit within 0.7% with the exception of the highest point which differed by 1.8%. The data of Eastman et al. vary from 3.6% high to 0.4% low. The entropy was obtained in a manner analogous to the heat of formation.

Transition Data

See the α -Ca table for details.

Melting Data

The melting point is that reported by Peterson and Fattore (4) and confirmed by Chioffi et al. (5). Earlier reports on less pure specimens ranged from 1083° to 1122°K . The heat of melting was measured by Chioffi et al. (5) using an adiabatic high temperature calorimeter, and is in agreement with that reported by Kubaschewski (6) of 2.07 ± 0.1 kcal/mol from enthalpy data.

References:

1. R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946. Quoted in Ref. 6.
2. E. Zalesinski and R. Zulinski, Bull. Intern. Acad. Polon. 1928A, 479 (1928).
3. E. D. Eastman, A. M. Williams and T. F. Young, J. Amer. Chem. Soc. 46, 1178 (1924).
4. D. T. Peterson and V. G. Fattore, J. Phys. Chem. 65, 2062 (1961).
5. P. Chioffi, G. J. Gartner, E. R. Stevens, and Y. Saito, J. Chem. Eng. Data 11, 571 (1966).
6. O. Kubaschewski, Z. Elektrochem. 54, 275 (1950).

Calcium (Ca)

(Liquid)

GFW = 40.08

T, °K	Cp°	S°	$-(C_p^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
100						
200						
298	7.200	12.105	12.105	.000	2.606	1.956 = 1.435
300	7.200	12.149	12.105	.013	2.607	1.953 = 1.423
400	7.200	14.221	12.387	.733	2.690	1.723 = .941
500	7.200	15.827	12.921	1.453	2.764	1.473 = .644
600	7.200	17.140	13.518	2.173	2.833	1.208 = .440
700	7.200	18.250	14.117	2.893	2.900	.932 = .171
800	7.200	19.159	14.620	3.613	2.967	.657 = -.107
900	7.200	19.968	15.033	4.333	2.855	.439 = -.347
1000	7.200	20.618	15.765	5.053	2.310	.250 = -.546
1100	7.200	21.504	16.256	5.773	2.072	.022 = -.774
1200	7.200	22.131	16.720	6.493	.000	.000
1300	7.200	22.607	17.158	7.213	.000	.000
1400	7.200	23.039	17.577	7.933	.000	.000
1500	7.200	23.737	17.968	8.653	.000	.000
1600	7.200	24.202	18.344	9.373	.000	.000
1700	7.200	24.639	18.701	10.093	.000	.000
1800	7.200	25.039	19.049	10.813	.000	.000
1900	7.200	25.419	19.382	11.533	.000	.000
2000	7.200	25.609	19.682	12.253	36.453	2.742 = .528
2100	7.200	26.160	19.982	12.973	36.235	6.891 = .717
2200	7.200	26.495	20.271	13.693	36.019	8.750 = .866
2300	7.200	26.725	20.546	14.413	35.800	13.008 = 1.165
2400	7.200	27.023	20.816	15.133	35.600	15.039 = 1.314
2500	7.200	27.415	21.074	15.853	35.398	15.039 = 1.314
2600	7.200	27.698	21.323	16.573	35.204	17.042 = 1.433
2700	7.200	27.969	21.564	17.293	35.019	19.048 = 1.542
2800	7.200	28.244	21.798	18.013	34.834	21.054 = 1.651
2900	7.200	28.484	22.028	18.733	34.641	23.061 = 1.736
3000	7.200	28.726	22.244	19.453	34.533	25.039 = 1.823

CALCIUM (Ca)

(LIQUID)

GFW = 40.08

 $S^\circ_{298.15} = 12.105$ gibbs/mol $\Delta H^\circ_{298.15} = 2.606 \pm 0.1$ kcal/mol $\Delta H_m^\circ = 2.04 \pm 0.10$ kcal/mol $T_m = 1112 \pm 2^\circ\text{K}$ $\Delta H_v^\circ = 36.9668$ kcal/mol $T_b = 1767.4 \pm 15^\circ\text{K}$

Heat of Formation

Obtained from that of β -Ca by adding ΔH_m° and the difference between $H_{1112} - H_{298}$ for β -Ca and liquid.

Heat Capacity and Entropy

The heat capacity was derived as constant from the enthalpy values of R. Jauch, Diplomarbeit, Techn. Hochschule Stuttgart, 1946, quoted by O. Kubaschewski, Z. Elektrochem. 51, 275 (1950). The entropy was obtained in a manner analogous to the heat of formation.

Melting Data

See the β -Ca table for details.

Vaporization Data

T_b is calculated from the free energy crossovers of the Ca(l) and Ca(g) tables, and ΔH_v° is the difference between $\Delta H^\circ_{1767.4}$ for liquid and gas.

Ca

Dec. 31, 1968

Ca

Ca

(IDEAL GAS)

Ca

Ca

Ca

Ground State Configuration $1s^2$
 $S^{\circ}_{298.15} = 36.992 \pm 0.005$ gibbs/mol
 $\Delta H^{\circ}_0 = 42.74 \pm 0.3$ kcal/mol
 $\Delta H^{\circ}_{298.15} = 42.85 \pm 0.30$ kcal/mol

Electronic Levels and Quantum Weights
 $\epsilon_i, \text{ cm}^{-1}$ g_i $\epsilon_i, \text{ cm}^{-1}$ g_i

Heat of Formation
The vapor pressure over solid and liquid calcium has been reported by several authors. The results of our analysis of their data are presented in the following table. By using free energy functions based on the α crystal at 298°K all the data yield $\Delta H^{\circ}_{298.15}$ (Ca, c) which is $\Delta H^{\circ}_{298.15}$ (Ca, g).

Heat Capacity and Entropy
The electronic levels and quantum weights were obtained from Moore (13), and were cut off at 45000 cm^{-1} , which is approximately the ionization limit minus KT for the maximum temperature. All of the unobserved terms in the spectrum are estimated to occur between 47000 cm^{-1} and the ionization limit.

References:
1. N. B. Pilling, Phys. Rev. **18**, 362 (1921).
2. O. Ruff and H. Hartmann, Z. Anorg. Chem. **133**, 29 (1924).
3. H. Hartmann and R. Schneider, Z. Anorg. Chem. **180**, 275 (1929).
4. H. Hartmann, Phys. Rev. **35**, 683 (1934).
5. P. E. Debye, Proc. Phys. Soc. (London) **57B**, 783 (1954).
6. D. H. Tomlin, Proc. Phys. Soc. (London) **67B**, 787 (1954).
7. Yu. A. Priselkov and An. N. Nesmeyanov, Dokl. Akad. Nauk SSSR **95**, 1207 (1954).
8. J. F. Smith and R. L. Smythe, Acta Met., **2**, 261 (1955).
9. J. F. Smith, USAC IS-440, Iowa State University, Ames, Iowa, 1962.
10. V. G. Maslovets and L. P. Fuchkov, Russ. J. Appl. Chem. (English Transl.) **38**, 937 (1965).
11. V. G. Maslovets and L. P. Fuchkov, Russ. J. Appl. Chem. (English Transl.) **38**, 937 (1965).
12. J. C. Bonchansky and H. E. J. Schins, J. Phys. Chem. **71**, 215 (1967).
13. C. E. Moore, U. S. Natl. Bur. Stds. Circular 467, 1949.

Calcium (Ca)

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

(Ideal Gas)

Ca

Ca

Calcium Monochloride (CaCl)

GFW = 75.533

Ground State Configuration $2s^2$

$S^{\circ}_{298.15} = 57.7 \pm 0.2$ gibbs/mol

$\Delta H^{\circ}_f = -25.0 \pm 3$ kcal/mol

$\Delta H^{\circ}_{f,298.15} = -25.0 \pm 3$ kcal/mol

Electronic Levels and Quantum Heights

State	ϵ_i , cm ⁻¹	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	16093.3	2
	16162.8	2
$B^2\Sigma$	16850.6	2
$C^2\Pi$	26498.9	2
	26574.7	2
$D^2\Sigma$	31107.8	2
$E^2\Sigma$	34286.4	2
$F^2\Pi$	35675	2
	35700	2
$G^2\Delta$	36705	2
	36710	2

$\omega_e x_e = 1.31$ cm⁻¹ $\sigma = 1$

$\omega_e = 369.8$ cm⁻¹ $\omega_e x_e = 1.31$ cm⁻¹ $q_e = 10.00071$ cm⁻¹ $r_e = 2.439$ Å

Heat of Formation

N. D. Potter (1) investigated mass spectrometrically the gaseous equilibria among Ca, CaCl, and CaCl₂. Ion intensities were measured 2.5 eV above the ionization threshold. Using the equilibrium constants $K = I(\text{Ca})I(\text{CaCl}_2)/I(\text{CaCl})^2$ which we calculated from the reported ion intensities for the reaction $\text{Ca(g)} + \text{CaCl}_2(\text{g}) \rightleftharpoons 2\text{CaCl(g)}$ in the temperature range 1252°-1557°K, we obtain $\Delta H^{\circ}_{f,298} = 15.81$ kcal/mol by the third law method. The third law drift is -2.8 ± 3.5 eu. The heat of formation is derived as $\Delta H^{\circ}_{f,298}(\text{CaCl, g}) = -27.0$ kcal/mol.

K. F. Zmbov (2) determined by mass spectrometry the heat of the above reaction as 24.4 ± 1.3 kcal/mol with a drift of 12.5 ± 9.4 eu. This yields the heat of formation, $\Delta H^{\circ}_{f,298}(\text{CaCl, g}) = -22.7$ kcal/mol.

D. L. Hildenbrand (2) also determined the equilibrium constants for the reaction (a) $\text{Ca(g)} + \text{CaCl}_2(\text{g}) \rightleftharpoons 2\text{CaCl(g)}$ and the reaction (b) $\text{Ca(g)} + \text{AlCl}_3(\text{g}) \rightleftharpoons \text{CaCl(g)} + \text{Al(g)}$ by mass spectrometry in the temperature range 1219-1353°K. Third law analysis of the reported equilibrium constants gives $\Delta H^{\circ}_{f,298} = 21.08$ kcal/mol and drift = -1.4 ± 1.8 eu for reaction (a); $\Delta H^{\circ}_{f,298} = 24.20$ kcal/mol and drift = 0.5 ± 1.3 eu for reaction (b). From third law $\Delta H^{\circ}_{f,298}$ of (a) and (b), we derived $\Delta H^{\circ}_{f,298}(\text{CaCl, g})$ as -24.4 and -23.3 kcal/mol, respectively, using all JANAF functions. Hildenbrand has also derived a corrected $D_0(\text{Ca-Cl}) = 95.0$ kcal/mol from a linear Birge-Sponer extrapolation of the ground state vibrational levels with correction for its ionicity. This corrected $D_0(\text{Ca-Cl})$ yields the heat of formation, $\Delta H^{\circ}_{f,298}(\text{CaCl, g}) = -23.9$ kcal/mol.

Ryabova and Gurvich (3) reported $D_0(\text{Ca-Cl}) = 102 \pm 6$ kcal/mol from flame spectra studies. This leads to $\Delta H^{\circ}_{f,298}(\text{CaCl, g}) = -30.8$ kcal/mol.

D. L. Hildenbrand (5) determined the dissociation energy of $\text{CaCl}_2(\text{g})$ by electron impact as $D_0(\text{CaCl-Cl}) = 5.04 \pm 0.02$ eV which, combined with JANAF $\Delta H^{\circ}_{f,298}$ of $\text{CaCl}_2(\text{g})$ and Cl(g) gives $\Delta H^{\circ}_{f,298}(\text{CaCl, g}) = -23.1$ kcal/mol.

A weighted average, $\Delta H^{\circ}_{f,298}(\text{CaCl, g}) = -25 \pm 3$ kcal/mol, is adopted in the tabulation.

Heat Capacity and Entropy

The vibrational constants (ω_e and $\omega_e x_e$), electronic levels and ground state configuration were taken from Herzberg (4). Morgan and Barrow (5) made rotational analysis of the $C^2\Pi-X^2\Sigma$ system and reported $B_e = 0.1516$ cm⁻¹ and $r_e = 2.439$ Å for the ground state. The value of q_e is calculated from the Morse potential function. The F and G states were reported by Schutte (6).

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. D. L. Hildenbrand, "Dissociation Energies and Chemical Bonding in the Alkaline-Earth Chlorides from Mass Spectrometric Studies," J. Chem. Phys., in press.
3. V. G. Ryabova and L. V. Gurvich, Teplofiz. Vysokikh Temp. Akad. Nauk SSSR 3, 652 (1965).
4. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc. New York, 1950.
5. E. Morgan and R. F. Barrow, Nature 185, 754 (1960).
6. D. L. Hildenbrand, CFTA Publication No. 189, Vol. 1 page 86, Aug. 1969.
7. K. F. Zmbov, Chem. Phys. Lett. 1, 191 (1969).
8. M. Schutte, Naturwiss. 40, 528 (1953).

June 30, 1970

CaCl

T, °K	C_p°	g°	$-(G^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	ΔH°	ΔG°	Log Kp
0	+0.00	INFINITE	2.292	24.824	24.824	24.824	INFINITE
100	7.244	49.066	64.976	1.591	24.705	26.973	58.949
200	8.116	54.379	59.476	-0.819	24.638	29.195	31.903
298	8.554	57.707	57.707	+0.000	24.638	31.300	22.944
300	8.559	57.760	57.707	-0.016	25.004	31.340	22.831
400	8.719	60.243	58.044	-0.879	25.192	33.424	18.262
500	8.822	62.200	58.687	-1.757	25.387	35.458	15.499
600	8.885	63.815	59.411	-2.642	25.587	37.453	13.642
700	8.916	65.083	60.183	-3.528	25.792	39.410	11.828
800	8.931	66.182	60.887	-4.428	26.000	41.339	10.068
900	8.937	67.039	61.522	-5.325	26.219	43.249	8.369
1000	8.936	67.687	62.162	-6.225	27.182	44.972	6.829
1100	8.928	68.247	62.768	-7.127	27.666	46.727	5.484
1200	8.914	68.728	63.348	-8.035	28.182	48.502	4.337
1300	8.891	69.130	63.884	-8.936	28.730	49.793	3.373
1400	8.861	69.459	64.399	-9.833	29.305	51.263	2.586
1500	8.826	69.720	64.889	-10.751	30.820	52.754	1.946
1600	8.786	69.924	65.355	-11.661	31.084	54.208	1.404
1700	8.742	70.081	65.798	-12.562	31.348	55.644	0.944
1800	8.694	70.197	66.220	-13.455	31.604	57.066	0.564
1900	8.642	70.272	66.633	-14.339	31.854	58.478	0.264
2000	8.586	70.317	67.024	-15.214	32.100	59.878	0.014
2100	8.526	70.335	67.400	-16.081	32.342	61.266	
2200	8.462	70.328	67.758	-16.936	32.580	62.642	
2300	8.394	70.306	68.100	-17.780	32.814	64.008	
2400	8.322	70.268	68.444	-18.614	33.044	65.366	
2500	8.246	70.215	68.788	-19.438	33.270	66.716	
2600	8.166	70.148	69.122	-20.252	33.492	68.058	
2700	8.082	70.068	69.446	-21.056	33.710	69.392	
2800	8.000	70.000	69.760	-21.850	33.924	70.716	
2900	7.918	69.948	69.965	-22.635	34.134	72.030	
3000	7.836	69.912	70.142	-23.410	34.340	73.334	
3100	7.754	69.890	70.298	-24.176	34.542	74.628	
3200	7.672	69.880	70.436	-24.932	34.740	75.912	
3300	7.590	69.880	70.558	-25.678	34.934	77.186	
3400	7.508	69.890	70.666	-26.414	35.124	78.450	
3500	7.426	69.912	70.760	-27.140	35.310	79.704	
3600	7.344	69.948	70.840	-27.856	35.492	80.948	
3700	7.262	69.996	70.906	-28.562	35.670	82.182	
3800	7.180	69.960	70.958	-29.258	35.844	83.406	
3900	7.098	69.936	71.000	-29.944	36.014	84.620	
4000	7.016	69.924	71.032	-30.620	36.180	85.824	
4100	6.934	69.932	71.054	-31.286	36.342	87.018	
4200	6.852	69.950	71.066	-31.942	36.498	88.202	
4300	6.770	69.976	71.068	-32.588	36.648	89.376	
4400	6.688	69.960	71.060	-33.224	36.792	90.540	
4500	6.606	69.900	71.042	-33.850	36.930	91.694	
4600	6.524	69.800	71.014	-34.466	37.062	92.838	
4700	6.442	69.676	70.966	-35.072	37.188	93.972	
4800	6.360	69.528	70.900	-35.668	37.308	95.096	
4900	6.278	69.356	70.814	-36.254	37.422	96.210	
5000	6.196	69.160	70.708	-36.830	37.530	97.314	
5100	6.114	68.944	70.592	-37.396	37.632	98.408	
5200	6.032	68.708	70.456	-37.952	37.728	99.492	
5300	5.950	68.452	70.300	-38.498	37.818	100.566	
5400	5.868	68.176	70.124	-39.034	37.902	101.630	
5500	5.786	67.880	69.928	-39.560	37.980	102.684	
5600	5.704	67.564	69.704	-40.076	38.052	103.728	
5700	5.622	67.228	69.452	-40.582	38.118	104.762	
5800	5.540	66.872	69.172	-41.078	38.178	105.786	
5900	5.458	66.500	68.868	-41.564	38.232	106.800	
6000	5.376	66.116	68.540	-42.040	38.280	107.804	

Calcium Chloride (CaCl₂)

(Crystal)

GFW = 110.986

CALCIUM CHLORIDE (CaCl₂)

(CRYSTAL)

GFW = 110.986

 $\Delta H_f^\circ = -190.3 \pm 0.3$ kcal/mol $\Delta H_{298.15}^\circ = -190.2 \pm 0.3$ kcal/mol $\Delta H_m^\circ = 6.822 \pm 0.2$ kcal/mol $\Delta H_{298.15}^\circ = 77.5 \pm 2$ kcal/mol $S_{298.15}^\circ = 25.0 \pm 1$ gibbs/mol $T_m = 1045^\circ\text{K}$ CaCl₂

June 30, 1970

CaCl₂

T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	11.666	8.508	39.406	3.678	-190.313	-190.313	INFINITE
200	16.099	18.286	26.558	3.090	-190.655	-186.609	407.434
298	17.413	25.000	25.000	1.452	-190.485	-182.610	199.546
300	17.430	25.108	25.001	.032	-190.195	-174.805	131.087
400	18.080	30.222	25.694	1.611	-189.883	-174.734	130.208
500	18.440	34.298	27.021	3.639	-189.554	-174.961	95.594
600	18.690	37.682	28.523	5.495	-189.218	-167.641	61.063
700	19.340	43.139	31.524	6.292	-188.486	-160.527	41.258
800	19.860	45.466	32.945	11.251	-188.614	-157.001	36.125
900	20.500	47.570	34.302	13.266	-188.396	-153.501	33.548
1000	21.200	49.557	35.600	15.353	-188.166	-150.023	29.907
1100	22.600	53.212	38.033	19.733	-189.100	-142.431	24.002
1200	23.300	54.913	39.178	22.028	-188.429	-139.294	21.745
1300	24.000	56.544	40.282	24.393	-187.490	-135.612	19.748
1400	24.700	58.115	41.358	26.824	-186.483	-132.360	18.082
1500	25.400	59.628	42.404	29.324	-185.408	-129.522	16.574
1600	26.100	61.105	43.379	31.808	-184.267	-126.997	15.174
1700	26.800	62.535	44.349	34.253	-183.063	-124.723	13.761
1800	27.500	63.928	45.294	37.266	-181.800	-122.692	12.496

Heat of Formation

V. B. Parker (1) has selected the standard heat of formation as -190.2 kcal/mol which is adopted in the tabulation. The heat of formation was derived from two independent paths. The first path involves $\Delta H_{298}^\circ(\text{Ca}^{++}, \infty \text{H}_2\text{O}) = -129.74$ kcal/mol (1), $\Delta H_{298}^\circ(\text{Cl}^-, \infty \text{H}_2\text{O}) = -39.952$ kcal/mol (2) and the heat of solution of $\text{CaCl}_2(\text{c})$ in water (3, 4, 5, 6, 7). The second path involves the heats of reaction of $\text{Ca}(\text{c})$, $\text{CaO}(\text{c})$ and $\text{CaCl}_2(\text{c})$ in aqueous HCl solution (4, 5-20).

Heat Capacity and Entropy

Kelley and Moore (21) measured the low temperature heat capacities in the temperature range from 52.6° to 295.1°K and made an extrapolation to 0°K which yielded an entropy of 4.59 ± 0.4 eu at 50.12°K. We have adopted the measured heat capacities, but made our own extrapolation to 0°K by comparison with the measured heat capacities of $\text{BaCl}_2(\text{c})$ (22) and $\text{SrCl}_2(\text{c})$ (23) from 6° to 50°K. The extrapolation gives $S_{50}^\circ = 2.45 \pm 1$ eu, which is used in the table. Moore (24) measured high temperature enthalpy data from 403.7° to 1667°K by drop calorimetry. The low temperature heat capacities and high temperature enthalpy data are smoothly joined at 298°K. The deviations of the observed enthalpies from the adopted values are about 21 near 400-500°K and only a few tenths percent at higher temperatures. Dworkin and Bredig (25) determined drop-calorimetrically $H_{1045}^\circ - H_{298}^\circ = 14.3$ kcal/mol, which is in very good agreement with the adopted value of 14.2 kcal/mol.

Melting Data

The adopted melting point 1045°K was determined by T. V. Tokareva (26). Dworkin and Bredig determined the heat of fusion $\Delta H_{1045}^\circ = 6.78 \pm 0.1$ kcal/mol by drop calorimetry. Chiotti, Gartner, Stevens and Saito (27) also measured the heat of fusion $\Delta H_{1055}^\circ = 6.79 \pm 0.2$ kcal/mol in an adiabatic calorimeter. The adopted heat of fusion, 6.822 kcal/mol, is calculated from the difference between the observed relative enthalpy of the liquid and the adopted value for the crystal at the melting point.

Sublimation Data

The heat of sublimation is calculated from the heats of formation of $\text{CaCl}_2(\text{c})$ and $\text{CaCl}_2(\text{g})$.

References

1. V. B. Parker, U. S. Natl. Bur. Std. private communication, Jan. 7, 1969.
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. Pickering, J. Chem. Soc. 53, 875 (1888).
4. Samoilov, Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk 1952, 626.
5. Ditté, Compt. Rend. 85, 1103 (1877).
6. Baud, Ann. Chim. Phys. 1, 8 (1904).
7. Berthelot and Ilosvay, Ann. Chim. Phys. 29, 295 (1883).
8. Kapustinaki and Samoilov, Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk 1950, 367.
9. P. Ehrlich, K. Peik and E. Koch, Z. Anorg. Allgem. Chem. 324, 113 (1963).
10. Vedenev, Zh. Fiz. Khim. 26, 1808 (1952).
11. Young, J. Amer. Chem. Soc. 65, 773 (1944).
12. Torgeson and Shomate, J. Amer. Chem. Soc. 69, 2103 (1947).
13. Taylor and Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
14. Wells and Taylor, J. Res. Natl. Bur. Std. 19, 215 (1937).
15. Backstrom, J. Amer. Chem. Soc. 51, 2678 (1929).
16. Thorvaldson, Brown, and Peaker, J. Amer. Chem. Soc. 51, 2678 (1929).
17. Guntz and Benoit, Ann. Chim. 20, 5 (1923).
18. Biltz and Wagner, Z. Anorg. Chem. 134, 1 (1924).
19. Geiseler and Buchner, Z. Anorg. Allgem. Chem. 343, 286 (1966).
20. Kocherov, Gertman and Geld, Zh. Neorg. Khim. 4, 1106 (1959).
21. K. X. Kelley and G. E. Moore, J. Amer. Chem. Soc. 55, 1284 (1933).
22. R. M. Goodman and E. F. Westrum, Jr., J. Chem. Eng. Data 11, 294 (1966).
23. D. F. Smith, T. E. Gardner, B. B. Letson and A. R. Taylor, Jr., U. S. Bur. Mines RI 6316, 1963.
24. G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943).
25. A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 57, 697 (1953).
26. M. V. Tokareva, Zh. Neorg. Khim. 2, 1591 (1957).
27. P. Chiotti, G. J. Gartner, E. R. Stevens and Y. Saito, J. Chem. Eng. Data 11, 571 (1966).

$S_{298.15}^{\circ} = 29.608 \pm 1.2$ gibbs/mol
 $\Delta H_f^{\circ} = -185.013 \pm 0.5$ kcal/mol
 $\Delta H_m^{\circ} = 6.822 \pm 0.2$ kcal/mol
 $\Delta H_v^{\circ} = 56.2$ kcal/mol

$T_m = 1045^{\circ}\text{K}$
 $T_b = 2208.6^{\circ}\text{K}$

Heat of Formation
The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between H_{1045}° and H_{298}° for the crystal and the liquid.

Heat Capacity and Entropy
The constant heat capacity above the assumed glass transition at 700°K is derived from high temperature enthalpy data in a drop calorimeter from the melting point up to 1667°K by G. E. Moore, J. Amer. Chem. Soc. 65, 1700 (1943). Below the glass transition point, the heat capacity is assumed to be the same as that of the crystal. A. S. Dworin and M. A. Bredig, J. Phys. Chem. 67, 697 (1963), reported $C_p(l) = 23.6$ gibbs/mol from enthalpy measurements in a short temperature range by drop calorimetry.

The entropy $S_{298.15}^{\circ} = 29.608$ gibbs/mol is calculated in a manner analogous to that of the heat of formation.

Melting Data
See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which $\Delta G = 0$ for $\text{CaCl}_2(l) + \text{CaCl}_2(g)$. The heat of vaporization is the difference in ΔH_f° between liquid and gas.

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^{\circ}}$	$-(G^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	$\frac{\text{kcal/mol}}{\Delta H^{\circ}}$	ΔG°	Log Kp
0							
100							
200							
298	17.413	29.608	29.608	.000	-185.013	-174.991	128.272
300	17.430	29.715	29.608	.032	-185.004	-174.929	127.936
400	16.080	34.629	30.301	1.811	-184.696	-171.617	93.767
500	16.440	38.605	31.628	3.439	-184.367	-168.343	73.600
600	16.670	42.289	33.131	5.495	-184.031	-165.218	60.181
700	16.870	45.643	34.777	7.828	-183.684	-162.253	49.253
800	17.040	48.663	36.541	10.428	-183.328	-159.442	40.383
900	17.180	51.369	38.406	13.279	-182.959	-156.775	32.906
1000	17.300	53.731	40.362	16.379	-182.576	-154.244	26.645
1100	17.400	55.796	42.489	19.692	-182.180	-151.847	21.380
1200	17.490	57.526	44.849	23.201	-181.771	-149.576	16.986
1300	17.570	58.961	47.375	26.902	-181.340	-147.425	13.322
1400	17.640	60.136	49.999	30.794	-180.888	-145.384	10.253
1500	17.700	61.099	52.744	34.765	-180.416	-143.443	7.645
1600	17.750	61.880	55.541	38.715	-180.000	-141.592	5.341
1700	17.790	62.411	58.311	42.644	-179.640	-139.821	3.301
1800	17.820	62.731	61.061	46.544	-179.330	-138.120	1.500
1900	17.840	62.880	63.791	50.394	-179.060	-136.479	0.000
2000	17.850	62.960	66.501	54.194	-178.830	-134.888	
2100	17.850	62.960	69.181	57.944	-178.630	-133.347	
2200	17.850	62.960	71.831	61.644	-178.460	-131.856	
2300	17.850	62.960	74.441	65.294	-178.310	-130.415	
2400	17.850	62.960	77.011	68.894	-178.180	-129.024	
2500	17.850	62.960	79.541	72.444	-178.070	-127.683	
2600	17.850	62.960	82.031	75.944	-177.980	-126.392	
2700	17.850	62.960	84.481	79.394	-177.910	-125.151	
2800	17.850	62.960	86.891	82.694	-177.860	-123.960	
2900	17.850	62.960	89.261	85.844	-177.830	-122.819	
3000	17.850	62.960	91.591	88.844	-177.810	-121.728	

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

Bond Distance: Ca-Cl = 2.51 Å
Bond Angle: Cl-Ca-Cl = 180°
Rotational Constant: $B_0 = 0.0377 \text{ cm}^{-1}$

Heat of Formation

Second and third law analyses of vapor pressure data are given below. The selected third law heat of vaporization is taken from Novikov's measurement (1) as $\Delta H_{298}^\circ = 72.30$ kcal/mol which is combined with ΔH_{298}° of the liquid to give $\Delta H_{298}^\circ(\text{CaCl}_2, g) = 112.7 \pm 1$ kcal/mol.

Third law analyses indicate zero drift for Novkov's data, positive and negative drifts for Hildenbrand's (2) and Bautista's (3) data, respectively. Their heats are in agreement within 1 kcal. Wartenberg (4) reported there was no boiling at 1819°K at 12 mm Hg pressure, and his value ($\Delta H_{298}^\circ = 71.1 \pm 0.7$ kcal/mol) serves as a guide for the minimum heat of vaporization.

Investigator	Method	Temperature Range, °K	Number of Points	ΔH_{298}° (kcal/mol)	Drift e.u.
Langeauista and Margrave (3)	Langmuir	952-993	7	2nd law 75.25 (80.34)*	3rd law 73.39 (78.57)* -1.7±6.9
Torsion Effusion 0.0096 cm ² Orifice Torsion Effusion 0.015 cm ² Orifice		1142-1228 1111-1281	12 17	64.99 68.71	71.24 71.24 2.0±0.2
Torsion Effusion Combined		1111-1281	29	68.91	71.24 2.4±0.3
Knudsen Effusion Boiling Point Boiling Point		1069-1225 1819 1591-1701	4 1 5	59.37 --- 72.25	71.03 >71.10 72.30 0.0±1.2
Langmuir Knudsen Effusion		973-1023 1073-1273	6 8	78.0 61.8	69.01 69.78 -8.0 +8.0

Value in parentheses is the heat of sublimation.

Heat Capacity and Entropy

The linear structure and vibrational frequencies were determined by D. White and co-workers (6) in the matrix-infrared-spectrometric studies. The linear structure is consistent within experimental error with the electric-quadrupole-deflection studies (7), and electron-diffraction data (8). Hayes (9) has qualitatively rationalized the linear structure through molecular orbital theory.

The bond length was measured by Akishin and Spiridonov (8). The moment of inertia is $74.174 \times 10^{-39} \text{ g cm}^2$.

References

1. G. I. Novikov and F. G. Gavryuchenkov, Zh. Neorg. Khim. 9, 260 (1964).
2. D. L. Hildenbrand and N. D. Potter, J. Phys. Chem. 67, 2231 (1963).
3. R. G. Bautista and J. L. Margrave, J. Phys. Chem. 67, 2411 (1963).
4. H. V. Vartenberg and O. Boase, Z. Elektrochem. 28, 364 (1922).
5. E. W. Dawing, Aluminum Laboratories, quoted in ref. (2).
6. Unpublished work cited by D. L. Hildenbrand, "Nuclear Reaction Energies and Chemical Bonding in the Alkaline-Earth Chlorides from Mass Spectrometric Studies," J. Chem. Phys., in press.
7. L. Wharton, R. A. Berg and W. Klumper, J. Chem. Phys. 39, 2023 (1963); 39, 2299 (1963).
8. P. A. Akshin and V. P. Spiridonov, Kristallografiya 2, 475 (1957).
9. E. F. Hayes, J. Phys. Chem. 70, 3740 (1966).
10. E. E. Lukashenko and G. A. Reutova, Zhur. Fiz. Khim. 44, 800 (1970).

Calcium Monofluoride (CaF)
$$GFW = 59.0784$$

Caf

$$\Delta H_f^\circ = -64.8 \pm 2 \text{ kcal/mol}$$
$$\Delta H_{298}^{\circ} = -65.0 \pm 2 \text{ kcal/mol}$$

Ground State Configuration $2\Sigma^+$

$$S_{298.15}^{\circ} = 54.86 \pm 0.1 \text{ gibbs/mol}$$

Ground State

CALCIUM MONOFLUORIDE (CaF)

(IDEAL GAS)

GFW = 59,0784

T, °K	C _p ^a	S ^b - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K _p
100	6.000	INFINITE	2.182	64.756	64.756	INFINITE
150	6.990	46.776	1.601	64.762	64.762	166.216
200	7.510	51.754	1.050	64.613	69.105	75.515
250	8.045	54.860	+0.000	65.000	71.173	52.171
300	8.053	54.910	+0.15	65.004	71.212	51.878
350	8.059	54.926	+0.30	65.003	71.212	51.878
400	8.059	54.919	+0.45	65.003	71.212	51.878
450	8.059	54.919	+0.60	65.003	71.212	51.878
500	8.059	54.919	+0.75	65.003	71.212	51.878
600	8.059	54.919	+0.90	65.003	71.212	51.878
700	8.702	60.745	56.493	2.552	77.187	28.115
800	8.864	62.073	57.199	3.426	79.101	24.697
900	8.997	63.270	57.686	4.300	80.957	22.116
1000	9.091	64.344	58.053	5.194	82.766	19.470
1100	9.152	65.253	58.319	6.085	84.531	16.840
1200	9.192	66.105	59.760	6.979	86.259	14.130
1300	9.216	66.864	60.322	7.875	87.943	11.350
1400	9.236	67.551	60.855	8.774	89.586	8.503
1500	9.253	68.271	61.361	9.674	91.191	5.587
1600	9.269	68.947	61.843	10.577	92.758	2.612
1700	9.284	69.577	62.302	11.481	94.288	-0.413
1800	9.298	70.166	62.740	12.387	95.780	-1.441
1900	9.312	70.715	63.160	13.294	97.235	-2.476
2000	9.326	71.236	63.561	14.202	98.655	-3.520
2100	9.340	71.730	63.947	15.112	100.038	-4.572
2200	9.354	72.198	64.317	16.023	101.384	-5.632
2300	9.368	72.647	64.674	16.936	102.695	-6.700
2400	9.382	73.079	65.017	17.851	103.972	-7.776
2500	9.396	73.496	65.349	18.767	105.216	-8.860
2600	9.410	73.899	65.669	19.683	106.428	-9.952
2700	9.424	74.283	65.979	20.600	107.608	-11.052
2800	9.438	74.650	66.279	21.528	108.756	-12.160
2900	9.452	75.004	66.570	22.453	109.873	-13.276
3000	9.466	75.344	66.852	23.381	110.959	-14.400
3100	9.480	75.676	67.126	24.311	112.006	-15.532
3200	9.494	75.996	67.393	25.244	113.024	-16.672
3300	9.508	76.306	67.652	26.183	114.013	-17.820
3400	9.522	76.606	67.904	27.125	114.974	-18.976
3500	9.536	76.896	68.150	28.070	115.916	-20.140
3600	9.550	77.176	68.390	29.020	116.830	-21.312
3700	9.564	77.446	68.624	29.975	117.716	-22.492
3800	9.578	77.706	68.852	30.935	118.574	-23.680
3900	9.592	77.956	69.076	31.900	119.412	-24.876
4000	9.606	78.206	69.294	32.871	120.224	-26.080
4100	9.620	78.456	69.508	33.847	121.012	-27.292
4200	9.634	78.706	69.718	34.830	121.776	-28.512
4300	9.648	78.956	69.923	35.819	122.524	-29.748
4400	9.662	79.206	70.124	36.814	123.256	-31.000
4500	9.676	79.456	70.321	37.816	123.972	-32.268
4600	9.690	79.706	70.514	38.824	124.672	-33.552
4700	9.704	79.956	70.704	39.840	125.356	-34.852
4800	9.718	80.206	70.891	40.863	126.024	-36.168
4900	9.732	80.456	71.074	41.893	126.676	-37.500
5000	9.746	80.706	71.253	42.931	127.312	-38.848
5100	9.760	80.956	71.432	43.976	127.936	-40.212
5200	9.774	81.206	71.607	45.028	128.548	-41.592
5300	9.788	81.456	71.778	46.088	129.148	-43.000
5400	9.802	81.706	71.947	47.156	129.736	-44.432
5500	9.816	81.956	72.114	48.231	130.312	-45.888
5600	9.830	82.206	72.278	49.314	130.876	-47.368
5700	9.844	82.456	72.446	50.405	131.432	-48.872
5800	9.858	82.706	72.610	51.503	131.980	-50.400
5900	9.872	82.956	72.772	52.609	132.520	-51.952
6000	9.886	83.206	72.930	53.723	133.052	-53.528
6100	9.900	83.456	73.086	54.843	133.576	-55.128
6200	9.914	83.706	73.240	55.969	134.100	-56.752
6300	9.928	83.956	73.394	57.100	134.616	-58.400
6400	9.942	84.206	73.548	58.236	135.124	-60.072
6500	9.956	84.456	73.702	59.376	135.624	-61.768
6600	9.970	84.706	73.856	60.520	136.116	-63.488
6700	9.984	84.956	74.010	61.668	136.600	-65.232
6800	9.998	85.206	74.164	62.820	137.076	-66.992
6900	10.012	85.456	74.318	63.976	137.544	-68.768
7000	10.026	85.706	74.472	65.136	138.004	-70.568
7100	10.040	85.956	74.626	66.300	138.456	-72.392
7200	10.054	86.206	74.780	67.468	138.900	-74.240
7300	10.068	86.456	74.934	68.640	139.336	-76.112
7400	10.082	86.706	75.088	69.816	139.764	-78.008
7500	10.096	86.956	75.242	71.000	140.184	-79.928
7600	10.110	87.206	75.396	72.188	140.596	-81.872
7700	10.124	87.456	75.550	73.380	141.000	-83.840
7800	10.138	87.706	75.704	74.576	141.396	-85.832
7900	10.152	87.956	75.858	75.776	141.784	-87.848
8000	10.166	88.206	76.012	76.980	142.164	-89.888
8100	10.180	88.456	76.166	78.188	142.536	-91.952
8200	10.194	88.706	76.320	79.400	142.900	-94.040
8300	10.208	88.956	76.474	80.616	143.256	-96.152
8400	10.222	89.206	76.628	81.836	143.604	-98.288
8500	10.236	89.456	76.782	83.060	143.944	-100.448
8600	10.250	89.706	76.936	84.288	144.276	-102.632
8700	10.264	89.956	77.090	85.520	144.600	-104.840
8800	10.278	90.206	77.244	86.756	144.916	-107.072
8900	10.292	90.456	77.398	87.996	145.224	-109.328
9000	10.306	90.706	77.552	89.240	145.524	-111.608
9100	10.320	90.956	77.706	90.488	145.816	-113.912
9200	10.334	91.206	77.860	91.740	146.100	-116.240
9300	10.348	91.456	78.014	92.996	146.376	-118.592
9400	10.362	91.706	78.168	94.256	146.644	-120.968
9500	10.376	91.956	78.322	95.520	146.904	-123.368
9600	10.390	92.206	78.476	96.788	147.156	-125.792
9700	10.404	92.456	78.630	98.060	147.400	-128.240
9800	10.418	92.706	78.784	99.336	147.640	-130.712
9900	10.432	92.956	78.938	100.616	147.876	-133.208
10000	10.446	93.206	79.092	101.900	148.104	-135.728

Dec. 31.1968

Dec. 31, 1968

Caf

Herzberg (6) gives the vibrational constants and electronic levels, Harvey (7) has reported a value for B_0 which corresponds to a bond length of 2.02 Å. The Morse potential function was used to calculate α_e .

References

1. J. N. Haste and J. L. Hargrave, *J. Chem. Eng. Data*, **13**, 428 (1968).
2. D. L. Hildenbrand and E. Murad, *J. Chem. Phys.*, **43**, 1400 (1965).
3. D. G. Blue, J. N. Green, R. G. Bautista, and J. L. Hargrave, *J. Phys. Chem.*, **67**, 877 (1963).
4. V. G. Ryabova and L. V. Gurvich, *Teplifiz. Vys. Temp.*, **2**, 934 (1964).
5. D. L. Hildenbrand and E. Murad, *J. Chem. Phys.*, **44**, 1524 (1966).
6. G. Herzberg, *Spectra of Diatomic Molecules*, D. Van Nostrand Co., Inc. New York, 1950.
7. A. Harvey, *Proc. Roy. Soc. (London)*, **133**, 336 (1931).

Calcium Difluoride (CaF₂)

(Crystal)

GFW = 78.0768

 $\Delta H_f^\circ = -292.3 \pm 1.5$ kcal/molCaF₂ $S_{298.15}^\circ = 16.39 \pm 0.08$ gibbs/mol $\Delta H_f^\circ = -293.0 \pm 1.5$ kcal/mol $T_m = 1424 \pm 20^\circ\text{K}$ (g-p) $\Delta H_f^\circ = 1.14 \pm 0.1$ kcal/mol $\Delta H_m^\circ = 7.10 \pm 0.1$ kcal/mol $\Delta H_{298.15}^\circ = 105.5 \pm 0.8$ kcal/mol

Heat of Formation

Torgeson and Sahama (1) measured the heat of solution of CaO in aqueous 20.1% HF as -54.96 ± 0.02 kcal/mol. Using ΔH_f° (CaO, c) = -151.79 kcal/mol (2), ΔH_f° (H₂O, l) = -68.317 kcal/mol (3) and ΔH_f° (HF, aq) = -76.60 kcal/mol (4), we obtain ΔH_f° (CaF₂, c) = -293.6 ± 0.6 kcal/mol.

Shvelyshev and Edeleva (5) report the solubility product of CaF₂ as $2.7 \pm 0.27 \times 10^{-11}$ in dilute HCl, which yields $\Delta G_{298}^\circ = 14.42$ kcal/mol for the reaction $\text{CaF}_2(\text{c}) + \text{Ca}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq})$. Using ΔG_f° (Ca²⁺, aq) = -132.30 kcal/mol (2) and ΔG_f° (F⁻, aq) = -66.95 kcal/mol (4) we obtain ΔG_f° (CaF₂, c) = -280.84 ± 0.6 kcal/mol, which using the adopted functions yields ΔH_f° (CaF₂, c) = -293.1 ± 0.6 kcal/mol.

Vechev and Vechev (17) have measured the ent of a high temperature solid state cell and report $\Delta G_{1200}^\circ = -17.6 \pm 0.2$ kcal/mol for the reaction $\text{CaO}(\text{c}) + \text{MgF}_2(\text{c}) + \text{CaF}_2(\text{c}) + \text{MgO}(\text{c})$. This reduces to $\Delta H_{298}^\circ = -17.6$ kcal/mol which, using JANAF values for MgO and MgF₂ and CaO from reference 2, yields ΔH_f° (CaF₂, c) = -294.4 ± 1.3 kcal/mol.

Kohlrausch (18) reported the solubility of CaF₂ and fluorapatite, which yield solubility products of 3.6×10^{-11} and 2.8×10^{-11} . From these we obtain, as above, ΔH_f° (CaF₂, c) = -292.9 and -293.1 kcal/mol.

Guntz (19) made measurements on the neutralization of $\text{Ca}(\text{OH})_2(\text{aq})$ and HF(aq) which yield ΔH_f° (CaF₂, c) = -293.1 kcal/mol, according to Parker (2).

A median value of ΔH_{298}° (CaF₂, c) = -293 ± 1.5 kcal/mol is adopted.

Heat Capacity and Entropy

Huffman and Norwood (8) have measured the low temperature heat capacity in the range 3.6° to 30°K . Eucken and Schwes (7) in the range 17° to 86°K and Todd (9) from 50° to 296.5°K . We have fitted a smooth polynomial curve through the data of references 6 and 8 and this yields $S_{298}^\circ = 16.39 \pm 0.08$ eu based on $S_{298}^\circ = 0.0002$ eu. The values of reference 7 deviate considerably at the lowest temperatures but are in reasonable agreement at higher temperatures.

The high temperature enthalpy of calcium fluoride has been reported by Naylor (3) to 1788°K , Kestnikov and Karetnikov (10) to 1273°K , and Lyashenko (11) to 1490°K . All the data are in approximate agreement and the more extensive results of Naylor on a very pure sample are adopted. The heat capacities, below 1424°K were derived from a polynomial fit of the enthalpy data of the form $H = at^4 + bt^3 + ct^2 + d/T + e/T^2$.

Transition Data

The temperature of transition is that reported by Naylor (3), the large uncertainty has been assigned since at 1424°K the enthalpies indicate complete conversion to $\beta\text{-CaF}_2$, and the next lower point is at 1402°K . Evidence in support of a transition in this region comes from Lyashenko (11) whose plot indicates a break between 1273° and 1413°K . In addition, SrCl_2 which has the fluorite structure has a transition near the melting point. The enthalpy of transition is that reported by Naylor (3).

Melting Data

McCreary (12) reports the melting point of a 99.1% pure sample as $1687 \pm 5^\circ\text{K}$. Porter and Brown (13) report $1675 \pm 5^\circ\text{K}$ as the melting point of 99.8% pure CaF₂ and Rogers et al. (14) obtained 1684°K as the melting point. The adopted melting point is $1691 \pm 5^\circ\text{K}$, for a sample of natural fluorite of high purity, was reported by Naylor (3). The heat of melting, 7100 cal, is that measured by Naylor (3). Three determinations from high temperature phase diagrams give 7250 ± 350 cal (15), 5500 cal (16) and 9800 cal (14).

Sublimation Data

See the CaF₂(g) table for details.

References:

1. D. R. Torgeson and T. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948).
2. V. B. Parker, Natl. Bur. Std., private communication Jan. 1969.
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. Consistent with the ΔH_f° (g) value.
5. S. Shvelyshev and E. Edeleva, Vysokiy Uchebn. Zavedeni, Khim. i Khim. Tekhnol. 5, 871 (1962).
6. D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).
7. A. Eucken and F. Schwes, Ber. Deut. Physik. Ges. 15, 578 (1913).
8. S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949).
9. B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945).
10. B. F. Kestnikov and G. A. Karetnikov, Legkie Metal. 3, 29 (1934) and 16 (1935).
11. V. S. Lyashenko, Zh. Fiz. Khim. 43, 1613 (1969).
12. W. J. McCreary, J. Am. Chem. Soc. 77, 2113 (1955).
13. B. Porter and E. A. Brown, J. Am. Ceram. Soc. 45, 49 (1962).
14. P. S. Rogers, J. W. Tomlinson and F. D. Richardson, Met. Soc. Conf. 8, 909 (1961).
15. F. Debove, Compt. Rend. 252, 2192 (1961).
16. D. Vechev and A. Vechev, Compt. Rend. 243, 360 (1956).
17. D. Vechev and A. Vechev, Zh. Fiz. Khim. 44, 129 (1970).
18. F. Kohlrausch, Z. Physik. Chem. 64, 129 (1909).
19. A. Guntz, Ann. Chim. Phys. 3, 5 (1884).

Calcium Difluoride (CaF₂)

(Liquid) GFW = 78.0768

CALCIUM DIFLUORIDE (CaF₂)

(LIQUID)

GFW = 78.0768

 $S_{298.15}^{\circ} = 22.125$ gibbs/mol $\Delta H_{298.15}^{\circ} = -283.477 \pm 1.5$ kcal/mol $T_m = 1691 \pm 5^{\circ}\text{K}$ $\Delta H_m^{\circ} = 7.10 \pm 0.1$ kcal/mol $T_b = 2806.5 \pm 30^{\circ}\text{K}$ $\Delta H_v^{\circ} = 73.78 \pm 0.8$ kcal/mol

Heat of Formation

The heat of formation is obtained from that of the crystal by adding the heat of melting and the difference between $H_{1691} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived from the heat content measurements of B. F. Naylor, J. Am. Chem. Soc. 57, 150 (1943). The heat capacity is constant in the real liquid range but at 1000°K a glass transition is assumed below which it follows that of the crystal. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which $\Delta G = 0$ for the vaporization process. The heat of vaporization is the difference in $\Delta H_{T_b}^{\circ}$ between liquid and gas.

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log K ^e
0							
100	16.393	22.125	22.125	.000	-283.477	-272.668	199.871
200	16.437	22.227	22.126	.030	-283.472	-272.601	199.590
300	16.479	22.328	22.127	.054	-283.465	-272.534	199.309
400	16.519	22.428	22.128	.078	-283.457	-272.467	199.028
500	16.557	22.527	22.129	.102	-283.449	-272.400	198.747
600	16.594	22.625	22.130	.126	-283.441	-272.333	198.466
700	16.629	22.722	22.131	.150	-283.433	-272.266	198.185
800	16.663	22.818	22.132	.174	-283.425	-272.199	197.904
900	16.696	22.914	22.133	.198	-283.417	-272.132	197.623
1000	16.728	23.009	22.134	.222	-283.409	-272.065	197.342
1100	16.759	23.103	22.135	.246	-283.401	-272.000	197.061
1200	16.789	23.196	22.136	.270	-283.393	-271.933	196.780
1300	16.818	23.288	22.137	.294	-283.385	-271.866	196.499
1400	16.846	23.379	22.138	.318	-283.377	-271.800	196.218
1500	16.873	23.469	22.139	.342	-283.369	-271.733	195.937
1600	16.899	23.558	22.140	.366	-283.361	-271.666	195.656
1700	16.924	23.646	22.141	.390	-283.353	-271.600	195.375
1800	16.948	23.733	22.142	.414	-283.345	-271.533	195.094
1900	16.971	23.819	22.143	.438	-283.337	-271.466	194.813
2000	16.994	23.904	22.144	.462	-283.329	-271.400	194.532
2100	17.016	23.988	22.145	.486	-283.321	-271.333	194.251
2200	17.037	24.071	22.146	.510	-283.313	-271.266	193.970
2300	17.058	24.153	22.147	.534	-283.305	-271.200	193.689
2400	17.078	24.234	22.148	.558	-283.297	-271.133	193.408
2500	17.097	24.314	22.149	.582	-283.289	-271.066	193.127
2600	17.116	24.393	22.150	.606	-283.281	-271.000	192.846
2700	17.134	24.471	22.151	.630	-283.273	-270.933	192.565
2800	17.151	24.548	22.152	.654	-283.265	-270.866	192.284
2900	17.168	24.624	22.153	.678	-283.257	-270.800	192.003
3000	17.184	24.699	22.154	.702	-283.249	-270.733	191.722
3100	17.199	24.773	22.155	.726	-283.241	-270.666	191.441
3200	17.214	24.846	22.156	.750	-283.233	-270.600	191.160
3300	17.228	24.918	22.157	.774	-283.225	-270.533	190.879
3400	17.241	24.989	22.158	.798	-283.217	-270.466	190.598
3500	17.254	25.059	22.159	.822	-283.209	-270.400	190.317
3600	17.266	25.128	22.160	.846	-283.201	-270.333	190.036
3700	17.277	25.196	22.161	.870	-283.193	-270.266	189.755
3800	17.288	25.263	22.162	.894	-283.185	-270.200	189.474
3900	17.298	25.329	22.163	.918	-283.177	-270.133	189.193
4000	17.308	25.394	22.164	.942	-283.169	-270.066	188.912

CALCIUM DIFLUORIDE (CaF₂) (IDEAL GAS) GFW = 78.0768

Point Group = C_{2v}

$\Delta H_f^\circ = -187 \pm 2$ kcal/mol

$\Delta H_f^\circ = -187.5 \pm 2$ kcal/mol

$S_{298.15}^\circ = 65.41 \pm 0.5$ gibbs/mol

$\Delta H_{298.15}^\circ = -187.5 \pm 2$ kcal/mol

Ground State Quantum Weight = 1

Calcium Difluoride (CaF₂)

(Ideal Gas) GFW = 78.0768

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.000	0.000	INFINITE	3.025	-187.044	-187.044	INFINITE
100	9.365	53.694	75.485	2.179	-187.127	-188.046	410.974
200	11.121	60.738	66.501	1.153	-187.343	-188.076	206.396
298	12.253	65.412	65.412	0.000	-187.500	-188.597	138.131
300	12.266	65.488	65.412	0.023	-187.503	-189.611	138.131
400	12.675	69.110	65.902	1.263	-187.650	-190.290	103.970
500	13.209	72.022	66.864	2.569	-187.797	-190.833	83.457
600	13.668	74.469	67.915	3.920	-187.940	-191.346	69.770
700	13.956	76.526	69.001	5.268	-188.105	-191.833	59.987
800	13.619	78.339	70.027	6.626	-188.406	-192.468	52.635
900	13.678	79.947	71.068	7.991	-188.969	-193.155	46.904
1000	13.721	81.381	72.030	9.361	-189.389	-193.598	42.311
1100	13.753	82.700	72.941	10.735	-189.665	-193.997	38.544
1200	13.778	83.920	73.805	12.110	-189.897	-194.354	35.249
1300	13.797	85.051	74.624	13.490	-190.022	-194.555	32.474
1400	13.812	86.024	75.402	14.870	-190.069	-194.695	30.362
1500	13.825	86.978	76.143	16.252	-190.018	-194.816	28.356
1600	13.835	87.910	76.848	17.635	-190.170	-194.722	26.598
1700	13.841	88.820	77.515	19.020	-190.305	-194.525	25.043
1800	13.851	89.501	78.151	20.404	-190.375	-194.205	23.590
1900	13.857	90.250	78.782	21.789	-190.613	-192.183	22.106
2000	13.862	90.961	79.373	23.175	-190.654	-190.158	20.780
2100	13.866	91.637	79.941	24.562	-190.699	-188.134	19.579
2200	13.874	92.289	80.484	25.950	-190.740	-186.075	17.491
2300	13.879	92.916	81.004	27.336	-190.805	-184.005	15.786
2400	13.877	93.469	81.521	28.723	-190.869	-182.042	16.577
2500	13.879	94.056	82.011	30.111	-190.940	-180.006	15.736
2600	13.881	94.600	82.485	31.499	-191.021	-177.967	14.959
2700	13.885	95.116	82.948	32.876	-191.116	-175.929	14.258
2800	13.885	95.608	83.388	34.256	-191.216	-173.879	13.572
2900	13.887	96.076	83.816	35.627	-191.335	-171.827	12.946
3000	13.889	96.587	84.236	37.003	-191.471	-169.776	12.368
3100	13.890	97.043	84.642	38.442	-191.624	-167.717	11.824
3200	13.892	97.501	85.020	39.880	-191.795	-165.653	11.313
3300	13.893	97.961	85.379	41.320	-191.990	-163.583	10.843
3400	13.893	98.326	85.794	42.610	-192.214	-161.506	10.401
3500	13.894	98.729	86.157	43.999	-192.461	-159.420	9.955
3600	13.895	99.120	86.512	45.388	-192.735	-157.329	9.551
3700	13.897	99.501	86.854	46.746	-193.038	-155.233	9.187
3800	13.897	99.874	87.186	48.100	-193.368	-153.133	8.867
3900	13.897	100.232	87.523	49.557	-193.741	-151.010	8.442
4000	13.898	100.584	87.847	50.947	-194.140	-148.881	8.135
4100	13.899	100.927	88.162	52.337	-194.574	-146.745	7.822
4200	13.900	101.262	88.470	53.727	-195.043	-144.597	7.528
4300	13.900	101.590	88.770	55.117	-195.547	-142.439	7.258
4400	13.901	101.909	89.066	56.507	-196.087	-140.265	6.987
4500	13.901	102.221	89.355	57.897	-196.663	-138.083	6.704
4600	13.901	102.527	89.638	59.287	-197.273	-135.886	6.456
4700	13.902	102.826	90.016	60.677	-197.920	-133.677	6.216
4800	13.902	103.119	90.390	62.067	-198.607	-131.456	5.986
4900	13.902	103.405	90.755	63.457	-199.333	-129.208	5.763
5000	13.902	103.686	90.716	64.848	-200.058	-126.954	5.549
5100	13.903	103.961	90.973	66.238	-200.836	-124.687	5.343
5200	13.903	104.231	91.226	67.628	-201.664	-122.398	5.144
5300	13.903	104.496	91.476	69.018	-202.542	-120.094	4.951
5400	13.903	104.746	91.717	70.409	-203.465	-117.784	4.767
5500	13.904	104.911	91.957	71.799	-204.435	-115.468	4.587
5600	13.904	105.262	92.182	73.190	-205.449	-113.098	4.414
5700	13.904	105.706	92.421	74.580	-206.508	-110.730	4.246
5800	13.905	106.145	92.658	75.970	-207.612	-108.362	4.083
5900	13.905	106.587	92.875	77.361	-208.761	-105.950	3.928
6000	13.905	106.921	93.086	78.751	-209.917	-103.534	3.771

Dec. 31, 1968

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	Points	2nd law	3rd law	Drift
1463	1668	9	106.2 ± 3.7	105.66 ± 0.9
1246	1498	6	99.6 ± 2.5	106.00 ± 1.0
1421	1689	34	102.4 ± 0.3	104.00 ± 0.2
1823		1	106.4	106.4
2086	2208	7	106.7 ± 4.8	105.22 ± 0.5
1242	1669	19	104.7 ± 0.5	-0.7 ± 2.2

$\Delta H_{298.15}^\circ = 1.2836 \times 10^{-114} \text{ g}^{-3} \text{ cm}^6$
 Bond Distance: Ca-F = 2.1 Å
 Bond Angle: F-Ca-F = 135 ± 7°
 Product of the Moments of Inertia: $I_A I_B I_C = 1.2836 \times 10^{-114} \text{ g}^{-3} \text{ cm}^6$
 $\sigma = 2$

The heat of formation is obtained from that of the crystal by adding $\Delta H_{298.15}^\circ$. The vapor pressure data of five authors was analysed by 2nd and 3rd law methods to give $\Delta H_{298.15}^\circ$ as listed below. Note that the drifts are small and both positive and negative confirming the correctness of the functions used.

Reference	Range °K	Points	2nd law	3rd law	Drift
Freeman (1)	1463 - 1668	9	106.2 ± 3.7	105.66 ± 0.9	-0.2 ± 2.3
Blue et al. (2)	1246 - 1498	6	99.6 ± 2.5	106.00 ± 1.0	4.1 ± 2.0
Schulz and Searcy (3)	1421 - 1689	34	102.4 ± 0.3	104.00 ± 0.2	1.0 ± 0.2
Pottier (4)	1823	1	106.4	106.4	
Ruff and LeBoucher (5)	2086 - 2208	7	106.7 ± 4.8	105.22 ± 0.5	-0.7 ± 2.2
Blue et al. (2) *	1242 - 1669	19	104.7 ± 0.5		

* This set was not analysed by the third law since the absolute pressures were adjusted by the authors to match their weight loss values.

A median value of 105.5 ± 0.5 kcal/mol is adopted for the heat of sublimation which yields $\Delta H_{298.15}^\circ(\text{CaF}_2, \text{g}) = -187.5 \pm 2$ kcal/mol.

Heat Capacity and Entropy

The bond length was measured by Akishin and Spiridonov (6), but the diffraction patterns were interpreted as indicating a linear molecule. The vibrational frequencies and bond angle are those reported by Calder (7) using matrix isolation spectroscopy and isotopically enriched materials.

The individual moments are $I_A = 2.092 \times 10^{-39}$, $I_B = 2.3749 \times 10^{-38}$, and $I_C = 2.5840 \times 10^{-38} \text{ g cm}^2$.

References

1. R. D. Freeman, Tech. Doc. Rept. ASD TDR 63-754, Part II, Oklahoma State University, 1965.
2. G. D. Blue, J. W. Green, R. G. Bautista and J. L. Margrave, J. Phys. Chem. **67**, 877 (1963).
3. D. A. Schulz and A. W. Searcy, J. Phys. Chem. **67**, 103 (1963).
4. R. W. Pottier, quoted in Reference 1.
5. O. Ruff and L. LeBoucher, Z. Anorg. Chem. **213**, 376 (1934).
6. P. A. Akishin and V. P. Spiridonov, Kristallografiya, **2**, 475 (1957).
7. G. V. Calder, Natl. Bur. Std. Rept. 9389, July 1966.

Point Group [C_{∞v}]

$$\Delta H_f^\circ = 88.5 \pm 15 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = 87.7 \pm 15 \text{ kcal/mol}$$

$$S_{298.15}^\circ = [55.4 \pm 2] \text{ gibbs/mol}$$

Ground State Quantum Weight = [1]

Calcium Monohydroxide Uniprotonated Ion (CaOH⁺)

GFW = 57.08682

(Ideal Gas)

T, °K	C _p ^a	S ^b	-(C _p ^a - H ₂₉₈)/T	H ^c - H ₂₉₈	ΔH ^c	ΔG ^d	Log K ^e
0							
100							
200							
298	10.993	55.380	55.380	.000	87.700	88.620	- 62.028
300							
350	11.009	58.688	58.390	-.020	87.708	88.600	- 61.631
400	11.607	59.714	59.821	1.157	87.099	88.522	- 65.635
500	12.056	61.162	59.673	2.345	86.322	88.367	- 36.003
600	12.312	63.944	57.884	3.588	86.660	88.185	- 29.557
700	12.506	65.097	56.833	4.805	89.004	79.864	- 24.935
800	12.643	65.815	56.151	5.981	89.173	80.000	- 24.935
900	12.743	66.180	60.525	7.360	89.173	77.268	- 18.592
1000	12.816	66.410	61.410	8.630	89.282	75.917	- 16.592
1100	13.118	71.283	62.552	9.935	89.344	74.517	- 16.817
1200	13.253	72.630	63.053	11.293	87.576	73.367	- 13.666
1300	13.357	73.692	63.513	12.610	86.195	70.972	- 11.070
1400	13.427	74.602	63.943	13.929	86.195	70.972	- 11.070
1500	13.465	75.427	65.238	15.284	88.509	69.731	- 10.160
1600	13.705	76.308	65.902	16.669	88.484	68.484	- 9.459
1700	13.796	77.142	66.539	18.078	89.182	67.187	- 8.836
1800	13.854	77.934	67.138	19.460	89.182	67.187	- 8.836
1900	13.956	78.683	67.738	20.800	89.182	67.331	- 7.748
2000	14.023	79.403	68.303	22.199	88.642	68.045	- 7.438
2100	14.085	80.088	68.848	23.604	88.642	68.045	- 7.438
2200	14.181	80.745	69.374	25.014	88.642	68.672	- 7.157
2300	14.313	81.368	69.882	26.432	88.642	69.455	- 6.900
2400	14.450	81.960	70.372	27.859	88.642	70.740	- 6.662
2500	14.582	82.562	70.850	29.280	88.642	71.342	- 6.238
2600	14.722	83.173	71.311	30.711	88.642	71.957	- 5.871
2700	14.857	83.664	71.750	32.144	88.642	72.532	- 5.471
2800	14.980	84.129	72.173	33.572	88.642	73.059	- 5.049
2900	15.100	84.569	72.583	35.000	88.642	73.532	- 4.602
3000	15.217	84.982	72.978	36.428	88.642	74.050	- 4.130
3100	15.332	85.366	73.359	37.856	88.642	74.512	- 3.641
3200	15.447	85.729	73.726	39.284	88.642	74.918	- 3.136
3300	15.561	86.076	74.081	40.712	88.642	75.368	- 2.613
3400	15.675	86.406	74.426	42.140	88.642	75.860	- 2.072
3500	15.787	86.717	74.756	43.568	88.642	76.392	- 1.513
3600	15.898	87.018	75.076	45.000	88.642	76.964	- 0.938
3700	16.008	87.309	75.386	46.432	88.642	77.576	- 0.358
3800	16.117	87.590	75.687	47.864	88.642	78.228	0.228
3900	16.225	87.861	75.978	49.296	88.642	78.920	0.803
4000	16.332	88.122	76.260	50.728	88.642	79.652	1.378
4100	16.438	88.373	76.542	52.160	88.642	80.424	1.953
4200	16.544	88.614	76.815	53.592	88.642	81.236	2.528
4300	16.649	88.845	77.078	55.024	88.642	82.088	3.103
4400	16.754	89.066	77.331	56.456	88.642	82.980	3.678
4500	16.858	89.277	77.574	57.888	88.642	83.912	4.253
4600	16.962	89.478	77.807	59.320	88.642	84.884	4.828
4700	17.065	89.669	78.030	60.752	88.642	85.896	5.403
4800	17.168	89.850	78.243	62.184	88.642	86.948	5.978
4900	17.270	89.999	78.446	63.616	88.642	88.040	6.553
5000	17.372	90.138	78.639	65.048	88.642	89.172	7.128
5100	17.474	90.267	78.822	66.480	88.642	90.344	7.703
5200	17.575	90.386	78.995	67.912	88.642	91.556	8.278
5300	17.676	90.495	79.158	69.344	88.642	92.808	8.853
5400	17.776	90.594	79.311	70.776	88.642	94.100	9.428
5500	17.876	90.683	79.454	72.208	88.642	95.432	10.003
5600	17.975	90.762	79.587	73.640	88.642	96.804	10.578
5700	18.074	90.831	79.710	75.072	88.642	98.216	11.153
5800	18.172	90.890	79.823	76.504	88.642	99.668	11.728
5900	18.269	90.939	79.926	77.936	88.642	101.160	12.303
6000	18.366	90.978	80.019	79.368	88.642	102.692	12.878

June 30, 1970

D. E. Jensen (1) determined the heat of reaction $\Delta H_r^\circ = 35 \pm 10$ kcal/mol for $\text{Ca(g)} + \text{OH(g)} \rightarrow \text{CaOH}^+(\text{g}) + e^-$ in atmospheric pressure hydrogen-nitrogen-oxygen flames using the microwave cavity resonance method. This value was calculated assuming a bent model for CaOH; the value is not significantly changed, within the uncertainty, by the change in configuration. Combining ΔH_r° with JANAF heats of formation of Ca(g) and OH(g) and electron, we obtain $\Delta H_f^\circ(\text{CaOH}^+, \text{g}) = 87.7$ kcal/mol, which is adopted in the table. This corresponds to an ionization potential of 6.11 eV.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that gaseous NaOH, KOH, CaOH, RbOH are linear (2, 3, 4). This evidence also confirms the prediction of A. D. Walsh (5) that "HAB" molecules with 10 or less valence electrons (CaOH⁺ has 8 valence electrons) will be linear in their ground state. The molecule of CaOH⁺ has an isoelectronic structure of KOH.

The bond distances O-H and Ca-O are assumed to be the same as those in $\text{H}_2\text{O(g)}$ and CaO(g) , respectively (6, 7). The moment of inertia is 7.1284×10^{-39} g cm².

The Ca-O stretching frequency 733 cm⁻¹ is estimated from those of CaO(g) (8) and CaF(g) (9). The O-H stretching frequency, 3600 cm⁻¹, is estimated from those of $\text{H}_2\text{O(g)}$ (6) and $\text{CaOH}_2(\text{g})$ (10). The bending vibrational frequency, 370 cm⁻¹, is estimated by comparison with those of NaOH, KOH, RbOH (2, 4).

The enthalpy change between 0° and 298°K is 7.630 kcal/mol.

References

1. D. E. Jensen, Combustion and Flame **13**, 261 (1968).
2. N. Acquista, S. Abramowitz and D. R. Lide, J. Chem. Phys. **43**, 780 (1965).
3. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. **44**, 3131 (1966).
4. N. Acquista and S. Abramowitz, Natl. Bur. Stds. Report 9805, July 1968.
5. A. D. Walsh, J. Chem. Soc. **1953**, 2288 (1953).
6. JANAF $\text{H}_2\text{O(g)}$ table, dated Mar. 31, 1961.
7. M. Hultin and A. Lagerqvist, Arkiv. Fysik, **2**, 471 (1950).
8. JANAF CaF(g) table, dated Dec. 31, 1968.
9. L. Brewer and R. Hauge, J. Mol. Spectry. **25**, 330 (1968).
10. O. Oehler and H. H. Günthard, J. Chem. Phys. **51**, 4714 (1969).

Calcium Monohydroxide (CaOH)

(Ideal Gas) GFW = 57.08737

CALCIUM MONOHYDROXIDE (CaOH)

(IDEAL GAS)

GFW = 57.08737

Point Group [C_{∞v}] $\Delta H_f^\circ = -52.5 \pm 5 \text{ kcal/mol}$ $S_{298.15}^\circ = [56.8 \pm 2] \text{ gibbs/mol}$ $\Delta H_f^\circ_{298.15} = -53.3 \pm 5 \text{ kcal/mol}$

T, °K	Cp°	gibbs/mol S°	(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	7.000	INFINITE	-	2.433	-52.512	-	INFINITE
100	7.821	46.095	INFINITE	-	52.512	-	INFINITE
200	9.483	57.591	57.730	1.919	-52.759	-51.738	117.445
298	10.993	56.757	56.757	0.000	-53.059	-50.660	59.664
300	11.009	56.825	56.767	0.020	-53.305	-50.303	40.538
400	12.535	62.740	57.564	1.020	-53.305	-55.316	40.298
500	12.056	62.740	57.564	2.135	-53.305	-58.546	24.716
600	12.312	64.962	59.022	3.564	-53.840	-57.104	20.400
700	12.506	66.475	60.010	4.805	-53.992	-57.636	17.995
800	12.673	68.056	60.975	5.964	-54.075	-58.117	15.877
900	12.825	69.697	61.913	7.064	-54.117	-58.542	14.216
1000	12.976	71.317	62.787	8.130	-54.205	-58.936	12.403
1100	13.118	72.660	63.629	9.935	-55.640	-59.300	11.742
1200	13.253	73.408	64.430	11.253	-57.005	-59.440	10.629
1300	13.379	74.073	65.193	12.585	-58.004	-59.562	10.017
1400	13.497	74.687	65.915	13.840	-58.727	-59.670	9.416
1500	13.606	75.260	66.615	15.064	-59.270	-59.764	8.810
1600	13.705	75.786	67.280	16.250	-59.644	-59.866	8.177
1700	13.797	76.269	67.916	17.409	-59.823	-59.936	7.705
1800	13.880	76.710	68.520	18.540	-59.926	-59.976	7.209
1900	13.956	77.115	69.100	19.640	-59.954	-59.996	6.709
2000	14.026	77.488	69.661	20.710	-59.961	-59.996	6.209
2100	14.093	77.826	70.206	21.760	-59.954	-59.976	5.709
2200	14.153	78.129	70.729	22.790	-59.936	-59.936	5.209
2300	14.210	78.394	71.230	23.800	-59.904	-59.880	4.709
2400	14.263	78.626	71.710	24.790	-59.858	-59.826	4.209
2500	14.315	78.830	72.170	25.760	-59.800	-59.760	3.709
2600	14.365	79.006	72.610	26.710	-59.736	-59.696	3.209
2700	14.413	79.154	73.030	27.640	-59.664	-59.624	2.709
2800	14.461	79.284	73.430	28.560	-59.584	-59.544	2.209
2900	14.506	79.396	73.810	29.470	-59.496	-59.456	1.709
3000	14.554	79.490	74.170	30.370	-59.400	-59.360	1.209
3100	14.601	79.563	74.506	31.260	-59.296	-59.256	0.709
3200	14.648	79.617	74.816	32.140	-59.184	-59.144	0.209
3300	14.695	79.654	75.106	33.010	-59.064	-59.024	-0.309
3400	14.743	79.676	75.376	33.870	-58.936	-58.896	-0.809
3500	14.791	79.686	75.626	34.720	-58.800	-58.760	-1.309
3600	14.840	79.686	75.856	35.560	-58.656	-58.616	-1.809
3700	14.889	79.676	76.066	36.390	-58.504	-58.464	-2.309
3800	14.939	79.654	76.256	37.210	-58.344	-58.304	-2.809
3900	14.987	79.622	76.430	38.020	-58.176	-58.136	-3.309
4000	15.039	79.580	76.590	38.820	-58.000	-58.000	-3.809
4100	15.089	79.526	76.736	39.610	-57.816	-57.776	-4.309
4200	15.139	79.460	76.866	40.390	-57.624	-57.584	-4.809
4300	15.190	79.384	76.980	41.160	-57.424	-57.384	-5.309
4400	15.240	79.300	77.080	41.930	-57.216	-57.176	-5.809
4500	15.289	79.206	77.166	42.690	-56.996	-56.956	-6.309
4600	15.338	79.106	77.240	43.440	-56.764	-56.724	-6.809
4700	15.386	79.000	77.300	44.180	-56.520	-56.480	-7.309
4800	15.436	78.886	77.346	44.910	-56.264	-56.224	-7.809
4900	15.483	78.766	77.376	45.630	-55.996	-55.956	-8.309
5000	15.529	78.640	77.396	46.340	-55.716	-55.676	-8.809
5100	15.575	78.506	77.406	47.040	-55.424	-55.384	-9.309
5200	15.620	78.366	77.406	47.730	-55.120	-55.080	-9.809
5300	15.663	78.216	77.396	48.410	-54.804	-54.764	-10.309
5400	15.705	78.056	77.376	49.080	-54.476	-54.436	-10.809
5500	15.746	77.886	77.346	49.740	-54.136	-54.096	-11.309
5600	15.786	77.710	77.300	50.390	-53.784	-53.744	-11.809
5700	15.825	77.526	77.240	51.030	-53.416	-53.376	-12.309
5800	15.862	77.336	77.166	51.660	-53.036	-52.996	-12.809
5900	15.897	77.140	77.080	52.280	-52.644	-52.604	-13.309
6000	15.932	76.940	76.980	52.890	-52.240	-52.200	-13.809

Electronic Levels and Quantum Heights

ϵ_i , cm ⁻¹	g_i
0	[2]
[16000]	[2]
[16100]	[2]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
[733] (1)	[3600] (1)
[320] (2)	[3600] (1)

Bond Distance: Ca-O = [1.82] Å O-H = [0.96] Å
 Bond Angle: Ca-O-H = [180°]
 Rotational Constant: B₀ = [0.3926] cm⁻¹

σ = 1

Heat of Formation

Cotton and Jenkins (1) determined the equilibrium constants in the temperature range 1570°K-2030°K for the reaction $\text{Ca}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CaOH}(g) + \text{H}(g)$ by atomic absorption spectroscopy in a fuel-rich hydrogen-nitrogen-oxygen flame. Using all JANAF functions, third law analyses of the data give $\Delta H_f^\circ_{298} = 13.8 \text{ kcal/mol}$ and the drift $1.9 \pm 2.9 \text{ eu}$. This leads to the heat of formation, $\Delta H_f^\circ(\text{CaOH}, g) = -53.3 \text{ kcal/mol}$ which is adopted in the tabulation. The bond dissociation energy, $D_0(\text{Ca-OH})$, is 104.6 kcal/mol .

Ryabova and Gurvich (2) reported the bond dissociation energy $D_0(\text{Ca-OH})$ as 100 kcal/mol . Schofield and Sugden (3) found $D_0(\text{Ca-OH})_2$ as $217 \pm 12 \text{ kcal/mol}$. Using the relation $D_0(\text{H-X})/D_0(\text{H-X})_2 = 0.47$ suggested by Kent, McDonald and Hargrave (4), we obtain $D_0(\text{Ca-OH}) = 102 \text{ kcal/mol}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that gaseous NaOH, KOH, CaOH and RbOH are linear (5, 6, 7). This evidence also confirms the prediction of A. D. Walsh (8) that "HAB" molecules with 10 or less valence electrons (CaOH has 9 valence electrons) will be linear in their ground state.

The ground state is assumed to be $^2\Sigma$ by analogy with isoelectronic CaF (9). The electronic levels are estimated from band spectra of CaOH reported by Gaydon (10).

The bond distances O-H and Ca-O are assumed to be the same as those in $\text{H}_2\text{O}(g)$ and $\text{CaO}(g)$, respectively (10, 11).

The moment of inertia is $7.1295 \times 10^{-39} \text{ g cm}^2$.

The O-H stretching frequency, 3600 cm^{-1} , is estimated from those of $\text{H}_2\text{O}(g)$ (10) and $\text{CaOH}(g)$ (12). The bending frequency, 320 cm^{-1} , is estimated by comparison with those of NaOH, CaOH and RbOH (5, 7). The Ca-O stretching frequency, 733 cm^{-1} , is estimated to be the same as that of $\text{CaO}(g)$ observed by Hultin and Lagerqvist (11) and Brewer and Hauge (13).

References

1. D. H. Cotton and D. R. Jenkins, Trans. Faraday Soc. 64, 2388 (1968).
2. V. G. Ryabova and L. V. Gurvich, Teplofizika Vysokikh Temperatur, 3, 318, (1965).
3. K. Schofield and T. M. Sugden, Trans. Faraday Soc. 62, 566 (1966).
4. R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966).
5. N. Acquista, S. Abramowitz and D. R. Lide, J. Chem. Phys. 49, 780 (1968).
6. R. L. Kuczkowski and D. R. Lide, J. Chem. Phys. 44, 3131 (1966).
7. N. Acquista and S. Abramowitz, Matl. Bur. Stde. Report 9905, July, 1968.
8. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
9. JANAF CaF(g) table dated Dec. 31, 1968.
10. JANAF $\text{H}_2\text{O}(g)$ table dated Mar. 31, 1961.
11. M. Hultin and Lagerqvist, Arkiv Fysik, 2, 471 (1950).
12. O. Oehler and H. H. Günthard, J. Chem. Phys. 51, 4714 (1969).
13. L. Brewer and R. Hauge, J. Mol. Spectry. 25, 330 (1968).
14. A. G. Gaydon, Proc. Roy. Soc. (London) A231, 437 (1955).

T, °K.	C _p	S° - (F° - H° ₃₀₀)/T	H° - H° ₃₀₀	ΔH _f °	Log K _p
0	4.000	INFINITE	1.459	29,520	INFINITE
100	5.038	37.412	26.805	26,316	28,780
200	5.219	39.456	26,922	25,102	18,400
300	5.223	39.466	26,924	25,079	18,269
400	5.220	39.463	26,923	25,078	18,268
500	5.218	39.461	26,922	25,077	18,267
600	5.216	39.459	26,921	25,076	18,266
700	5.214	39.457	26,920	25,075	18,265
800	5.212	39.455	26,919	25,074	18,264
900	5.210	39.453	26,918	25,073	18,263
1000	5.208	39.451	26,917	25,072	18,262
1100	5.206	39.449	26,916	25,071	18,261
1200	5.204	39.447	26,915	25,070	18,260
1300	5.202	39.445	26,914	25,069	18,259
1400	5.200	39.443	26,913	25,068	18,258
1500	5.198	39.441	26,912	25,067	18,257
1600	5.196	39.439	26,911	25,066	18,256
1700	5.194	39.437	26,910	25,065	18,255
1800	5.192	39.435	26,909	25,064	18,254
1900	5.190	39.433	26,908	25,063	18,253
2000	5.188	39.431	26,907	25,062	18,252
2100	5.186	39.429	26,906	25,061	18,251
2200	5.184	39.427	26,905	25,060	18,250
2300	5.182	39.425	26,904	25,059	18,249
2400	5.180	39.423	26,903	25,058	18,248
2500	5.178	39.421	26,902	25,057	18,247
2600	5.176	39.419	26,901	25,056	18,246
2700	5.174	39.417	26,900	25,055	18,245
2800	5.172	39.415	26,899	25,054	18,244
2900	5.170	39.413	26,898	25,053	18,243
3000	5.168	39.411	26,897	25,052	18,242
3100	5.166	39.409	26,896	25,051	18,241
3200	5.164	39.407	26,895	25,050	18,240
3300	5.162	39.405	26,894	25,049	18,239
3400	5.160	39.403	26,893	25,048	18,238
3500	5.158	39.401	26,892	25,047	18,237
3600	5.156	39.399	26,891	25,046	18,236
3700	5.154	39.397	26,890	25,045	18,235
3800	5.152	39.395	26,889	25,044	18,234
3900	5.150	39.393	26,888	25,043	18,233
4000	5.148	39.391	26,887	25,042	18,232
4100	5.146	39.389	26,886	25,041	18,231
4200	5.144	39.387	26,885	25,040	18,230
4300	5.142	39.385	26,884	25,039	18,229
4400	5.140	39.383	26,883	25,038	18,228
4500	5.138	39.381	26,882	25,037	18,227
4600	5.136	39.379	26,881	25,036	18,226
4700	5.134	39.377	26,880	25,035	18,225
4800	5.132	39.375	26,879	25,034	18,224
4900	5.130	39.373	26,878	25,033	18,223
5000	5.128	39.371	26,877	25,032	18,222
5100	5.126	39.369	26,876	25,031	18,221
5200	5.124	39.367	26,875	25,030	18,220
5300	5.122	39.365	26,874	25,029	18,219
5400	5.120	39.363	26,873	25,028	18,218
5500	5.118	39.361	26,872	25,027	18,217
5600	5.116	39.359	26,871	25,026	18,216
5700	5.114	39.357	26,870	25,025	18,215
5800	5.112	39.355	26,869	25,024	18,214
5900	5.110	39.353	26,868	25,023	18,213
6000	5.108	39.351	26,867	25,022	18,212

March 31, 1961

Electronic Levels and Multiplicities

E ₁ cm. ⁻¹	E ₂ cm. ⁻¹	E ₃ cm. ⁻¹	E ₄ cm. ⁻¹	E ₅ cm. ⁻¹	E ₆ cm. ⁻¹
0	4	84,480.91	4	94,477.93	5
862.5	2	84,684.27	2	94,659.28	6
71,954	6	84,115.68	6	94,969.43	2
72,484.2	4	84,117.38	4	94,727.91	8
72,822.64	2	84,643.69	6	94,822.75	6
74,221.44	4	84,984.04	4	95,303.43	4
74,861.24	2	85,239.98	2	95,530.51	2
82,914.54	6	85,439.04	4	95,140.05	6
83,126.59	4	85,913.44	2	95,176.	8
83,360.55	2	85,730.68	4	95,336.31	6
83,889.64	8	94,509.67	4	95,702.01	4
84,127.90	6	94,464.5	2	95,535.28	2

Heat of Formation

Bands in the visible for the $\text{Cl} - \text{Cl}^+$ transitions have been observed by A. Elliott, Proc. Roy. Soc. Soc. 32, 1517 (1936) have measured several lines in the same system. These data lead to a convergence limit of 20,831 ± 20 cm.⁻¹ from which the dissociation energy is obtained assuming excited and normal Cl atoms as the dissociation products of the A state. The assigned accuracy estimation reflects the uncertain knowledge of the products. The value in parenthesis is a precision measure and would apply if the dissociation products were those assumed. See R. G. Alkin and N. S. Baylis, Trans. Far. Soc. 33, 1333 (1937) for further details on the dissociation products.

Heat Capacity and Entropy

The electronic energy levels are listed by C. E. Moore, Nat. Bur. Stands. Circ. 467, (1949).

Chlorine Unipositive Ion (Cl⁺)
(Ideal Gas) Mol. Wt. = 35.45245

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
100	5.487	40.021	40.021	•000	330.400	325.125	- 238.311
200	5.491	40.035	40.035	•010	330.612	325.090	- 236.617
300	5.495	40.050	40.050	•060	331.252	323.154	- 176.554
400	5.499	40.064	40.064	•135	331.689	321.055	- 140.526
500	5.503	40.078	40.078	•230	332.126	318.829	- 116.128
600	5.507	40.092	40.092	•345	332.563	316.499	- 98.611
700	5.511	40.106	40.106	•480	333.000	314.082	- 85.799
800	5.515	40.120	40.120	•635	333.437	311.589	- 75.660
900	5.519	40.134	40.134	•810	333.874	309.029	- 67.535
1000	5.523	40.148	40.148	•1000	334.311	306.412	- 60.876
1100	5.527	40.162	40.162	•1400	334.748	303.742	- 55.316
1200	5.531	40.176	40.176	•1800	335.185	301.022	- 50.604
1300	5.535	40.190	40.190	•2200	335.622	298.252	- 46.556
1400	5.539	40.204	40.204	•2600	336.059	295.458	- 43.006
1500	5.543	40.218	40.218	•3000	336.496	292.617	- 39.968
1600	5.547	40.232	40.232	•3400	336.933	289.743	- 37.247
1700	5.551	40.246	40.246	•3800	337.370	286.834	- 34.825
1800	5.555	40.260	40.260	•4200	337.807	283.896	- 32.654
1900	5.559	40.274	40.274	•4600	338.244	280.930	- 30.697
2000	5.563	40.288	40.288	•5000	338.681	277.932	- 28.923
2100	5.567	40.302	40.302	•5400	339.118	274.911	- 27.309
2200	5.571	40.316	40.316	•5800	339.555	271.863	- 25.832
2300	5.575	40.330	40.330	•6200	340.000	268.793	- 24.476
2400	5.579	40.344	40.344	•6600	340.445	265.700	- 23.226
2500	5.583	40.358	40.358	•7000	340.890	262.585	- 22.071
2600	5.587	40.372	40.372	•7400	341.335	259.449	- 21.000
2700	5.591	40.386	40.386	•7800	341.780	256.293	- 20.004
2800	5.595	40.400	40.400	•8200	342.225	253.117	- 19.074
2900	5.599	40.414	40.414	•8600	342.670	250.000	- 18.206
3000	5.603	40.428	40.428	•9000	343.115	246.870	- 17.392
3100	5.607	40.442	40.442	•9400	343.560	243.724	- 16.628
3200	5.611	40.456	40.456	•9800	344.005	240.567	- 15.909
3300	5.615	40.470	40.470	•10200	344.450	237.400	- 15.231
3400	5.619	40.484	40.484	•10600	344.895	234.225	- 14.591
3500	5.623	40.498	40.498	•11000	345.340	231.040	- 13.986
3600	5.627	40.512	40.512	•11400	345.785	227.845	- 13.412
3700	5.631	40.526	40.526	•11800	346.230	224.640	- 12.866
3800	5.635	40.540	40.540	•12200	346.675	221.425	- 12.351
3900	5.639	40.554	40.554	•12600	347.120	218.200	- 11.859
4000	5.643	40.568	40.568	•13000	347.565	214.965	- 11.390
4100	5.647	40.582	40.582	•13400	348.010	211.720	- 10.943
4200	5.651	40.596	40.596	•13800	348.455	208.465	- 10.516
4300	5.655	40.610	40.610	•14200	348.900	205.200	- 10.108
4400	5.659	40.624	40.624	•14600	349.345	201.935	- 9.717
4500	5.663	40.638	40.638	•15000	349.790	198.660	- 9.343
4600	5.667	40.652	40.652	•15400	350.235	195.375	- 8.984
4700	5.671	40.666	40.666	•15800	350.680	192.080	- 8.639
4800	5.675	40.680	40.680	•16200	351.125	188.775	- 8.309
4900	5.679	40.694	40.694	•16600	351.570	185.460	- 7.991
5000	5.683	40.708	40.708	•17000	352.015	182.135	- 7.684
5100	5.687	40.722	40.722	•17400	352.460	178.800	- 7.390
5200	5.691	40.736	40.736	•17800	352.905	175.455	- 7.105
5300	5.695	40.750	40.750	•18200	353.350	172.100	- 6.831
5400	5.699	40.764	40.764	•18600	353.795	168.735	- 6.567
5500	5.703	40.778	40.778	•19000	354.240	165.360	- 6.311
5600	5.707	40.792	40.792	•19400	354.685	161.975	- 6.065
5700	5.711	40.806	40.806	•19800	355.130	158.580	- 5.826
5800	5.715	40.820	40.820	•20200	355.575	155.175	- 5.595
5900	5.719	40.834	40.834	•20600	356.020	151.760	- 5.371
6000	5.723	40.848	40.848	•21000	356.465	148.335	- 5.152

June 30, 1965

Cl⁺

MOL. WT. = 35.45245

(IDEAL GAS)

CHLORINE UNIPOSITIVE ION (Cl⁺)

Ground State Configuration ³P₂
ΔH_f^o 0 = 328.7 ± .5 kcal./mole⁻¹
ΔH_f^o 298.15 = 330.6 ± .5 kcal/mole

Electronic Levels and Quantum Weight				
E _i , cm. ⁻¹	g _i	E _i , cm. ⁻¹	g _i	
0.0	5	27900.0	1	
897.0	3	93366.8	5	
986.0	1	93988.7	3	
11652.0	5	94332.8	1	

Heat of Formation.

The heat of formation was calculated from the equation Cl(g) - e⁻ → Cl⁺(g) with the JANAF auxiliary value for Cl(g); using an I.P. = 1.04931 X 10⁵ cm.⁻¹ (300.206 kcal/mole) obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, loc. cit. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H^o-H₂₉₈^o value at 0°K. is -1.526 kcal./mole.

Cl⁺

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	(H°-H° ₂₉₈)	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.968	36.628	36.628	0.000	-55.900	-57.389	42.066
100	4.968	36.628	36.628	0.000	-55.900	-57.389	41.813
200	4.968	36.628	36.628	0.009	-55.907	-57.398	41.597
300	4.968	36.628	36.628	0.066	-56.322	-57.834	41.350
400	4.968	36.628	36.628	0.206	-56.749	-58.262	41.077
500	4.968	36.628	36.628	0.421	-57.184	-58.690	40.786
600	4.968	36.628	36.628	0.712	-57.622	-59.118	40.477
700	4.968	36.628	36.628	1.079	-58.066	-59.546	40.150
800	4.968	36.628	36.628	1.523	-58.510	-59.974	39.805
900	4.968	36.628	36.628	2.044	-58.958	-60.402	39.441
1000	4.968	36.628	36.628	2.642	-59.406	-60.830	39.059
1100	4.968	36.628	36.628	3.317	-59.856	-61.258	38.660
1200	4.968	36.628	36.628	4.069	-60.307	-61.686	38.245
1300	4.968	36.628	36.628	4.898	-60.759	-62.114	37.815
1400	4.968	36.628	36.628	5.704	-61.212	-62.542	37.370
1500	4.968	36.628	36.628	6.587	-61.666	-62.970	36.911
1600	4.968	36.628	36.628	7.547	-62.121	-63.398	36.438
1700	4.968	36.628	36.628	8.584	-62.576	-63.826	35.952
1800	4.968	36.628	36.628	9.698	-63.032	-64.254	35.453
1900	4.968	36.628	36.628	10.889	-63.489	-64.682	34.941
2000	4.968	36.628	36.628	12.157	-63.947	-65.110	34.415
2100	4.968	36.628	36.628	13.502	-64.406	-65.538	33.876
2200	4.968	36.628	36.628	14.924	-64.865	-65.966	33.324
2300	4.968	36.628	36.628	16.433	-65.326	-66.394	32.759
2400	4.968	36.628	36.628	18.029	-65.788	-66.822	32.182
2500	4.968	36.628	36.628	19.712	-66.251	-67.250	31.594
2600	4.968	36.628	36.628	21.483	-66.715	-67.678	30.995
2700	4.968	36.628	36.628	23.343	-67.180	-68.106	30.386
2800	4.968	36.628	36.628	25.292	-67.646	-68.534	29.767
2900	4.968	36.628	36.628	27.330	-68.114	-68.962	29.138
3000	4.968	36.628	36.628	29.457	-68.584	-69.390	28.500
3100	4.968	36.628	36.628	31.673	-69.055	-69.818	27.852
3200	4.968	36.628	36.628	33.978	-69.528	-70.246	27.195
3300	4.968	36.628	36.628	36.372	-70.001	-70.674	26.528
3400	4.968	36.628	36.628	38.855	-70.476	-71.102	25.852
3500	4.968	36.628	36.628	41.427	-70.953	-71.530	25.167
3600	4.968	36.628	36.628	44.088	-71.431	-71.958	24.472
3700	4.968	36.628	36.628	46.839	-71.910	-72.386	23.768
3800	4.968	36.628	36.628	49.680	-72.391	-72.814	23.055
3900	4.968	36.628	36.628	52.611	-72.872	-73.242	22.333
4000	4.968	36.628	36.628	55.633	-73.355	-73.670	21.603
4100	4.968	36.628	36.628	58.746	-73.839	-74.098	20.865
4200	4.968	36.628	36.628	61.950	-74.324	-74.526	20.119
4300	4.968	36.628	36.628	65.244	-74.809	-74.954	19.365
4400	4.968	36.628	36.628	68.628	-75.295	-75.382	18.603
4500	4.968	36.628	36.628	72.101	-75.782	-75.810	17.833
4600	4.968	36.628	36.628	75.660	-76.269	-76.238	17.055
4700	4.968	36.628	36.628	79.304	-76.758	-76.666	16.269
4800	4.968	36.628	36.628	83.032	-77.246	-77.094	15.474
4900	4.968	36.628	36.628	86.844	-77.734	-77.522	14.670
5000	4.968	36.628	36.628	90.740	-78.223	-77.950	13.857
5100	4.968	36.628	36.628	94.720	-78.712	-78.378	13.035
5200	4.968	36.628	36.628	98.784	-79.202	-78.806	12.205
5300	4.968	36.628	36.628	102.932	-79.691	-79.234	11.367
5400	4.968	36.628	36.628	107.164	-80.181	-79.662	10.521
5500	4.968	36.628	36.628	111.480	-80.670	-80.090	9.667
5600	4.968	36.628	36.628	115.880	-81.160	-80.518	8.805
5700	4.968	36.628	36.628	120.364	-81.649	-80.946	7.935
5800	4.968	36.628	36.628	124.932	-82.138	-81.374	7.057
5900	4.968	36.628	36.628	129.584	-82.627	-81.802	6.172
6000	4.968	36.628	36.628	134.320	-83.116	-82.230	5.281

June 30, 1965

CHLORINE UNINEGATIVE ION (Cl⁻) (IDEAL GAS) MOL. WT. = 35.45355

Ground State Configuration 1s₀
S°_{298.15} = 36.628 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = -54.8 ± .5 kcal. mole⁻¹
ΔH°_f 298.15 = -55.9 ± .5 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E ₁ , cm. ⁻¹	E ₁
0.0	1
93143.8	5
93750.639	3
94553.707	1
95399.870	3

Heat of Formation.

The heat of formation was calculated from the equation: Cl(g) + e⁻ → Cl⁻(g) with the JANAF auxiliary values for Cl(g); using the measured electron affinity = 3.613 e.v. (83.316 kcal./mole) obtained from R. S. Berry and C. W. Reimann, J. Chem. Phys. 39, 1540 (1963). Other calculated values for the electron affinity are: 3.70 e.v. reported by B. Edlen, J. Chem. Phys. 33, 98 (1960) and 3.56 e.v. reported by E. Clementi, A. D. McLean, D. L. Raimondi and M. Yoshimine, Phys. Rev. 133, A1274 (1964).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Argon. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The H°-H°₂₉₈ value at 0°K. is -1.481 kcal/mole.

Cesium Chloride (CsCl)

(Crystal)

GFW = 168.358

T, °K	Cp	gibbs/mol S° - (G° - H° ₂₉₈)/T	— kcal/mol H° - H° ₂₉₈	— kcal/mol ΔH°	ΔG°	Log Kp
0	0.00	INFINITE	2.074	-105.875	-105.875	INFINITE
100	10.530	11.029	2.167	-106.107	-103.679	226.589
200	11.581	15.294	2.314	-105.948	-101.300	110.696
298	12.534	24.183	2.400	-105.840	-99.038	72.597
300	12.541	24.261	2.403	-105.838	-98.996	72.119
400	13.400	35.915	2.637	-105.607	-95.567	52.141
500	13.600	46.915	2.840	-105.077	-91.157	41.160
600	14.125	53.441	3.024	-105.667	-91.603	33.439
700	14.550	55.654	3.184	-105.607	-89.479	27.537
800	14.875	57.671	3.326	-104.390	-87.266	23.040
900	15.125	59.500	3.452	-102.974	-85.034	19.074
1000	15.300	61.152	3.562	-101.474	-82.734	15.574
1100	15.580	63.772	3.6424	-119.167	-78.520	15.600
1200	15.700	65.133	3.7027	-118.550	-74.852	13.632
1300	15.820	66.394	3.7377	-117.952	-71.258	11.976
1400	15.940	67.571	3.776	-117.284	-67.662	10.364
1500	16.060	68.675	3.8135	-116.634	-64.147	9.346
1600	16.180	69.715	3.8491	-115.975	-60.670	8.287
1700	16.310	70.700	3.731	-115.305	-57.233	7.358
1800	16.430	71.636	3.648	-114.625	-53.834	6.337
1900	16.550	72.528	3.588	-113.938	-50.476	5.258
2000	16.670	73.375	3.5382	-113.241	-47.156	5.159

CESIUM CHLORIDE (CsCl)

(CRYSTAL)

GFW = 168.358

S°_{298.15} = 24.183 ± 0.005 gibbs/molΔH°_{298.15} = -105.84 ± 0.2 kcal/mol

Tt(α-β) = 743°K

ΔH° = 0.90 kcal/mol

Tm = 918°K

ΔHm° = 3.8 kcal/mol

ΔH°_{298.15}(to monomer) = 48.74 kcal/mol

Heat of Formation

The heat of solution (ΔHsoln) of CsCl(c) in water has been measured by Forcand (1, 2), Haigh (3), Samoilov (4, 5), and Rodnikova (6). Based on their results, Parker (7) derived the corresponding ΔHsoln_{298.15}(∞ H₂O) values as 4.30, 4.32, 4.08, 4.25, 4.18 and 4.18 kcal/mol. Borob'ev (8) determined the same quantity and reported ΔHsoln₂₉₈(CsCl, ∞ H₂O) = 4.20 ± 0.04 kcal/mol. Using this value, 4.20 kcal/mol, and ΔH°₂₉₈ = -61.69 (9) and -39.952 kcal/mol (10) for Cs(∞ H₂O) and Cl⁻(∞ H₂O), respectively, we evaluate ΔH°₂₉₈(CsCl, c) = -105.84 ± 0.2 kcal/mol, which is adopted.

Heat Capacity and Entropy

Taylor (11) measured the low temperature heat capacities, 7.19 - 299.38°K, with an adiabatic calorimeter; the sample purity was >99.95 per cent. Employing these data we derive the value S°₂₉₈ = 24.183 eu based on S°₁₉ = 0.091 eu.

The high temperature enthalpies, 385.2 - 904.9°K, were measured by Kaylor (21, 22, 23), using a Bunsen ice calorimeter and a CsCl sample of 99.8 per cent purity. The heat capacities derived from the reported enthalpy data at temperatures 385.2 - 740.5°K appear too low (less than the adopted Cp's systematically by 0.9 gibbs/mol) to join smoothly with the low temperature data at 298°K. The Cp values derived from the measured enthalpy data in the temperature range 760 - 920°K increase rapidly from 14.46 to 16.3 gibbs/mol. In order to rationalize this situation, we adopt the high temperature heat capacities, 298 - 743°K, for CsCl(α) obtained by linear extrapolation of the low temperature data. The Cp values for CsCl(β) are adjusted such that the rate of increase in heat capacities is linear and less rapid than the original one, and the total enthalpy remains essentially unchanged. The discrepancy between the high and low temperature Cp for CsCl(α) may be caused by the incomplete β → α phase conversion involved. In order to resolve this discrepancy, independent enthalpy measurements using a high purity sample with composition well characterized before and after each drop experiment seem necessary.

Transition Data

The temperature of transition (in °K) has been reported by many investigators as 718 (14), 752 (15), 745 (16), 742 (21), 742.5 (12), 743 (20), and 733 (17), using different methods and samples of different purity. The value adopted is 743°K. The heat of transition (in kcal/mol) was reported to be 1.8 (14), 1.55 (18), 1.4 (19), 0.80 (22), 0.58 (12), 0.90 (13), and 1.1 (17). A median value 0.90 kcal/mol is tentatively adopted.

Melting Data

See CsCl(4) table for details.

Heat of Sublimation

ΔH°₂₉₈ is calculated as the difference between ΔH°₂₉₈ for CsCl(g) and CsCl(c).

References

1. R. de Forcand, *Compt. Rend.* **143**, 98 (1906); 1 point, concentration m = 0.25 (19°K) where m is molality.
2. R. de Forcand, *Ann. Chim. Phys.* **8**, 24, 256 (1911); *Compt. Rend.* **152**, 27 (1911); 1 point, m = 0.50 (15°K).
3. E. Haigh, *Ann. Chem. Soc.* **23**, 258 (1901); 1 point, m = 0.50 (15°K).
4. O. Y. Rodnikova, *Zh. Neorg. Khim.* **3**, 2417 (1958); 6 points, m = 0.05 (25°K).
5. M. N. Rodnikova, *Zh. Neorg. Khim.* **3**, 2417 (1958); 6 points, m = 0.05 (15, 35°K).
6. O. Y. Samoilov and M. N. Rodnikova, *Stroenie Veshchestva i Spektroskopiya*, Akad. Nauk SSSR, 102 (1960); 3 points, m = 0.06 (15, 35°K).
7. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
8. A. Borob'ev, M. A. Abram, and S. M. Kuratov, *Russ. J. Inorg. Chem. (English Transl.)* **11**, 13 (1966).
9. S. E. Rodnikova, *Chem. Abstr.* **57**, 1386 (1957).
10. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
11. A. R. Taylor, Jr., T. E. Gardner, and D. F. Smith, U. S. Bur. Mines RI 6157 (1963).
12. C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
13. D. F. Smith, C. E. Kaylor, G. E. Walden, A. R. Taylor, Jr., and J. B. Gayle, U. S. Bur. Mines, RI 5832, 1961.
14. J. W. Wood, W. Wood, and J. W. Wood, *Proc. Roy. Soc. (London)* **A208**, 158 (1951).
15. J. W. Wood, W. Wood, and J. W. Wood, *Proc. Roy. Soc. (London)* **A208**, 158 (1951).
16. L. J. Wood, W. Wood, and J. W. Wood, *Proc. Roy. Soc. (London)* **A208**, 158 (1951).
17. A. J. Majumdar and R. Roy, *J. Inorg. Nucl. Chem.* **22**, 1961 (1965).
18. J. Krogh-Moe, *J. Am. Chem. Soc.* **82**, 2389 (1960).
19. J. Krogh-Moe, *J. Am. Chem. Soc.* **82**, 6196 (1960).
20. J. Johnson, Jr., A. Agron, and H. A. Bredig, *J. Am. Chem. Soc.* **77**, 2734 (1955).
21. C. E. Kaylor, Ph. D. Thesis, University of Alabama, 1959.

(Liquid)

GFW = 168.358

CESIUM CHLORIDE (CsCl)

(LIQUID)

GFW = 168.358

$$S_{298.15}^{\circ} = 24.309 \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = -103.84 \pm 2.0 \text{ kcal/mol}$$

$$T_m = 918^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 3.8 \pm 1 \text{ kcal/mol}$$

$$T_b = 1597.3^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = 27.52 \text{ kcal/mol of liquid (to equilibrium mixture)}$$

Heat of Formation

$\Delta H_f^{\circ}(s)$ is obtained from $\Delta H_f^{\circ}(c)$ by adding ΔH_m° and the difference between $H_{918}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The enthalpies of CsCl(l) at temperatures 923.6 - 1169.0°K were measured with a Bunsen ice calorimeter by Kaylor (1, 2). Dworkin (3) derived the heat capacity of CsCl(l) as 18.5 gibbs/mol from enthalpy data at temperatures 918 - 980°K. This value is adopted since it is in agreement with the enthalpy values reported by Kaylor et al. The heat capacity at temperatures above 1168 and below 923.6°K is assumed to be 18.5 gibbs/mol. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting temperature (in °K) of CsCl(c) has been determined by many investigators as 904 ± 3 (1), 919 (5), 912 (6), 911 (7), 918 (8), 916 (9), and 919 (13). The cause of the discrepancies is probably due to the difference in purity of the samples. The melting temperature adopted is 918°K.

The heat of melting (in kcal/mol) was reported to be 4.84 (14), 4.97 (15), 4.58 (10), 4.96 (11), and 4.78 (2), which were obtained calorimetrically. Using a modification of Kelley's method of obtaining heat of melting from freezing point data on binary systems involving CsCl (16), we derive the value of ΔH_m° as 3.6 - 4.0 kcal/mol, based on the following systems: CsCl-NaCl (5), CsCl-CuCl (9), CsCl-AgCl (9), CsCl-LiCl (9), and CsCl-Cs₃(PO₃)₃ (12). The heat of melting for CsCl(c) is tentatively adopted as 3.8 kcal/mol. The ΔH_m° values obtained calorimetrically are not used due to the uncertainties of the state of the sample before and after the enthalpy measurements.

Vaporization Data

T_b is the temperature at which the calculated total pressures of CsCl(g) and Cs₂Cl₂(g) equal one atmosphere. The vapor composition at T_b is derived as CsCl 80.4 per cent and Cs₂Cl₂ 19.6 per cent. The boiling point of CsCl(l) has been determined by several investigators as 1562 (17), 1572 (18), and 1576 (19). The heat required to vaporize one mole of liquid to the above vapor mixture at T_b is ΔH_v° .

References

1. C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
2. D. F. Smith, C. E. Kaylor, G. E. Walden, A. R. Taylor, Jr., and J. B. Gayle, U. S. Bur. Mines RI 5832, 1961.
3. A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 1, 1964.
4. T. Carnelley and Carleton-Williams, *J. Chem. Soc.* **37**, 125 (1880).
5. S. Zencuzny and F. Rambach, *Z. Anorg. Chem.* **55**, 415 (1910).
6. C. Sandomini, *Atti Acc. Linc. Ser. 5*, **21** II, 77 (1912).
7. E. Korring, *Z. Anorg. Chem.* **91**, 194 (1915).
8. T. W. Richards and W. B. Maldrum, *J. Am. Chem. Soc.* **39**, 1816 (1917).
9. B. F. Markov and I. D. Panchenko, *Russ. J. Gen. Chem. (English Transl.)* **25**, 1987 (1955).
10. C. E. Kaylor, Ph. D. Thesis, University of Alabama, 1958.
11. C. E. Kaylor, G. E. Walden, and D. F. Smith, *J. Phys. Chem.* **64**, 276 (1960).
12. G. A. Bukhalova and I. V. Mardirosova, *Russ. J. Inorg. Chem. (English Transl.)* **12**, 1158 (1967).
13. G. A. Bukhalova and D. V. Semantsova, *Russ. J. Inorg. Chem. (English Transl.)* **10**, 1027 (1965).
14. A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.* **64**, 269 (1960).
15. Determined by D. F. Smith, University of Alabama; quoted by Dworkin (14).
16. K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936.
17. O. Ruff and S. Mugdan, *Z. Anorg. Allgem. Chem.* **117**, 147 (1921).
18. I. G. Murgulescu and L. Topor, *Rev. Roum. Chim.* **12**, 1077 (1967).
19. H. von Wartenberg and H. Schulz, *Z. Elektrochem.* **27**, 568 (1921).

June 30, 1968

CICs

Cesium Chloride (CsCl)

(Ideal Gas) $\Delta H_f^\circ = 168.358$

CESIUM CHLORIDE (CsCl)

(IDEAL GAS)

GFW = 168.358

Ground State Configuration $1s^2$ $\Delta H_f^\circ = -56.9 \pm 1 \text{ kcal/mol}$ $\Delta H_f^\circ = -57.4 \pm 1 \text{ kcal/mol}$ $S_{298.15}^\circ = 61.175 \pm 0.005 \text{ gibbs/mol}$ $\Delta H_f^\circ = -57.4 \pm 1 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

 $\epsilon_i, \text{ cm}^{-1}$

0

 $\frac{g_i}{1}$ $\omega_e = 213.08 \pm 0.05 \text{ cm}^{-1}$
 $\omega_e x_e = 0.733 \pm 0.008 \text{ cm}^{-1}$
 $B_e = 0.07134 \text{ cm}^{-1}$
 $\sigma_e = 0.000332 \text{ cm}^{-1}$
 $\sigma = 1$
 $r_e = 2.906 \text{ \AA}$

Heat of Formation

The total pressures of CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$ over CsCl(c) and CsCl(l) in the temperature range 605 - 1577°K have been determined by manometric, transpiration and Knudsen effusion methods by many investigators. Based on the reported results, the partial pressures of CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$ are calculated using the derived free energy functions for CsCl(c), CsCl(l), CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$, and the heats of sublimation and vaporization which are adjusted so that the sum of the calculated partial pressures of CsCl(g) and $\text{Cs}_2\text{Cl}_2(\text{g})$ approaches the measured total pressures, and the evaluated second and third law ΔH_f° values are in reasonable agreement. The results obtained are presented in the table below. The value of ΔH_f° (CsCl, g) adopted is -57.4 \pm 1 kcal/mol.

Gaydon (10) reported $D_0(\text{Cs-Cl}) = 4.6 \pm 0.2 \text{ eV}$ or $106.08 \pm 4.61 \text{ kcal/mol}$. Using this D_0 value and $\Delta H_f^\circ = 19.683$ and 28.52 kcal/mol for Cs(g) and Cl(g), we evaluate $\Delta H_f^\circ = -59.4 \pm 4.6 \text{ kcal/mol}$ for CsCl(g), which is in fair agreement with the adopted value.

Investigator	Reaction*	Method	Temperature, °K	No. of Points	Second Law ΔH_f° , kcal/mol	Third Law ΔH_f° , kcal/mol	Drift eu kcal/mol
1. Niwa (1938)	1	A	793-893	11	46.81 \pm 0.35	49.92	3.7 \pm 0.4
2. Cogin (1948)	1	A	690-891	28	47.80 \pm 0.31	47.88	0.1 \pm 0.4
3. Treadwell (1953)	1	B	784-905	10	47.08 \pm 0.26	49.17	2.5 \pm 0.3
4. Mesnyanov (1960)	1	A	605-851	16	45.26 \pm 0.38	48.74	4.7 \pm 0.5
5. Martenyanov (1921)	2	C	1359-1577	9	46.36 \pm 0.50	46.27	-2.1 \pm 0.3
6. Ruff (1921)	2	C	1235-1568	7	51.61 \pm 1.08	46.17	-3.8 \pm 0.8
7. Flock (1926)	2	B	1098-1293	9	47.57 \pm 0.08	46.52	-0.9 \pm 0.1
8. Kangro (1938)	2	C	1133-1263	3	46.73 \pm 2.09	47.00	-1.4 \pm 1.7
9. Schrier (1938)	2	C	1165-1387	10	47.46 \pm 0.08	46.36	-0.9 \pm 0.1
16. Murgulescu (1967)	1	A	1174-1353	10	47.97 \pm 0.15	46.54	-1.1 \pm 0.1
*1 CsCl(c) = CsCl(g); 2 CsCl(l) = CsCl(g); A = Knudsen effusion; B = transpiration; and C = manometric.							
**Calculation based on the third law ΔH_f° value.							

Heat Capacity and Entropy

Clausen (11) studied the pure rotational spectra of CsCl(g) in the 0.36 - 3 mm range of the microwave region with the molecular-beam spectrometer, and derived the values of B_e , ω_e , $\omega_e x_e$, and r_e , which are adopted and corrected to the average isotopic species.

The Cs-Cl bond distance was measured as $3.06 \pm 0.03 \text{ \AA}$ by the electron diffraction method by Maxwell (12), which is not used. Similar values of B_e and ω_e were reported by Honig (13) and Rice (14), determined from microwave and infrared spectra, respectively. Barrow (15) gave $\omega_e = 240 \text{ cm}^{-1}$ (CsCl₃) which is significantly different from the adopted value 214.22 cm^{-1} for CsCl₃ and the value $209 \pm 6 \text{ cm}^{-1}$ reported by Rice (14). The moment of inertia is $3.924 \times 10^{-38} \text{ g cm}^2$.

References

1. K. Niwa, J. Fac. Sci., Hokkaido Univ., Ser. III, 2, 201 (1938).
2. E. P. Cogin, G. K. Niwa, J. Chem. Phys., 16, 1035 (1948).
3. W. D. Treadwell and W. Werner, Helv. Chim. Acta, 36, 1436 (1953).
4. A. N. Mesnyanov and L. A. Sazonov, Russ. J. Inorg. Chem. (English Transl.), 5, 248 (1960).
5. H. von Martenyanov and H. Schulz, Z. Elektrochem., 57, 568 (1953).
6. O. Ruff and S. Hugdan, Z. Anorg. Allgem. Chem., 117, 147 (1921).
7. F. Flock and W. H. Martenyanov, J. Chem. Soc., 1926, 2218 (1926).
8. K. Kangro, J. Fac. Sci., Hokkaido Univ., Ser. III, 2, 201 (1938).
9. E. Schrier, Ph. D. Thesis, Rensselaer Polytechnic Institute, 1938.
10. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.
11. P. L. Clausen and W. Gordy, Phys. Rev., 134, A863 (1964).
12. L. R. Maxwell, S. B. Hendricks and V. H. Nye, Phys. Rev., 52, 988 (1937).
13. G. Honig, M. Mandel, H. L. Sticht and C. H. Townes, Phys. Rev., 137, 134 (1956).
14. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London), A219, 120 (1953).
15. I. G. Murgulescu and L. Topor, Rev. Roum. Chim., 12, 1077 (1967).

June 30, 1968

CICs

COPPER MONOCHLORIDE (CuCl)

(CRYSTAL)

ClCu

MOL. WT. = 98.993

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0								
100								
200								
298	11.400	20.800	20.800	0.000	0.000	-33.000	-28.808	21.183
300	11.656	20.872	20.800	0.022	32.997	-32.997	-28.873	21.034
400	13.600	24.540	21.267	1.301	32.720	-27.535	-27.535	19.044
500	14.300	27.656	22.758	2.699	32.374	-26.275	-26.275	11.465
600	14.700	30.300	23.984	4.149	31.991	-25.092	-25.092	9.140
700	15.000	32.589	25.039	5.635	31.589	-23.872	-23.872	7.494
800	15.220	34.607	26.078	7.146	31.178	-22.604	-22.604	6.260
900	15.369	36.410	26.768	8.677	30.759	-21.005	-21.005	5.319
1000	15.540	38.039	27.615	10.224	30.338	-20.944	-20.944	4.577
1100	15.662	39.426	28.413	11.764	29.912	-20.025	-20.025	3.979
1200	15.777	40.694	29.164	13.356	29.486	-19.140	-19.140	3.497
1300	15.884	42.161	30.069	14.939	29.058	-18.301	-18.301	3.077
1400	15.983	43.442	31.033	16.532	31.815	-17.368	-17.368	2.714
1500	16.075	44.447	32.057	18.135	31.415	-16.371	-16.371	2.385

Mar. 31, 1966

$\Delta H_f^0 = 20.8 \pm 1.0$ cal. deg.⁻¹ mole⁻¹
 $T_m = 703^\circ K.$
 $\Delta H_f^0 = -35.0 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_m^0 = 2.445$ kcal. mole⁻¹
 $\Delta H_g^0 = 54.77 \pm 0.5$ kcal. mole⁻¹ of monomer
 $\Delta H_g^0 = 37.2 \pm 0.2$ kcal. mole⁻¹ of trimer

Heat of Formation.

There have been three calorimetric determinations of the heat of formation. Thomsen, "Thermochemische Untersuchungen", Barth, Leipzig (1882-1886) reported -32.875 kcal. mole⁻¹. Berthelot, Ann. Chim. Phys. 20, 504 (1880) reported -35.6 kcal. mole⁻¹ and H. V. Wartenberg and H. Werth, Z. physik. Chem. A 151, 109 (1930) reported -32.1 ± 0.4 kcal. mole⁻¹. In addition, values of the heat of formation have been derived from several sets of equilibrium data. A. A. Noyes and M. Chow, J. Am. Chem. Soc. 40, 739 (1918) from a study of cell potentials derived a $\Delta H_f^0 = 7.19$ kcal. for the reaction $Cu(c) + HCl(aq) \rightarrow CuCl(c) + 1/2 H_2(g)$ which yields ΔH_f^0 298 (CuCl) = -32.76 kcal. mole⁻¹. Several investigators have studied the reaction $2CuCl(c) + H_2(g) \rightarrow 2Cu(c) + 2HCl(g)$ and its reverse reaction. These include A. B. Begdasarian, Trans. Am. Electrochem. Soc. 51, 449 (1927) who reported equilibrium constants which result in 2nd and 3rd law heats of reaction of 24.3 and 23.2 kcal. mole⁻¹; A. F. Kapustinsky, J. Am. Chem. Soc. 59, 460 (1936) who obtained similarly 20.1 and 21.8 kcal. mole⁻¹; S. A. Shchukarev and M. A. Oranskaya, Z. Obshch. Khim. 24, 1926 (1954) obtained 25.4 and 21.5 kcal. mole⁻¹ for the 2nd and 3rd law heat of reaction. These yield values for ΔH_f^0 298 (CuCl) ranging from -32.1 to -34.8 . M. Watanabe, Bull. Inst. Phys. Chem. Res. 9, 94 (1929) from cell studies reports ΔH_f^0 298 (CuCl) = -34.6 kcal. mole⁻¹. A value of ΔH_f^0 298 can also be obtained from ΔH_f^0 (CuCl)₃(g), which is fixed independently and known with good precision. Using the 3rd law heat of sublimation of CuCl(c) to trimer determined by D. W. Magee, Doctoral Thesis, Ohio State University (1955) [See trimer table], we obtain ΔH_f^0 298 CuCl(c) = -33.01 ± 0.3 kcal. mole⁻¹. A weighted average of -33.0 ± 0.4 kcal. mole⁻¹ was adopted.

Heat Capacity and Entropy.

The entropy of CuCl was obtained from the several pieces of equilibrium data reported above and the adopted ΔH_f^0 298. A weighted average of 20.8 ± 1 cal./mol.-deg) was adopted for S_{298}^0 CuCl(c). The enthalpy and heat capacity above 298°K. have been reported by A. N. Krestovnikov and G. A. Krestnikov, Jour. Gen. Chem. (USSR) 6, 955 (1936). However these values were not adopted since they do not give reasonable heat capacities and other data by these workers is not in agreement with established values. Heat capacities equal to those of AgCl, as given by K. K. Kelley, U. S. Bureau of Mines Bulletin 584, Washington 1960, were adopted here above 298°K.

Melting Data.

The temperature and heat of melting were those selected by K. K. Kelley, U. S. Bur. Mines Bulletin 393 (1936), from phase studies. The heat of melting was reported by Krestovnikov and Krestnikov loc. cit. as 2.54 kcal. mole⁻¹.

Sublimation Data.

The heat of sublimation was calculated from the adopted heats of formation at 298° for the reaction $x CuCl(c) \rightarrow (CuCl)_x(g)$ where $x = 1$ or 3. See the respective gas tables for details.

ClCu

Copper Monochloride (CuCl)

(Liquid)

Mol. wt. = 98.993

ClCu

MOL. WT. = 98.993

COPPER MONOCHLORIDE (CuCl)

(LIQUID)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	16.000	22.407	22.407	0.000	-31.350	-27.727	20.329
200	16.000	22.506	22.407	0.030	-31.339	-27.705	20.183
300	16.000	27.109	23.035	1.530	-30.751	-26.584	14.525
400	16.000	30.679	24.220	3.230	-30.193	-25.606	11.192
500	16.000	33.594	25.557	4.830	-29.661	-24.730	9.011
600	16.000	36.093	26.857	6.330	-29.144	-23.960	7.411
700	16.000	38.193	28.162	7.830	-28.644	-23.254	6.353
800	16.000	40.084	29.384	9.330	-28.157	-22.609	5.490
900	16.000	41.770	30.540	11.230	-27.682	-22.019	4.812
1000	16.000	43.294	31.631	12.830	-27.216	-21.474	4.267
1100	16.000	44.667	32.632	14.330	-26.762	-20.974	3.820
1200	16.000	45.967	33.537	15.830	-26.317	-20.508	3.448
1300	16.000	47.153	34.351	17.230	-25.881	-20.077	3.118
1400	16.000	48.257	35.077	18.530	-25.450	-19.672	2.818
1500	16.000	49.280	35.721	20.830	-25.024	-19.284	2.550
1600	16.000	50.220	36.284	22.530	-24.602	-18.914	2.323
1700	16.000	51.174	37.824	24.030	-24.184	-18.566	2.135
1800	16.000	52.039	38.550	25.630	-23.769	-18.237	1.961
1900	16.000	52.860	39.245	27.230	-23.358	-17.924	1.806
2000	16.000	53.631	39.912	28.830	-22.950	-17.616	1.668
2100	16.000	54.351	40.553	30.430	-22.544	-17.314	1.544
2200	16.000	55.026	41.170	32.030	-22.140	-17.018	1.434
2300	16.000	55.656	41.765	33.630	-21.738	-16.726	1.333
2400	16.000	56.240	42.338	35.230	-21.336	-16.434	1.242
2500	16.000	56.780	42.892	36.830	-20.934	-16.142	1.160
2600	16.000	57.280	43.426	38.430	-20.532	-15.850	1.084
2700	16.000	57.740	43.940	40.030	-20.130	-15.558	1.016
2800	16.000	58.160	44.430	41.630	-19.728	-15.266	0.953
2900	16.000	58.540	44.890	43.230	-19.326	-14.974	0.893
3000	16.000	58.880	45.320	44.830	-18.924	-14.682	0.839

 $S_{298.15}^{\circ} = 22.4 \pm 1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_m = 703^{\circ}\text{K.}$ $\Delta H_f^{\circ} 298.15 = -31.35 \pm 0.4 \text{ kcal. mole}^{-1}$ $\Delta H_m^{\circ} = 2.445 \text{ kcal. mole}^{-1}$ $\Delta H_v^{\circ} = [5.18] \text{ kcal. mole}^{-1} \text{ (to equilibrium mixture)}$ $T_b = [1485]^{\circ}\text{K. (to equilibrium mixture)}$

Heat of Formation.

Calculated from $\Delta H_f^{\circ} 298$ of the crystal plus ΔH_m° and the difference between $H_m - H_m^{\circ} 298$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated to be constant at 8 cal. deg.⁻¹ gm. atom⁻¹. The entropy was calculated in a manner analogous to that of the heat of formation.

Boiling Data.

The boiling point and heat of vaporization were calculated from the respective liquid, monomer and trimer gas tables. The boiling point was taken as the point where the total pressure reached 1 atm. At this point the partial pressures are 0.021 atm. of monomer and 0.979 atm. of trimer.

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(H° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	Log K _p
0	7.000	0.000	INFINITE	-	2.264	21.798	INFINITE
100	7.000	48.115	21.398	1.264	21.398	21.798	16.984
200	7.972	53.387	21.403	1.264	21.403	21.798	16.984
298	8.428	56.667	21.770	1.264	21.770	21.798	11.126
300	8.433	56.719	21.767	1.264	21.767	21.798	11.027
400	8.657	59.179	21.611	1.264	21.611	21.798	10.706
500	8.776	61.125	21.441	1.264	21.441	21.798	10.385
600	8.854	62.723	21.255	1.264	21.255	21.798	10.065
700	8.905	64.101	21.059	1.264	21.059	21.798	9.745
800	8.942	65.293	20.851	1.264	20.851	21.798	9.425
900	8.968	66.328	20.635	1.264	20.635	21.798	9.105
1000	8.986	67.255	20.409	1.264	20.409	21.798	8.785
1100	9.017	68.153	20.175	1.264	20.175	21.798	8.465
1200	9.036	68.938	19.932	1.264	19.932	21.798	8.145
1300	9.052	69.610	19.681	1.264	19.681	21.798	7.825
1400	9.066	70.192	19.425	1.264	19.425	21.798	7.505
1500	9.084	70.660	19.162	1.264	19.162	21.798	7.185
1600	9.098	71.547	18.631	1.264	18.631	21.798	6.865
1700	9.112	72.099	18.241	1.264	18.241	21.798	6.545
1800	9.126	72.620	17.851	1.264	17.851	21.798	6.225
1900	9.139	73.114	17.461	1.264	17.461	21.798	5.905
2000	9.151	73.592	17.071	1.264	17.071	21.798	5.585
2100	9.164	74.030	16.681	1.264	16.681	21.798	5.265
2200	9.176	74.436	16.291	1.264	16.291	21.798	4.945
2300	9.188	74.864	15.901	1.264	15.901	21.798	4.625
2400	9.200	75.265	15.511	1.264	15.511	21.798	4.305
2500	9.212	75.652	15.121	1.264	15.121	21.798	3.985
2600	9.224	75.993	14.731	1.264	14.731	21.798	3.665
2700	9.236	76.341	14.341	1.264	14.341	21.798	3.345
2800	9.248	76.678	13.951	1.264	13.951	21.798	3.025
2900	9.260	77.006	13.561	1.264	13.561	21.798	2.705
3000	9.271	77.316	13.171	1.264	13.171	21.798	2.385
3100	9.283	77.621	12.781	1.264	12.781	21.798	2.065
3200	9.294	77.916	12.391	1.264	12.391	21.798	1.745
3300	9.306	78.202	11.991	1.264	11.991	21.798	1.425
3400	9.317	78.478	11.591	1.264	11.591	21.798	1.105
3500	9.329	78.750	11.191	1.264	11.191	21.798	0.785
3600	9.340	79.013	10.791	1.264	10.791	21.798	0.465
3700	9.352	79.269	10.391	1.264	10.391	21.798	0.145
3800	9.363	79.519	9.991	1.264	9.991	21.798	-0.175
3900	9.374	79.764	9.591	1.264	9.591	21.798	-0.495
4000	9.386	79.999	9.191	1.264	9.191	21.798	-0.815
4100	9.397	80.231	8.791	1.264	8.791	21.798	-1.135
4200	9.409	80.458	8.391	1.264	8.391	21.798	-1.455
4300	9.420	80.679	7.991	1.264	7.991	21.798	-1.775
4400	9.431	80.894	7.591	1.264	7.591	21.798	-2.095
4500	9.443	81.108	7.191	1.264	7.191	21.798	-2.415
4600	9.454	81.316	6.791	1.264	6.791	21.798	-2.735
4700	9.465	81.519	6.391	1.264	6.391	21.798	-3.055
4800	9.476	81.719	5.991	1.264	5.991	21.798	-3.375
4900	9.487	81.916	5.591	1.264	5.591	21.798	-3.695
5000	9.499	82.106	5.191	1.264	5.191	21.798	-4.015
5100	9.510	82.294	4.791	1.264	4.791	21.798	-4.335
5200	9.522	82.476	4.391	1.264	4.391	21.798	-4.655
5300	9.533	82.650	3.991	1.264	3.991	21.798	-4.975
5400	9.544	82.824	3.591	1.264	3.591	21.798	-5.295
5500	9.556	83.004	3.191	1.264	3.191	21.798	-5.615
5600	9.567	83.186	2.791	1.264	2.791	21.798	-5.935
5700	9.578	83.356	2.391	1.264	2.391	21.798	-6.255
5800	9.589	83.522	1.991	1.264	1.991	21.798	-6.575
5900	9.600	83.684	1.591	1.264	1.591	21.798	-6.895
6000	9.612	83.848	1.191	1.264	1.191	21.798	-7.215

Mar. 31, 1966

Ground State Configuration $1\Sigma^+$
 $S_{298.15}^0 = 56.667$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^0 = 21.80 \pm 0.4$ kcal. mole⁻¹
 $\Delta H_f^0 = 21.77 \pm 0.4$ kcal. mole⁻¹

Electronic Levels and Multiplicities

$$\frac{\epsilon_i, \text{cm.}^{-1}}{0} \frac{g_i}{1}$$

$\omega_e = 414.9$ cm.⁻¹
 $\omega_e x_e = 1.577$ cm.⁻¹
 $\sigma = 1$
 $r_e = 2.050$ Å
 $\alpha_e = 0.0001$ cm.⁻¹
 $B_e = 0.1761$ cm.⁻¹

Heat of Formation.

The heat of formation was obtained from the equilibrium data of I. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950). They studied the reaction $\text{Cu(c)} + \text{HCl(g)} \rightarrow \text{CuCl(g)} + \frac{1}{2} \text{H}_2\text{(g)}$ by measuring the amount of CuCl formed when various ratios of HCl:H₂ were passed over heated copper. Brewer and Lofgren analyzed the data by a least squares fitting technique and deduced partial pressures of monomer and trimer. The monomer pressures were subjected to second and third law analysis and gave $\Delta H_f^0 = 46.85 \pm 3.2$ and 43.83 ± 0.4 kcal. mole⁻¹ respectively. The 3rd law value yields $\Delta H_f^0 = 21.77 \pm 0.4$ kcal. mole⁻¹, which was adopted.

Heat Capacity and Entropy.

The molecular constants were corrected for normal isotopic abundance of both copper and chlorine and were calculated from the values for ⁶⁵Cu³⁵Cl given by R. K. Aundil, P. R. Rao and J. K. Brody, Nature 192, 444 (1961). The rotational constants were in good agreement with those reported by A. Lagerqvist and V. Lissarova-Girmanov for Cu⁶³Cl³⁵, Naturwissenschaften 48, 68 (1961).

Chlorine Monofluoride (ClF)

(Ideal Gas) Mol. Wt. = 54.4514

ClF

MOL. WT. = 54.4514

CHLORINE MONOFLUORIDE (ClF)

(IDEAL GAS)

Ground State Configuration $1\Sigma^+$
 $S_{298.15} = 52.064 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = -12.12 \pm 0.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = -12.14 \pm 0.6 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

State	ϵ_f , cm. ⁻¹	g_i
$1\Sigma^+$	0	1
$3\Pi^0$	19,592	1
$3\Pi_1$	19,592	2
$3\Pi_2$	19,592	2

$\lambda = 784.39 \text{ cm.}^{-1}$
 $\omega_e = 6.20 \text{ cm.}^{-1}$
 $\alpha_e = 0.004329 \text{ cm.}^{-1}$
 $\sigma = 1$
 $r_e = 1.62913 \text{ \AA}$

Heat of Formation

The $\Delta H_f^{298.15} = -12.14 \text{ kcal. mole}^{-1}$ was calculated from the dissociation energy ($D_0^0 = 58.99$) obtained from the visible band spectra measured by H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2a, 359 (1947) and A. L. Wahrhaftig, J. Chem. Phys. 10, 248 (1941). The convergence limit of $21,512 \pm 20 \text{ cm.}^{-1}$ for the A state leads to the selected D_0^0 assuming that the products are $\text{Cl}(^2P_{3/2})$ and $\text{F}(^2P_{3/2})$ or to $D_0^0 = 60.36$ assuming $\text{Cl}(^2P_{3/2})$ and $\text{F}(^2P_{1/2})$. Calorimetric values bracket the two possibilities but more weight was given to the results of Wicke.

Method	Reaction	Observation
1 Spectroscopic	$\text{ClF} = \text{Cl}(^2P_{3/2}) + \text{F}(^2P_{3/2})$	$\Delta H_f^{298} \text{ kcal. mole}^{-1}$
2 Spectroscopic	$\text{ClF} = \text{Cl}(^2P_{3/2}) + \text{F}(^2P_{1/2})$	$D_0^0 = 58.99$
3 Calorimetric	$1/2 \text{ Cl}_2 + 1/2 \text{ F}_2 = \text{ClF}$	$D_0^0 = 60.36$
4 Explosion method	$1/2 \text{ Cl}_2 + 1/2 \text{ F}_2 = \text{ClF}$	$\Delta H_{293}^0 = -11.6 \pm 0.1$
5a Calorimetric	$\text{NaCl} + \text{ClF} = \text{NaF} + \text{Cl}_2$	$\Delta H_{290}^0 = -11.7$
5b Calorimetric	$\text{NaCl} + 0.5 \text{ F}_2 = \text{NaF} + 0.5 \text{ Cl}_2$	$\Delta H_{290}^0 = -24.5 \pm 0.5$
		$\Delta H_{290}^0 = -39.5 \pm 0.5$

Sources
 1, 2 H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2a, 359 (1947).

3 E. Wicke, Nachr. Acad. Wiss. Gottigen Math-Physik Klasse p. 89 (1946).

4 E. Wicke and H. Fritz, Z. Elektrochem. 57, 9 (1953).

5a, 5b H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2a, 362 (1947).

*Based on $\Delta H_f^{298}(\text{NaCl}(c)) = -98.26$ and $\Delta H_f^{298}(\text{NaF}(c)) = -137.1 \text{ kcal. mole}^{-1}$

**Based on the difference between the two calorimetric reactions of reference 5a, 5b.

Heat Capacity and Entropy

The rotational constants were obtained from the microwave spectrum by D. A. Gilbert, A. Roberts and P. A. Orszold, Phys. Rev. 76, 1723 (1949) and by D. A. Gilbert and A. Roberts Phys. Rev. 77, 742 (1950). The vibrational constants were obtained from the analysis vibration-rotation fine structure in the infrared by A. H. Nielsen and E. A. Jones, J. Chem. Phys. 19, 1117 (1951).

The rotational and vibrational constants were adjusted to $\text{Cl}^{35} = 75.4\%$ and $\text{Cl}^{37} = 24.6\%$.

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.000	INFINITE	-	2.129	-12.117	-12.117	INFINITE
100	6.961	44.228	58.559	12.349	-12.349	-12.349	26.766
200	7.621	52.064	72.750	12.514	-12.514	-12.514	19.554
298	7.868	52.064	72.750	12.514	-12.514	-12.514	9.160
300	7.677	52.111	72.064	0.014	-12.140	-12.140	9.105
400	8.067	54.376	52.370	0.803	-12.152	-12.616	6.893
500	8.134	56.207	52.960	1.623	-12.161	-12.731	5.565
600	8.513	57.743	53.633	2.466	-12.169	-12.844	4.678
700	8.639	59.065	54.316	3.324	-12.175	-12.956	4.045
800	8.729	60.225	54.984	4.193	-12.183	-13.068	3.570
900	8.798	61.258	55.625	5.069	-12.189	-13.179	3.200
1000	8.851	62.187	56.235	5.952	-12.196	-13.288	2.904
1100	8.894	63.033	56.815	6.839	-12.203	-13.397	2.652
1200	8.930	63.808	57.366	7.730	-12.211	-13.505	2.459
1300	8.960	64.524	57.890	8.625	-12.219	-13.612	2.288
1400	8.986	65.189	58.388	9.522	-12.227	-13.719	2.142
1500	9.010	65.810	58.862	10.422	-12.235	-13.825	2.014
1600	9.031	66.392	59.315	11.324	-12.245	-13.931	1.903
1700	9.051	66.940	59.747	12.228	-12.254	-14.035	1.804
1800	9.069	67.458	60.161	13.134	-12.265	-14.141	1.717
1900	9.086	67.949	60.559	14.042	-12.275	-14.244	1.638
2000	9.102	68.416	60.940	14.951	-12.287	-14.349	1.568
2100	9.117	68.860	61.306	15.862	-12.298	-14.452	1.504
2200	9.132	69.284	61.660	16.775	-12.311	-14.553	1.446
2300	9.146	69.691	62.000	17.689	-12.324	-14.655	1.393
2400	9.160	70.080	62.329	18.604	-12.338	-14.755	1.344
2500	9.173	70.454	62.646	19.521	-12.354	-14.856	1.299
2600	9.186	70.814	62.963	20.439	-12.370	-14.955	1.257
2700	9.199	71.161	63.251	21.358	-12.388	-15.054	1.218
2800	9.211	71.496	63.540	22.278	-12.406	-15.153	1.183
2900	9.224	71.820	63.820	23.200	-12.426	-15.252	1.149
3000	9.236	72.133	64.081	24.123	-12.447	-15.351	1.118
3100	9.248	72.436	64.346	25.047	-12.470	-15.447	1.089
3200	9.260	72.729	64.613	25.973	-12.494	-15.540	1.061
3300	9.271	73.014	64.883	26.899	-12.519	-15.634	1.035
3400	9.283	73.291	65.107	27.827	-12.546	-15.728	1.011
3500	9.295	73.561	65.345	28.756	-12.574	-15.824	0.988
3600	9.306	73.823	65.577	29.686	-12.603	-15.915	0.966
3700	9.318	74.078	65.803	30.617	-12.634	-16.006	0.945
3800	9.329	74.326	66.024	31.549	-12.666	-16.095	0.926
3900	9.340	74.569	66.240	32.483	-12.699	-16.184	0.907
4000	9.351	74.806	66.451	33.417	-12.734	-16.278	0.889
4100	9.363	75.037	66.658	34.353	-12.769	-16.367	0.872
4200	9.374	75.262	66.860	35.290	-12.806	-16.451	0.856
4300	9.385	75.483	67.058	36.228	-12.842	-16.538	0.841
4400	9.396	75.699	67.252	37.167	-12.881	-16.623	0.826
4500	9.407	75.910	67.442	38.107	-12.919	-16.708	0.811
4600	9.418	76.117	67.628	39.048	-12.958	-16.792	0.798
4700	9.429	76.320	67.811	39.991	-12.998	-16.876	0.785
4800	9.440	76.518	67.990	40.934	-13.038	-16.955	0.772
4900	9.451	76.713	68.166	41.879	-13.079	-17.036	0.760
5000	9.462	76.904	68.339	42.824	-13.120	-17.118	0.748
5100	9.472	77.092	68.509	43.771	-13.161	-17.200	0.737
5200	9.483	77.276	68.676	44.719	-13.202	-17.277	0.726
5300	9.494	77.456	68.840	45.668	-13.244	-17.351	0.715
5400	9.505	77.634	69.001	46.617	-13.286	-17.423	0.706
5500	9.516	77.808	69.160	47.569	-13.327	-17.495	0.696
5600	9.527	77.980	69.316	48.521	-13.369	-17.568	0.686
5700	9.537	78.149	69.469	49.474	-13.412	-17.641	0.677
5800	9.548	78.315	69.620	50.428	-13.453	-17.713	0.668
5900	9.559	78.478	69.769	51.383	-13.494	-17.788	0.659
6000	9.570	78.639	69.915	52.340	-13.537	-17.861	0.651

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

ClF

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ keal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	6.500	INFINITE	2.208	-170.046	-170.046	INFINITE
100	6.530	51.950	74.135	-170.170	-170.071	302.551
200	12.399	64.367	1.366	-170.711	-170.963	196.645
298	15.019	64.037	1.000	-180.200	-179.980	131.922
300	15.056	64.130	0.98	-180.209	-179.979	131.108
400	16.935	66.492	6.449	-180.681	-179.832	99.231
500	17.591	72.519	65.851	-182.611	-179.422	78.421
600	18.195	75.762	67.241	-183.086	-178.736	65.101
700	18.595	76.620	66.668	-183.520	-177.977	55.564
800	18.869	81.121	70.071	-183.595	-177.335	48.395
900	19.062	85.173	72.721	-184.629	-175.587	38.329
1000	19.212	85.373	72.721	-184.629	-175.587	38.329
1100	19.320	87.209	73.956	-184.973	-174.446	34.858
1200	19.404	88.694	75.132	-185.311	-173.475	31.993
1300	19.475	90.450	76.251	-185.485	-172.480	28.994
1400	19.536	92.411	77.315	-185.582	-171.460	25.860
1500	19.570	94.244	78.335	-186.289	-170.402	22.626
1600	19.606	94.508	79.306	-186.604	-169.331	23.128
1700	19.632	95.697	80.236	-187.010	-168.566	21.287
1800	19.650	96.864	81.166	-187.416	-167.802	19.409
1900	19.661	98.094	82.117	-187.821	-167.037	17.509
2000	19.714	99.856	83.591	-188.137	-166.261	15.332
2100	19.731	100.773	84.351	-188.139	-165.752	14.996
2200	19.735	101.691	85.129	-188.139	-165.752	13.761
2300	19.753	103.691	86.792	-188.139	-165.752	12.562
2400	19.761	103.597	86.476	-188.139	-165.752	11.407
2500	19.770	104.073	87.138	-188.139	-165.752	10.291
2600	19.776	104.619	87.779	-188.139	-165.752	9.858
2700	19.785	105.236	88.401	-188.139	-165.752	9.060
2800	19.788	105.816	89.016	-188.139	-165.752	8.310
2900	19.794	106.403	89.589	-188.139	-165.752	7.603
3000	19.800	107.553	90.158	-188.139	-165.752	6.963
3100	19.805	108.181	90.712	-188.139	-165.752	6.360
3200	19.809	108.781	91.250	-188.139	-165.752	5.815
3300	19.813	109.356	91.781	-188.139	-165.752	5.284
3400	19.815	109.956	92.286	-188.139	-165.752	4.763
3500	19.816	110.515	92.765	-188.139	-165.752	4.261
3600	19.821	111.056	93.271	-188.139	-165.752	3.867
3700	19.821	111.598	93.709	-188.139	-165.752	3.446
3800	19.827	112.131	94.166	-188.139	-165.752	3.049
3900	19.829	112.603	94.664	-188.139	-165.752	2.682
4000	19.831	113.093	95.108	-188.139	-165.752	2.307
4100	19.831	113.593	95.108	-188.139	-165.752	1.964
4200	19.832	113.371	95.542	-188.139	-165.752	1.638
4300	19.834	113.493	95.986	-188.139	-165.752	1.326
4400	19.834	114.093	96.464	-188.139	-165.752	1.041
4500	19.836	114.639	96.790	-188.139	-165.752	0.783
4600	19.840	115.375	97.189	-188.139	-165.752	0.541
4700	19.842	115.902	97.560	-188.139	-165.752	0.310
4800	19.843	116.420	97.964	-188.139	-165.752	0.041
4900	19.843	116.939	98.386	-188.139	-165.752	-0.210
5000	19.845	117.530	98.711	-188.139	-165.752	-0.461
5100	19.846	117.423	99.074	-188.139	-165.752	-0.736
5200	19.847	117.408	99.430	-188.139	-165.752	-1.011
5300	19.849	117.408	99.786	-188.139	-165.752	-1.286
5400	19.849	117.408	100.142	-188.139	-165.752	-1.561
5500	19.849	117.408	100.498	-188.139	-165.752	-1.836
5600	19.850	117.408	100.854	-188.139	-165.752	-2.111
5700	19.850	117.408	101.210	-188.139	-165.752	-2.386
5800	19.851	120.315	101.763	-188.139	-165.752	-2.661
5900	19.852	120.649	102.075	-188.139	-165.752	-2.936
6000	19.852	120.649	102.075	-188.139	-165.752	-3.211

December 31, 1960.

DILITHIUM CHLORIDE FLUORIDE (Li₂ClF)

Mol. Wt. = 68.34

ΔH_f⁰ 298.15 = [-180.2] kcal. mole⁻¹

S_{298.15}⁰ = [64.037] cal. deg.⁻¹ mole⁻¹

ΔH_f⁰ 298.15 from National Bureau of Standards Report No. 6297, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine (Revised)", January, 1959. Cp from R. R. Koppang, C. W. Sherwood, and G. S. Bahn, Marquardt Corp., Van Nuys, Calif., "Some Provisional Tables of Species Thermodynamic Properties", October, 1959.

Magnesium Chloride Fluoride (MgClF)

(Ideal Gas) Mol. Wt. = 78.7634

CIFMg

MAGNESIUM CHLORIDE FLUORIDE (MgClF) (IDEAL GAS) MOL. WT. = 78.7634

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+∞	INFINITE	-2.947	-135.599	-135.599	INFINITE
100	9.089	51.367	-2.943	-135.599	-135.599	297.765
200	10.923	28.726	-2.943	-135.599	-135.599	149.557
298	11.979	22.756	-2.943	-135.599	-135.599	100.591
300	11.945	62.830	+0.022	-136.003	-137.222	99.966
400	12.619	66.367	63.234	-136.186	-137.602	75.182
500	13.015	69.229	64.156	-136.375	-137.933	60.290
600	13.259	71.625	65.207	-136.580	-138.226	50.349
700	13.418	73.682	66.274	-136.803	-138.482	43.236
800	13.526	75.481	67.315	-137.056	-138.707	37.893
900	13.603	77.079	68.313	-137.344	-138.896	33.728
1000	13.659	78.515	69.262	-137.659	-139.050	30.350
1100	13.701	79.819	70.164	-140.117	-138.764	27.570
1200	13.733	81.013	71.019	-140.471	-138.626	25.227
1300	13.759	82.113	71.830	-140.852	-138.456	23.277
1400	13.779	83.134	72.602	-141.264	-138.258	21.508
1500	13.796	84.085	73.336	-141.651	-138.035	19.722
1600	13.809	84.976	74.036	-142.008	-137.779	18.159
1700	13.821	85.813	74.704	-142.336	-137.494	16.779
1800	13.830	86.604	75.344	-142.636	-137.179	15.553
1900	13.838	87.352	75.956	-142.908	-136.836	14.455
2000	13.845	88.062	76.544	-143.154	-136.468	13.467
2100	13.851	88.737	77.108	-143.380	-136.074	12.573
2200	13.856	89.382	77.652	-143.586	-135.658	11.760
2300	13.861	89.998	78.175	-143.774	-135.222	11.017
2400	13.865	90.588	78.680	-143.944	-134.770	10.337
2500	13.869	91.154	79.168	-144.096	-134.302	9.710
2600	13.872	91.698	79.639	-144.232	-133.820	9.132
2700	13.874	92.221	80.096	-144.354	-133.326	8.596
2800	13.877	92.726	80.538	-144.462	-132.820	8.099
2900	13.879	93.213	80.967	-144.556	-132.302	7.635
3000	13.881	93.684	81.383	-144.636	-131.772	7.203
3100	13.883	94.139	81.787	-144.702	-131.230	6.798
3200	13.885	94.580	82.180	-144.756	-130.676	6.418
3300	13.886	95.007	82.562	-144.800	-130.112	6.051
3400	13.888	95.421	82.934	-144.834	-129.538	5.725
3500	13.889	95.824	83.297	-144.858	-128.954	5.408
3600	13.890	96.215	83.650	-144.874	-128.360	5.109
3700	13.891	96.596	83.995	-144.882	-127.758	4.825
3800	13.892	96.966	84.332	-144.882	-127.148	4.557
3900	13.893	97.327	84.660	-144.874	-126.526	4.302
4000	13.894	97.679	84.981	-144.858	-125.894	4.059
4100	13.895	98.022	85.295	-144.834	-125.252	3.829
4200	13.895	98.357	85.602	-144.800	-124.600	3.609
4300	13.896	98.684	85.903	-144.756	-123.946	3.399
4400	13.897	99.003	86.197	-144.702	-123.292	3.198
4500	13.897	99.316	86.485	-144.636	-122.630	3.007
4600	13.898	99.621	86.767	-144.558	-121.958	2.823
4700	13.898	99.920	87.044	-144.468	-121.286	2.647
4800	13.899	100.213	87.315	-144.368	-120.614	2.478
4900	13.899	100.499	87.581	-144.258	-119.942	2.316
5000	13.900	100.780	87.842	-144.138	-119.270	2.160
5100	13.900	101.055	88.099	-144.008	-118.598	2.010
5200	13.900	101.325	88.351	-143.868	-117.926	1.866
5300	13.901	101.590	88.598	-143.718	-117.254	1.727
5400	13.901	101.850	88.841	-143.558	-116.582	1.593
5500	13.902	102.105	89.080	-143.388	-115.910	1.463
5600	13.902	102.355	89.315	-143.208	-115.238	1.338
5700	13.902	102.601	89.545	-143.018	-114.566	1.217
5800	13.902	102.843	89.773	-142.818	-113.894	1.100
5900	13.903	103.081	89.996	-142.608	-113.222	0.987
6000	13.903	103.314	90.216	-142.388	-112.550	0.877

Dec. 31, 1960; Mar. 31, 1966

Point Group C_{2v} ΔH_f⁰ = [-135.6 ± 5] kcal. mole⁻¹

S_{298.15} = [82.76] cal. deg.⁻¹ mole⁻¹ ΔH_f⁰ 298.15 = [-136.0 ± 5] kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e cm.⁻¹

[719](1)

[205](1)

[453](1)

Bond Distances: Mg-Cl = [2.18] Å Mg-F = [1.77] Å

Bond Angle: Cl-Mg-F = [170]°

Product of the Moments of Inertia: I_AI_BI_C = [1.5643 X 10⁻¹¹⁵] g.³ cm.⁶

Heat of Formation

The heat of formation is based on an estimated ΔH_f⁰ 298 = 0 for the reaction MgCl₂(g) + MgF₂(g) → 2MgClF(g), using ΔH_f⁰ 298.15 = -95.85 and -176.2 kcal. mole⁻¹ for MgCl₂(g) and MgF₂(g), respectively.

Heat Capacity and Entropy

The bond angle is taken to be the value we have adopted for MgCl₂(g). The Mg-Cl and Mg-F bond distances are assumed to be the same as those in MgCl₂(g) and MgF₂(g). The vibration frequencies are the averages of those for MgCl₂(g) and MgF₂(g). The three principal moments of inertia are: I_A = 0.0977 X 10⁻³⁵, I_B = 39.956 X 10⁻³⁹ and I_C = 40.054 X 10⁻³⁹ g. cm.²

CIFMg

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	(H ^o -H ₂₉₈)/T	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	3.178	-	3.034	-	3.034	INFINITE
100	12.073	51.000	67.926	1.365	2.715	-	2.715	2.095
200	15.517	66.653	66.653	1.000	5.120	-	12.090	6.661
300	15.373	66.749	66.653	1.029	5.125	-	12.106	6.664
400	16.132	71.602	67.297	1.722	5.268	-	16.002	6.835
500	20.000	75.863	68.593	3.635	5.312	-	23.631	10.416
600	21.319	79.633	70.125	5.704	5.226	-	29.653	10.401
700	22.271	82.994	71.728	7.886	5.076	-	35.455	11.069
800	22.967	86.016	73.328	10.130	4.894	-	41.231	11.263
900	23.467	88.753	74.863	12.474	4.683	-	46.983	11.408
1000	23.883	91.249	76.405	14.843	4.426	-	52.710	11.519
1100	24.189	93.540	77.860	17.248	4.175	-	58.410	11.604
1200	24.430	95.655	79.256	19.679	3.914	-	64.090	11.672
1300	24.624	97.619	80.594	22.132	3.649	-	69.746	11.725
1400	24.760	99.449	81.876	24.602	3.382	-	75.380	11.767
1500	24.859	101.164	83.106	27.087	3.112	-	80.990	11.801
1600	25.016	102.775	84.285	29.584	2.843	-	86.596	11.828
1700	25.105	104.294	85.418	32.090	2.574	-	92.179	11.850
1800	25.161	105.731	86.507	34.604	2.311	-	97.744	11.867
1900	25.246	107.094	87.555	37.125	2.051	-	103.297	11.881
2000	25.351	108.391	88.564	39.653	1.795	-	108.833	11.892
2100	25.349	109.626	89.538	42.185	1.544	-	114.359	11.901
2200	25.391	110.807	90.478	44.723	1.300	-	119.871	11.906
2300	25.428	111.936	91.367	47.264	1.060	-	125.374	11.913
2400	25.461	113.019	92.266	49.808	0.828	-	130.866	11.917
2500	25.489	114.059	93.117	52.356	0.605	-	136.347	11.919
2600	25.515	115.059	93.942	54.906	0.386	-	141.833	11.921
2700	25.538	116.023	94.742	57.458	0.176	-	147.289	11.922
2800	25.558	116.952	95.516	60.013	0.027	-	152.747	11.922
2900	25.577	117.849	96.273	62.570	0.223	-	158.199	11.922
3000	25.593	118.716	97.007	65.129	0.411	-	163.641	11.921
3100	25.608	119.556	97.721	67.689	0.593	-	169.082	11.920
3200	25.622	120.369	98.416	70.250	0.767	-	174.513	11.918
3300	25.635	121.158	99.093	72.813	0.935	-	179.937	11.916
3400	25.646	121.926	100.753	75.377	1.105	-	185.360	11.914
3500	25.657	122.667	100.398	77.942	1.249	-	190.776	11.912
3600	25.666	123.390	101.026	80.508	1.396	-	196.192	11.910
3700	25.675	124.093	101.640	83.075	1.537	-	201.600	11.907
3800	25.683	124.778	102.240	85.643	1.673	-	207.009	11.905
3900	25.691	125.445	102.827	88.212	1.803	-	212.404	11.902
4000	25.698	126.096	103.400	90.782	1.926	-	217.803	11.900
4100	25.704	126.730	103.961	93.352	2.043	-	223.200	11.897
4200	25.711	127.350	104.511	95.922	2.156	-	228.592	11.894
4300	25.716	127.955	105.049	98.494	2.264	-	233.986	11.892
4400	25.721	128.546	105.577	101.066	2.366	-	239.370	11.889
4500	25.726	129.124	106.093	103.636	2.464	-	244.755	11.886
4600	25.731	129.690	106.600	106.211	2.558	-	250.143	11.884
4700	25.735	130.243	107.097	108.784	2.646	-	255.525	11.881
4800	25.739	130.785	107.585	111.358	2.731	-	260.904	11.879
4900	25.743	131.316	108.064	113.932	2.812	-	266.277	11.876
5000	25.747	131.836	108.534	116.507	2.889	-	271.652	11.873
5100	25.750	132.346	108.996	119.082	2.961	-	277.029	11.871
5200	25.753	132.846	109.450	121.657	3.030	-	282.399	11.868
5300	25.756	133.336	109.896	124.232	3.097	-	287.779	11.866
5400	25.759	133.816	110.335	126.806	3.156	-	293.140	11.863
5500	25.762	134.290	110.766	129.384	3.220	-	298.516	11.861
5600	25.765	134.755	111.190	131.960	3.274	-	303.881	11.859
5700	25.767	135.211	111.608	134.537	3.327	-	309.248	11.857
5800	25.769	135.659	112.019	137.114	3.378	-	314.621	11.855
5900	25.771	136.093	112.423	139.691	3.425	-	319.982	11.852
6000	25.773	136.533	112.821	142.266	3.470	-	325.349	11.850

March 31, 1961

Phosphoryl Difluoride Chloride (POClF₂)

(Ideal Gas) Mol. Wt. = 120.432

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	INFINITE
100	9.119	56.627	84.368	- 3.393	- 226.287	- 226.287	- 226.287	INFINITE
200	13.155	66.184	73.486	- 2.576	- 226.961	- 226.961	- 226.961	490.116
298	16.453	72.081	72.081	- 1.460	- 227.565	- 227.565	- 227.565	221.847
300	16.453	72.081	72.081	- 1.460	- 227.565	- 227.565	- 227.565	159.917
300	16.453	72.081	72.081	- 1.460	- 227.565	- 227.565	- 227.565	159.917
400	18.960	77.287	72.081	- 0.930	- 228.007	- 228.007	- 228.007	158.886
500	20.684	81.715	74.119	- 0.700	- 228.300	- 228.300	- 228.300	117.721
600	21.889	85.599	75.715	- 0.593	- 228.482	- 228.482	- 228.482	92.380
700	22.743	89.041	77.378	- 0.516	- 228.595	- 228.595	- 228.595	75.732
800	23.360	91.160	78.031	- 0.461	- 228.673	- 228.673	- 228.673	63.835
900	23.815	92.815	78.684	- 0.418	- 228.720	- 228.720	- 228.720	56.361
1000	24.161	94.161	79.167	- 0.383	- 228.746	- 228.746	- 228.746	48.759
1100	24.427	95.427	79.573	- 0.353	- 228.751	- 228.751	- 228.751	41.216
1200	24.636	96.636	79.904	- 0.327	- 228.746	- 228.746	- 228.746	37.819
1300	24.802	97.802	80.166	- 0.303	- 228.732	- 228.732	- 228.732	34.582
1400	24.937	98.937	80.357	- 0.280	- 228.711	- 228.711	- 228.711	31.496
1500	25.047	100.047	80.483	- 0.259	- 228.684	- 228.684	- 228.684	28.561
1600	25.138	101.138	80.546	- 0.240	- 228.652	- 228.652	- 228.652	25.767
1700	25.215	102.215	80.546	- 0.223	- 228.616	- 228.616	- 228.616	23.111
1800	25.278	103.278	80.499	- 0.208	- 228.576	- 228.576	- 228.576	20.597
1900	25.328	104.328	80.406	- 0.194	- 228.533	- 228.533	- 228.533	18.224
2000	25.368	105.368	80.271	- 0.182	- 228.487	- 228.487	- 228.487	15.981
2100	25.423	106.423	80.100	- 0.172	- 228.437	- 228.437	- 228.437	13.866
2200	25.459	107.459	80.000	- 0.163	- 228.383	- 228.383	- 228.383	11.876
2300	25.490	108.490	79.875	- 0.155	- 228.326	- 228.326	- 228.326	10.000
2400	25.516	109.516	79.725	- 0.148	- 228.267	- 228.267	- 228.267	8.244
2500	25.542	110.542	79.550	- 0.142	- 228.206	- 228.206	- 228.206	6.608
2600	25.564	111.564	79.350	- 0.137	- 228.144	- 228.144	- 228.144	5.088
2700	25.583	112.583	79.125	- 0.132	- 228.081	- 228.081	- 228.081	3.684
2800	25.600	113.600	78.875	- 0.128	- 228.016	- 228.016	- 228.016	2.396
2900	25.614	114.614	78.600	- 0.125	- 227.952	- 227.952	- 227.952	1.232
3000	25.630	115.630	78.300	- 0.123	- 227.889	- 227.889	- 227.889	0.192
3100	25.643	116.643	77.975	- 0.121	- 227.826	- 227.826	- 227.826	- 0.816
3200	25.655	117.655	77.625	- 0.119	- 227.763	- 227.763	- 227.763	- 1.876
3300	25.665	118.665	77.250	- 0.117	- 227.699	- 227.699	- 227.699	- 2.996
3400	25.674	119.674	76.850	- 0.115	- 227.636	- 227.636	- 227.636	- 4.176
3500	25.684	120.684	76.425	- 0.113	- 227.572	- 227.572	- 227.572	- 5.416
3600	25.692	121.692	75.975	- 0.112	- 227.509	- 227.509	- 227.509	- 6.716
3700	25.700	122.700	75.500	- 0.111	- 227.446	- 227.446	- 227.446	- 8.066
3800	25.707	123.707	75.000	- 0.110	- 227.383	- 227.383	- 227.383	- 9.466
3900	25.714	124.714	74.475	- 0.109	- 227.320	- 227.320	- 227.320	- 10.916
4000	25.719	125.719	73.925	- 0.108	- 227.257	- 227.257	- 227.257	- 12.416
4100	25.724	126.724	73.350	- 0.107	- 227.194	- 227.194	- 227.194	- 13.966
4200	25.730	127.730	72.750	- 0.106	- 227.131	- 227.131	- 227.131	- 15.566
4300	25.734	128.734	72.125	- 0.105	- 227.068	- 227.068	- 227.068	- 17.216
4400	25.738	129.738	71.475	- 0.104	- 227.005	- 227.005	- 227.005	- 18.916
4500	25.743	130.743	70.800	- 0.103	- 226.942	- 226.942	- 226.942	- 20.666
4600	25.747	131.747	70.100	- 0.102	- 226.879	- 226.879	- 226.879	- 22.466
4700	25.751	132.751	69.375	- 0.101	- 226.816	- 226.816	- 226.816	- 24.316
4800	25.754	133.754	68.625	- 0.100	- 226.753	- 226.753	- 226.753	- 26.216
4900	25.758	134.758	67.850	- 0.100	- 226.690	- 226.690	- 226.690	- 28.166
5000	25.760	135.760	67.050	- 0.099	- 226.627	- 226.627	- 226.627	- 30.166
5100	25.763	136.763	66.225	- 0.098	- 226.564	- 226.564	- 226.564	- 32.216
5200	25.766	137.766	65.375	- 0.097	- 226.501	- 226.501	- 226.501	- 34.316
5300	25.768	138.768	64.500	- 0.096	- 226.438	- 226.438	- 226.438	- 36.466
5400	25.771	139.771	63.600	- 0.095	- 226.375	- 226.375	- 226.375	- 38.666
5500	25.773	140.773	62.675	- 0.094	- 226.312	- 226.312	- 226.312	- 40.916
5600	25.775	141.775	61.725	- 0.093	- 226.249	- 226.249	- 226.249	- 43.216
5700	25.777	142.777	60.750	- 0.092	- 226.186	- 226.186	- 226.186	- 45.566
5800	25.779	143.779	59.750	- 0.091	- 226.123	- 226.123	- 226.123	- 47.966
5900	25.781	144.781	58.725	- 0.090	- 226.060	- 226.060	- 226.060	- 50.416
6000	25.783	145.783	57.675	- 0.089	- 226.000	- 226.000	- 226.000	- 52.916

March 31, 1983

ClF₂OP

MOL. WT. = 120.432

PHOSPHORYL DIFLUORIDE CHLORIDE (POClF₂)

(IDEAL GAS)

Point Group C_s
 $\Delta H_f^0 = [-226] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 72.081 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = [-228] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 298.15$
Bond State Multiplicity = [1]

Vibrational Frequencies and Degeneracies	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
	274 (1)	424 (2)	948 (2)
	410 (1)	618 (1)	1358 (1)
		895 (1)	

Bond Distance: P-Cl = 2.01 ± 0.04 Å P-P = 1.51 ± 0.05 Å P-O = 1.55 ± 0.03 Å
Bond Angle: P-P-F = P-P-Cl = 103°
Product of the Moments of Inertia: I_AI_BI_C = 4.2790825 X 10⁻¹¹³ g.³ cm.⁶
 $\sigma = 1$

Heat of Formation.

The ΔH_f^0 298.15 of POClF₂ was estimated to be -228 kcal. mole⁻¹ from the ΔH_f^0 298.15 of POCl₃ by assuming bond energies of 120 kcal. for D(P-F) and 80 kcal. for D(P-Cl). The D(P-F) and D(P-Cl) values were taken from E. Neale and L. T. D. Williams, J. Chem. Soc., 2485 (1955) Part I and E. Neale, L. T. D. Williams and V. T. Moores, J. Chem. Soc., 422 (1956) Part II.

Essentially the same ΔH_f^0 298.15 may be obtained by assuming a $\Delta H_f^0 = 0$ for the following reaction:



Heat Capacity and Entropy.

The molecular constants were determined by L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc., 50, 1836 (1928) and by Q. Williams, J. Sheridan, and M. Gordy, J. Chem. Phys., 20, 164 (1952). Brockway and Beach used electron diffraction. Q. Williams et al. measured microwave spectra. Brockway and Beach assumed that the P-P-F and P-P-Cl angles were equal in POCl₂Cl and POClF₂. An analysis of Brockway and Beach's data by Q. Williams et al., indicates that the angles in POCl₂Cl, POClF₂, POCl₃, and POF₃ should be 103° rather than the reported 106° ± 3°. The principal moments of inertia calculated from these parameters were I_A = 3.24319 X 10⁻³⁸ g. cm.², I_B = 1.87015 X 10⁻³⁸ g. cm.², and I_C = 3.13496 g. cm.² X 10⁻³⁸.

The Raman spectra and vibrational frequencies for POCl₂Cl were reported by M. L. Delwaule and P. Francois, Compt. Rend. 222, 550 (1946). The frequencies were reassigned by M. L. Delwaule and P. Francois in J. Chim. Phys. 46, 87 (1949).

ClF₂OP

CHLORINE TRIFLUORIDE (ClF₃)

(IDEAL GAS)

MOL. WT. = 92.4482

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	- 3.262	- 36.970	- 36.970	INFINITE	
100	8.872	54.430	78.926	- 2.450	- 37.551	- 34.630	INFINITE
200	12.582	61.712	68.598	- 31.577	- 37.889	- 34.477	34.477
298	15.260	67.279	67.279	+0.000	- 37.970	- 28.416	20.859
300	15.298	67.374	67.280	+0.28	- 37.970	- 28.360	20.659
400	16.875	72.012	67.001	1.644	- 37.924	- 25.160	13.746
500	17.798	75.885	69.122	3.382	- 37.824	- 21.980	9.607
600	18.366	79.184	70.531	5.102	- 37.696	- 18.823	6.856
700	18.794	82.065	71.976	7.008	- 37.555	- 15.688	4.998
800	18.984	84.564	73.395	8.935	- 37.410	- 12.576	3.435
900	19.162	86.811	74.763	10.843	- 37.262	- 9.480	2.302
1000	19.291	88.637	76.071	12.766	- 37.113	- 6.402	1.399
1100	19.389	90.080	77.316	14.700	- 36.965	- 3.388	.663
1200	19.464	92.331	78.463	16.645	- 36.818	- 0.352	.000
1300	19.523	94.631	79.659	18.592	- 36.674	2.782	.663
1400	19.570	96.379	80.747	20.547	- 36.532	5.780	.902
1500	19.608	97.671	81.727	22.506	- 36.392	8.798	1.282
1600	19.640	97.997	82.705	24.468	- 36.257	11.806	1.613
1700	19.666	99.189	84.240	26.442	- 36.126	14.806	2.000
1800	19.688	100.314	84.535	28.402	- 35.993	17.795	2.401
1900	19.707	101.379	84.534	30.371	- 35.866	20.782	2.816
2000	19.723	102.390	86.218	32.343	- 35.742	23.762	3.256
2100	19.737	103.353	87.012	34.316	- 35.622	26.730	3.720
2200	19.749	104.273	87.516	36.285	- 35.506	29.682	4.200
2300	19.759	105.149	88.512	38.265	- 35.393	32.661	4.693
2400	19.768	105.980	89.223	40.242	- 35.284	35.617	5.103
2500	19.776	106.787	89.910	42.219	- 35.180	38.569	5.437
2600	19.784	107.573	90.576	44.197	- 35.079	41.517	5.800
2700	19.790	108.333	91.223	46.177	- 34.982	44.462	6.193
2800	19.796	109.040	91.841	48.155	- 34.888	47.401	6.610
2900	19.801	109.734	92.447	50.135	- 34.800	50.342	7.053
3000	19.806	110.406	93.034	52.115	- 34.717	53.270	7.521
3100	19.810	111.055	93.605	54.096	- 34.637	56.204	8.000
3200	19.814	111.684	94.160	56.069	- 34.562	59.132	8.493
3300	19.817	112.294	94.700	58.059	- 34.492	62.060	8.993
3400	19.820	112.886	95.227	60.041	- 34.425	64.984	9.500
3500	19.823	113.460	95.739	62.023	- 34.364	67.911	10.013
3600	19.826	114.019	96.240	64.005	- 34.306	70.832	10.530
3700	19.829	114.562	96.727	65.988	- 34.250	73.746	11.053
3800	19.831	115.091	97.204	67.971	- 34.202	76.671	11.580
3900	19.833	115.606	97.669	69.954	- 34.161	79.585	12.100
4000	19.835	116.108	98.124	71.938	- 34.120	82.504	12.613
4100	19.837	116.598	98.548	73.921	- 34.085	85.416	13.120
4200	19.838	117.076	99.003	75.905	- 34.050	88.320	13.620
4300	19.840	117.543	99.429	77.889	- 34.024	91.246	14.113
4400	19.841	117.999	99.846	79.873	- 34.002	94.159	14.600
4500	19.843	118.445	100.254	81.857	- 33.981	97.068	15.080
4600	19.844	118.881	100.655	83.841	- 33.964	99.981	15.553
4700	19.845	119.308	101.077	85.826	- 33.952	102.886	16.020
4800	19.846	119.726	101.432	87.811	- 33.942	105.803	16.480
4900	19.847	120.135	101.809	89.795	- 33.937	108.719	16.933
5000	19.848	120.536	102.180	91.780	- 33.934	111.628	17.380
5100	19.849	120.920	102.544	93.765	- 33.935	114.536	17.820
5200	19.850	121.311	102.920	95.750	- 33.940	117.440	18.253
5300	19.851	121.692	103.252	97.735	- 33.947	120.368	18.680
5400	19.852	122.063	103.597	99.720	- 33.958	123.273	19.100
5500	19.853	122.428	103.936	101.705	- 33.972	126.186	19.513
5600	19.853	122.785	104.269	103.691	- 33.989	129.102	19.920
5700	19.854	123.137	104.597	105.666	- 34.011	132.021	20.320
5800	19.855	123.482	104.920	107.661	- 34.033	134.921	20.713
5900	19.855	123.822	105.237	109.647	- 34.060	137.831	21.100
6000	19.856	124.155	105.550	111.632	- 34.090	140.750	21.480

Dec. 31, 1960; June 30, 1961; Sept. 30, 1965

Point Group C_{2v}
 $S_{298}^{298.15} = 67.279$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{\circ} 298.15 = -36.97 \pm 0.7$ kcal. mole⁻¹
 $\Delta H_f^{\circ} 298.15 = -37.97 \pm 0.7$ kcal. mole⁻¹
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm.⁻¹ ω , cm.⁻¹

752 (1) 703 (1)

528 (1) 434 (1)

326 (1) 364 (1)

Bond Distances: Cl-F₁ = Cl-F₂ = 1.688 Å Cl-F₃ = 1.598 Å

Bond Angle: F₁-Cl-F₂ = F₂-Cl-F₃ = 67° 29' F₃-Cl-F₁ = 185° 02'

Product of Moments of Inertia: I_AI_BI_C = 2.6923061 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation: $\Delta H_f^{\circ} 298.15 = -37.97$ kcal. mole⁻¹ was calculated from $\Delta H_f^{\circ} 298 = 25.63$ kcal. mole⁻¹ obtained by third law analysis of the equilibrium data of H. Schmitz and H. T. Schumacher, Z. Naturforsch. **2b**, 362 (1947) for the reaction ClF₃(g) = ClF(g) + F₂(g). Similar values are obtained from the equilibrium data of K. Schafer and E. Wicke, Z. Elektrochemie **52**, 205-209 (1948). Calorimetric values scatter widely, as summarized below; these were given little weight.

Source	Method	Reaction	Observation ₂₁	3rd Law Drift	ΔH _f ²⁹⁸ (kcal. mole ⁻¹)
1a	K ₂ (523-623°K)	ClF ₃ (g) → ClF(g) + F ₂ (g)	ΔH _r ²⁹⁸ = 25.83	0.8 ± 0.3	-37.97
2a	K ₂ (735°K)	ClF ₃ (g) → ClF(g) + F ₂ (g)	ΔH _r ²⁹⁸ = 25.77	---	-37.91
2b	K ₂ (570-680°K)	ClF ₃ (g) → ClF(g) + F ₂ (g)	ΔH _r ²⁹⁸ = 26.12	6 ± 3	-38.28
1b	Calorimetric	3NaCl + ClF ₃ → 3NaF + 2Cl ₂	ΔH _r ²⁹¹ = -76.5	---	-40.02
1c	Calorimetric	NaCl + 0.5 F ₂ → NaF + 0.5 Cl ₂	ΔH _r ²⁹¹ = -59.5	---	-42.0*
3	Calorimetric	3NaCl + ClF ₃ → 3NaF + 2Cl ₂	ΔH _r ²⁹⁸ = -86.8	---	-29.7
4	Calorimetric	0.5 F ₂ + NaCl → NaF + 0.5 Cl ₂	ΔH _r ²⁹³ = -59.3	---	-31.1**
5	Flow reaction	0.5 Cl ₂ (g) + 1.5 F ₂ (g) = ClF ₃ (g)	ΔH _r ⁴⁷³ = -26.4	---	-26.4

*From combination of 1b and 1c. **From combination of 3 and 4.

Sources

- 1 H. Schmitz and H. T. Schumacher Z. Naturforsch. **2b**, 362 (1947).
- 2a (Hot wire) K. Schafer and E. Wicke, Z. Elektrochem. **52**, 205 (1948).
- 2b (From the Graph) K. Schafer and E. Wicke, Z. Elektrochem. **52**, 205 (1948).
- 3 H. v. Wartenberg Z. anorg. allgem. Chem. **25B**, 356 (1949).
- 4 H. v. Wartenberg and O. Fitzer, A. anorg. allgem. Chem. **152**, 313 (1928).
- 5 C. F. Swinehart, private communication from the Harshaw Chemical Co., March, 1963.

Heat Capacity and Entropy.

The structural constants were obtained from the microwave study of D. P. Smith, J. Chem. Phys. **21**, 609 (1953). The planar distorted "m" structure is similar to that derived from X-ray studies of the solid by R. D. Burbank and P. N. Bensey, J. Chem. Phys. **21**, 802 (1953). Fundamental frequencies are taken from the infrared and Raman spectra of H. H. Claassen, B. Weinstein and J. G. Malm, J. Chem. Phys. **28**, 285 (1958). These data confirm the "m" structure as opposed to the pyramidal structure used in earlier spectral analyses.

Claassen, et al., loc. cit., calculate thermodynamic functions virtually identical with the JANAF values. These authors also correct the third law entropy reported by J. W. Gitsard, H. A. Bernhardt and G. D. Oliver, J. Am. Chem. Soc. **73**, 5725 (1951) from measurements of heat capacity (14-285°K.) and vapor pressure (228-303°K.). The entropy at the normal boiling point becomes $S_{284.91}^{\circ} = 67.04$ cal. deg.⁻¹ mole⁻¹ when a non-ideality correction consistent with the normal boiling point becomes $S_{284.91}^{\circ} = 67.04$ cal. deg.⁻¹ mole⁻¹. The corresponding statistical entropy, $S_{284.91}^{\circ} = 66.59$ cal. deg.⁻¹ mole⁻¹, is consistent with the third law value within the probable error in the entropy of the liquid and the entropy of vaporization. The three principal moments of inertia are: I_A = 6.114 X 10⁻³⁹, I_B = 1.61545 X 10⁻³⁸ and I_C = 2.42859 X 10⁻³⁸ g. cm.²



Chlorotrifluorosilane (ClSiF₃)
(Ideal Gas) Mol. Wt. = 120.547

INTERIM TABLE

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	0.000	INFINITE	0.000	0.000	0.000	INFINITE
100	11.114	57.324	66.166	3.971	-313.953	-313.953	-313.953	16.656
200	15.857	66.792	73.394	3.064	-314.521	-314.521	-314.521	16.615
298	18.671	73.751	77.751	2.000	-315.000	-315.000	-315.000	16.615
300	19.018	73.868	73.751	0.935	-315.002	-315.002	-315.002	16.615
400	22.095	79.664	76.025	2.038	-315.006	-315.006	-315.006	16.615
500	22.431	84.507	76.025	2.038	-315.073	-315.073	-315.073	16.615
600	23.305	86.660	77.814	6.519	-315.039	-315.039	-315.039	16.615
700	23.994	92.319	79.432	8.661	-314.983	-314.983	-314.983	16.615
800	24.405	96.819	81.154	13.736	-314.843	-314.843	-314.843	16.615
1000	24.821	101.023	84.813	16.210	-314.771	-314.771	-314.771	16.615
1100	24.967	103.397	86.396	16.701	-314.699	-314.699	-314.699	16.615
1200	25.117	105.577	87.905	21.266	-314.627	-314.627	-314.627	16.615
1300	25.261	107.843	90.214	25.263	-314.551	-314.551	-314.551	16.615
1400	25.391	109.843	92.122	28.783	-314.471	-314.471	-314.471	16.615
1500	25.508	111.211	93.274	31.322	-314.385	-314.385	-314.385	16.615
1600	25.614	112.850	94.471	33.667	-314.294	-314.294	-314.294	16.615
1700	25.709	114.393	95.619	35.616	-314.198	-314.198	-314.198	16.615
1800	25.797	115.850	96.714	37.263	-314.098	-314.098	-314.098	16.615
1900	25.878	117.140	97.778	38.724	-313.994	-313.994	-313.994	16.615
2000	25.958	118.530	98.778	40.006	-313.885	-313.885	-313.885	16.615
2100	26.033	119.768	99.779	41.082	-313.771	-313.771	-313.771	16.615
2200	26.104	120.980	99.779	46.642	-313.642	-313.642	-313.642	16.615
2300	26.172	122.111	100.725	49.205	-313.506	-313.506	-313.506	16.615
2400	26.237	123.169	101.611	50.783	-313.363	-313.363	-313.363	16.615
2500	26.299	124.257	102.523	54.334	-313.213	-313.213	-313.213	16.615
2600	26.357	125.264	103.379	56.901	-313.056	-313.056	-313.056	16.615
2700	26.411	126.233	104.207	59.469	-312.893	-312.893	-312.893	16.615
2800	26.461	127.169	105.011	62.039	-312.724	-312.724	-312.724	16.615
2900	26.507	128.081	105.788	64.611	-312.549	-312.549	-312.549	16.615
3000	26.551	128.941	106.546	67.180	-312.368	-312.368	-312.368	16.615
3100	26.592	129.764	107.284	69.752	-312.174	-312.174	-312.174	16.615
3200	26.631	130.561	108.000	72.325	-311.968	-311.968	-311.968	16.615
3300	26.668	131.333	108.697	74.896	-311.751	-311.751	-311.751	16.615
3400	26.703	132.086	109.371	77.466	-311.524	-311.524	-311.524	16.615
3500	26.737	132.808	110.037	80.046	-311.287	-311.287	-311.287	16.615
3600	26.771	133.433	110.683	82.621	-311.040	-311.040	-311.040	16.615
3700	26.803	134.063	111.313	85.196	-310.783	-310.783	-310.783	16.615
3800	26.834	134.693	111.928	87.772	-310.516	-310.516	-310.516	16.615
3900	26.864	135.326	112.528	90.348	-310.239	-310.239	-310.239	16.615
4000	26.893	135.947	113.116	92.925	-309.952	-309.952	-309.952	16.615
4100	26.922	136.563	113.690	95.502	-309.655	-309.655	-309.655	16.615
4200	26.950	137.174	114.252	98.079	-309.348	-309.348	-309.348	16.615
4300	26.977	137.781	114.802	100.656	-309.031	-309.031	-309.031	16.615
4400	26.999	138.381	115.347	103.233	-308.704	-308.704	-308.704	16.615
4500	27.021	138.974	115.886	105.812	-308.367	-308.367	-308.367	16.615
4600	27.043	139.563	116.416	108.390	-308.020	-308.020	-308.020	16.615
4700	27.064	140.149	116.939	110.969	-307.663	-307.663	-307.663	16.615
4800	27.085	140.728	117.457	113.547	-307.296	-307.296	-307.296	16.615
4900	27.105	141.302	117.971	116.126	-306.919	-306.919	-306.919	16.615
5000	27.125	141.871	118.480	118.705	-306.532	-306.532	-306.532	16.615
5100	27.144	142.436	118.984	121.284	-306.135	-306.135	-306.135	16.615
5200	27.163	143.000	119.491	123.864	-305.728	-305.728	-305.728	16.615
5300	27.181	143.563	119.994	126.444	-305.311	-305.311	-305.311	16.615
5400	27.199	144.126	120.497	129.024	-304.884	-304.884	-304.884	16.615
5500	27.217	144.689	121.000	131.603	-304.447	-304.447	-304.447	16.615
5600	27.234	145.252	121.503	134.183	-303.999	-303.999	-303.999	16.615
5700	27.251	145.815	122.006	136.763	-303.542	-303.542	-303.542	16.615
5800	27.268	146.378	122.509	139.343	-303.075	-303.075	-303.075	16.615
5900	27.284	146.941	123.012	141.923	-302.608	-302.608	-302.608	16.615
6000	27.300	147.504	123.515	144.503	-302.131	-302.131	-302.131	16.615

Chlorotrifluorosilane (ClSiF₃) (Ideal Gas)

Mol. Wt. = 120.547
 ΔH_f^0 298.15 = [-315 ± 15] kcal. mole⁻¹
 S^0 298.15 = [73.8 ± 4] cal. deg.⁻¹ mole⁻¹
 Point Group C_{3v}
 Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ν , cm. ⁻¹
[870] (1)
[550] (1)
[275] (1)
[900] (2)
[400] (2)
[200] (2)

Moments of Inertia: $I_A = [19.9 \times 10^{-39}]$ g. cm.²
 $I_B = [33.9 \times 10^{-39}]$ g. cm.²
 $I_C = [33.9 \times 10^{-39}]$ g. cm.²
 $\sigma = 3$

Heat of Formation. ΔH_f^0 298.15 was estimated in Henderson and Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. The molecular constants were estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.



(Ideal Gas) GFW = 130.445

CHLORINE PENTAFLUORIDE (ClF₅)

(IDEAL GAS)

OPW = 130.445

Point Group C_{4v} $\Delta H_f^\circ = [-54.9 \pm 15] \text{ kcal/mol}$
 $S_{298.15}^\circ = 74.241 \text{ gibbs/mol}$
 $\Delta H_f^\circ_{298.15} = [-57 \pm 15] \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
712 (1)	468 (1)	732 (2)
541 (1)	346 (1)	[440](2)
486 (1)	375 (1)	302 (2)

Bond Distance: (Cl-F)_{base} = 1.72 Å

Bond Angle: F-I-F = 90°

Product of Moments of Inertia: $I_{AB}I_C = 2.47289 \times 10^{-113} \text{ g}^3 \text{ cm}^6$

σ = 4

Heat of Formation.

The heat of formation was estimated by assuming that the ratio $[A.B.E.(ClF_3) - A.B.E.(ClF_3)]/[A.B.E.(ClF_3) - A.B.E.(ClF_5)]$ was equal to $[A.B.E.(BrF) - A.B.E.(BrF_3)]/[A.B.E.(BrF_3) - A.B.E.(BrF_5)]$, where A.B.E. represents average bond energy. All values were taken from these tables. A.B.E.(ClF₅) was thus calculated to be 36 kcal/mol which leads to $\Delta H_f^\circ = -57 \pm 15 \text{ kcal/mol}$.

Heat Capacity and Entropy.

O. M. Begun, W. H. Fletcher and D. P. Smith, J. Chem. Phys. 42, 2236 (1965), have reported the infrared spectra of the gas and the Raman spectra of the liquid. Their assignments have been adopted here, including one frequency ν_6 obtained from a valence force-field treatment. The values are consistent with those for IF₅(g) and BrF₅(g). D. P. Smith, Science 141, 1039 (1963), had previously reported three infrared bands. The structure of the molecule has not been determined but the spectra can only be interpreted assuming C_{4v} symmetry; this is in accord with IF₅ and BrF₅(g). Begun et al. assumed a square pyramidal structure with the chlorine in the base of the pyramid. There is some evidence that the chlorine may not lie in the basal plane but this would not appreciably affect the calculations. The structure adopted was that given by Begun et al. The individual moments of inertia are $I_A = I_B = 25.7380 \times 10^{-39} \text{ g cm}^2$ and $I_C = 37.3298 \times 10^{-39} \text{ g cm}^2$.

June 30, 1966

Iron Monochloride (FeCl)

(Ideal Gas) Mol. Wt. = 91.300

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	2.480	59.492	59.492	INFINITE
100	8.232	52.018	1.731	59.977	57.181	-12.046
200	8.821	57.954	0.863	60.054	54.340	-59.377
298	9.136	61.537	0.000	60.000	51.543	-57.761
300	9.141	61.593	0.017	59.998	51.491	-57.509
400	9.478	68.437	1.866	59.954	48.671	-56.591
500	9.631	70.581	3.598	59.725	45.686	-55.056
600	9.616	68.093	6.365	59.511	43.137	-53.712
700	9.520	66.560	9.148	59.235	40.429	-52.622
800	9.315	70.831	14.006	58.876	37.765	-51.816
900	8.921	76.182	20.626	58.451	35.153	-51.153
1000	8.314	72.954	28.911	57.753	32.602	-50.602
1100	9.522	73.861	37.595	56.882	30.134	-50.087
1200	9.532	74.090	47.067	56.221	27.725	-50.049
1300	9.545	75.453	58.145	55.901	25.365	-50.040
1400	9.561	76.811	70.643	55.565	23.059	-50.055
1500	9.572	78.021	84.213	55.216	20.716	-50.118
1600	9.584	77.439	98.708	54.851	18.428	-50.217
1700	9.595	78.021	113.330	54.180	16.168	-50.348
1800	9.605	78.569	128.061	53.694	13.968	-50.503
1900	9.615	79.081	142.891	53.282	11.838	-50.678
2000	9.619	79.562	157.720	49.552	9.873	-50.873
2100	9.623	80.052	172.547	48.414	8.036	-51.086
2200	9.627	80.499	187.375	47.854	6.129	-51.314
2300	9.630	80.927	202.203	47.289	4.283	-51.556
2400	9.632	81.336	217.032	46.720	2.560	-51.811
2500	9.632	81.730	231.862	46.155	0.968	-52.078
2600	9.633	82.108	246.691	45.566	-0.566	-52.356
2700	9.633	82.472	261.521	44.981	-2.047	-52.644
2800	9.632	82.822	276.351	44.391	-3.527	-52.941
2900	9.632	83.160	291.181	43.795	-5.007	-53.248
3000	9.631	83.487	306.011	43.194	-6.487	-53.564
3100	9.631	83.802	320.841	42.588	-7.967	-53.890
3200	9.630	84.108	335.671	41.969	-9.447	-54.226
3300	9.629	84.405	350.501	41.353	-10.927	-54.572
3400	9.628	84.692	365.331	40.737	-12.407	-54.928
3500	9.628	84.971	380.161	40.122	-13.887	-55.294
3600	9.628	85.242	395.000	39.506	-15.367	-55.669
3700	9.628	85.506	409.839	38.881	-16.847	-56.054
3800	9.628	85.763	424.679	38.256	-18.327	-56.449
3900	9.628	86.013	439.519	37.631	-19.807	-56.854
4000	9.629	86.257	454.359	36.996	-21.287	-57.269
4100	9.630	86.495	469.200	36.351	-22.767	-57.694
4200	9.631	86.727	484.041	35.696	-24.247	-58.129
4300	9.632	86.951	498.881	35.041	-25.727	-58.574
4400	9.634	87.175	513.721	34.376	-27.207	-59.029
4500	9.638	87.391	528.561	33.701	-28.687	-59.494
4600	9.638	87.603	543.401	33.026	-30.167	-59.969
4700	9.640	87.810	558.241	32.351	-31.647	-60.454
4800	9.642	88.013	573.081	31.676	-33.127	-60.949
4900	9.645	88.212	587.921	30.996	-34.607	-61.454
5000	9.648	88.407	602.761	30.316	-36.087	-61.969
5100	9.651	88.598	617.601	29.636	-37.567	-62.494
5200	9.654	88.786	632.441	28.956	-39.047	-63.029
5300	9.658	88.969	647.281	28.276	-40.527	-63.574
5400	9.661	89.150	662.121	27.596	-42.007	-64.129
5500	9.665	89.327	676.961	26.916	-43.487	-64.694
5600	9.669	89.501	691.801	26.236	-44.967	-65.269
5700	9.673	89.673	706.641	25.556	-46.447	-65.854
5800	9.678	89.841	721.481	24.876	-47.927	-66.449
5900	9.682	89.999	736.321	24.196	-49.407	-67.054
6000	9.687	90.169	751.161	23.516	-50.887	-67.669

June 30, 1965

CIFe

IRON MONOCHLORIDE (FeCl) (IDEAL GAS) MOL. WT. = 91.300

Ground State Configuration 6Σ
 $S_{298.15}^{\circ} = [61.537] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} 0 = 60 \pm 20 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = 60 \pm 20 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ_i , cm. ⁻¹	$\frac{g_i}{6}$
0	[200]
[200]	[8]
[1000]	[8]
[4000]	[8]

$\omega_e x_e = 1.19 \text{ cm.}^{-1}$
 $\omega_e = 404.92 \text{ cm.}^{-1}$
 $\omega_e = [0.17795] \text{ cm.}^{-1}$
 $r_e = [2.09]$

Heat of Formation.

The dissociation energy (D_0°) of FeCl(g) was reported as $3 \pm 2 \text{ e.v.}$ ($69 \pm 46 \text{ kcal. mole}^{-1}$) by A. G. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., London, 1953. The corresponding $\Delta H_f^{\circ} 298.15$ (FeCl, g) was evaluated to be $56 \pm 46 \text{ kcal. mole}^{-1}$. By comparing $D(\text{Fe-O}) = 101 \text{ kcal. mole}^{-1}$ in FeO(g) with the coordinate bond energies obtained in organic complexes and iron carbonyl halides of $E(\text{Fe-O}) = 59.4$ and $E(\text{Fe-Cl}) = 37.3 \text{ kcal. mole}^{-1}$, reported by M. M. Jones, B. J. Yow and W. R. May, Inorg. Chem. 1, 166 (1962), the $D(\text{Fe-Cl})$ in FeCl(g) was estimated as $101 \times (37.3/59.4) = 63.5 \text{ kcal. mole}^{-1}$, yielding $\Delta H_f^{\circ} 298.15$ (FeCl, g) = $64 \text{ kcal. mole}^{-1}$. The adopted value of $\Delta H_f^{\circ} 298.15$ for FeCl(g) is $60 \pm 20 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The ground state configuration, ω_e and $\omega_e x_e$ (corrected to the average isotopic species) were obtained from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc., New York, 1950. The Fe-Cl bond distance was assumed to be the same as that in FeCl₂(g). Hence the values of B_e and ω_e were calculated. The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe²⁺(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, G. E. Leroy and T. C. James, J. Chem. Phys. 35, 1670 (1961). The total 30 for the quantum weight was obtained from the ground multiplet of Fe²⁺ and was split arbitrarily. The entropy values may be in error by a few entropy units due to the uncertainties in the low lying electronic levels. The principal moment of inertia is $1.5728 \times 10^{-38} \text{ g. cm.}^2$.

CIFe

Hydrogen Chloride (HCl)

(Ideal Gas) Mol. Wt. = 36.465

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	+0.00	+0.00	INFINITE	- 2.065	- 22.019	- 22.019	INFINITE
100	6.959	50.835	50.835	- 22.019	- 22.019	- 22.019	48.709
200	6.961	41.865	41.865	- 22.019	- 22.019	- 22.019	10.696
298	6.964	41.865	41.865	- 22.019	- 22.019	- 22.019	10.696
300	6.964	41.865	41.865	- 22.019	- 22.019	- 22.019	10.696
400	6.973	46.688	46.688	- 22.064	- 22.782	- 22.782	16.596
500	7.004	46.688	46.688	- 22.129	- 23.012	- 23.012	10.151
600	7.069	46.688	46.688	- 22.288	- 23.420	- 23.420	8.530
700	7.167	50.630	50.630	- 22.423	- 23.602	- 23.602	7.368
800	7.289	51.595	51.595	- 22.505	- 23.774	- 23.774	6.494
900	7.423	52.461	52.461	- 22.505	- 23.936	- 23.936	5.812
1000	7.559	53.250	53.250	- 22.505	- 24.093	- 24.093	5.265
1100	7.693	53.977	53.977	- 22.505	- 24.241	- 24.241	4.816
1200	7.819	54.652	54.652	- 22.505	- 24.390	- 24.390	4.442
1300	7.936	55.283	55.283	- 22.505	- 24.534	- 24.534	4.124
1400	8.043	55.875	55.875	- 22.505	- 24.675	- 24.675	3.852
1500	8.141	56.433	56.433	- 22.505	- 24.813	- 24.813	3.615
1600	8.229	56.961	56.961	- 22.505	- 24.950	- 24.950	3.408
1700	8.310	57.463	57.463	- 22.505	- 25.086	- 25.086	3.225
1800	8.382	57.940	57.940	- 22.505	- 25.221	- 25.221	3.062
1900	8.449	58.395	58.395	- 22.505	- 25.353	- 25.353	2.916
2000	8.509	58.830	58.830	- 22.505	- 25.486	- 25.486	2.785
2100	8.564	59.246	59.246	- 22.505	- 25.618	- 25.618	2.666
2200	8.614	59.646	59.646	- 22.505	- 25.750	- 25.750	2.558
2300	8.660	60.030	60.030	- 22.505	- 25.880	- 25.880	2.459
2400	8.703	60.399	60.399	- 22.505	- 26.007	- 26.007	2.368
2500	8.742	60.755	60.755	- 22.505	- 26.137	- 26.137	2.285
2600	8.778	61.099	61.099	- 22.505	- 26.266	- 26.266	2.208
2700	8.812	61.431	61.431	- 22.505	- 26.394	- 26.394	2.136
2800	8.844	61.752	61.752	- 22.505	- 26.521	- 26.521	2.068
2900	8.874	62.063	62.063	- 22.505	- 26.647	- 26.647	1.998
3000	8.902	62.364	62.364	- 22.505	- 26.773	- 26.773	1.930
3100	8.928	62.656	62.656	- 22.505	- 26.897	- 26.897	1.865
3200	8.953	62.940	62.940	- 22.505	- 27.021	- 27.021	1.804
3300	8.976	63.216	63.216	- 22.505	- 27.144	- 27.144	1.748
3400	8.999	63.484	63.484	- 22.505	- 27.266	- 27.266	1.695
3500	9.020	63.745	63.745	- 22.505	- 27.387	- 27.387	1.644
3600	9.041	64.000	64.000	- 22.505	- 27.509	- 27.509	1.592
3700	9.061	64.248	64.248	- 22.505	- 27.629	- 27.629	1.540
3800	9.079	64.490	64.490	- 22.505	- 27.749	- 27.749	1.488
3900	9.096	64.726	64.726	- 22.505	- 27.866	- 27.866	1.440
4000	9.115	64.956	64.956	- 22.505	- 27.981	- 27.981	1.392
4100	9.132	65.182	65.182	- 22.505	- 28.101	- 28.101	1.348
4200	9.148	65.402	65.402	- 22.505	- 28.216	- 28.216	1.304
4300	9.164	65.617	65.617	- 22.505	- 28.329	- 28.329	1.260
4400	9.179	65.828	65.828	- 22.505	- 28.441	- 28.441	1.216
4500	9.195	66.035	66.035	- 22.505	- 28.551	- 28.551	1.172
4600	9.210	66.237	66.237	- 22.505	- 28.667	- 28.667	1.128
4700	9.224	66.435	66.435	- 22.505	- 28.775	- 28.775	1.084
4800	9.238	66.629	66.629	- 22.505	- 28.885	- 28.885	1.040
4900	9.252	66.820	66.820	- 22.505	- 28.993	- 28.993	0.996
5000	9.265	67.007	67.007	- 22.505	- 29.102	- 29.102	0.952
5100	9.278	67.191	67.191	- 22.505	- 29.208	- 29.208	0.908
5200	9.291	67.371	67.371	- 22.505	- 29.313	- 29.313	0.864
5300	9.304	67.548	67.548	- 22.505	- 29.416	- 29.416	0.820
5400	9.316	67.722	67.722	- 22.505	- 29.521	- 29.521	0.776
5500	9.329	67.894	67.894	- 22.505	- 29.622	- 29.622	0.732
5600	9.341	68.061	68.061	- 22.505	- 29.724	- 29.724	0.688
5700	9.353	68.227	68.227	- 22.505	- 29.828	- 29.828	0.644
5800	9.365	68.390	68.390	- 22.505	- 29.928	- 29.928	0.600
5900	9.376	68.550	68.550	- 22.505	- 30.027	- 30.027	0.556
6000	9.388	68.707	68.707	- 22.505	- 30.121	- 30.121	0.512

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1964

HYDROGEN CHLORIDE (HCl)

(IDEAL GAS)

Ground State Configuration $1\sigma +$ $\Delta F_f^0 = -22.019 \pm 0.05 \text{ kcal. mole}^{-1}$ $\Delta F_f^0 = -22.019 \pm 0.05 \text{ kcal. mole}^{-1}$ $\Delta F_f^0 = -22.019 \pm 0.05 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weights

ϵ_1 , cm. ⁻¹	ϵ_1	ϵ_1
0	1	1
$W_f X_e = 52.06 \text{ cm.}^{-1}$	$W_f X_e = 52.06 \text{ cm.}^{-1}$	$W_f X_e = 52.06 \text{ cm.}^{-1}$
$B_e = 10.5884 \text{ cm.}^{-1}$	$B_e = 10.5884 \text{ cm.}^{-1}$	$B_e = 10.5884 \text{ cm.}^{-1}$

Heat of Formation

The selected value, Rossini's flow calorimetric measurement (1) of the direct combination of the elements, is essentially the same as that in the revised version (2) of NBS Circular 500. JANAP analyses of the more recent measurements are summarized below, while the earlier measurements have been reviewed by Rossini (1).

Experimenters	Date	Method	References
Johnson, Ambrose	1963	Comparison of HCl, H ₂ SO ₄ and SO ₂ by solution calorimetry	2, 3, 4, 5, 6, 7, 8, 9, 10
Lecher, et al.	1949-52	Catalytic combination in flow calorimeter	11, 12
Roth, Richter	1934	Direct combination in bomb calorimeter	13
von Wartenberg, Hanisch	1932	Direct combination in flow calorimeter	14
Rossini	1932	Direct combination in flow calorimeter	1
- - -	1922-63	ΔF_f^0 from e.m.f. and ΔF_f^0 from statistical mechanics	15, 16, 17, 18, 19, 20
Lewis	1906	Equilibria for reaction $\text{HCl(g)} + \frac{1}{2} \text{O}_2(\text{g}) = \frac{1}{2} \text{H}_2\text{O(g)} + \frac{1}{2} \text{Cl}_2(\text{g})$	21

The direct combination values of Roth-Richter (13) and von Wartenberg - Hanisch (14) are 0.7% less negative than that of Rossini; however, all of the other methods favor the more negative value. The Roth - Richter value may be affected by errors in the measurement of the extent of reaction by HCl titration (9,22), since a set of experiments based on determination of the amount of H₂ gave a value of -22.02 kcal. mole⁻¹.

Rossini's value is confirmed by a variety of independent methods. The solution calorimetry (3), though it is related through a complex reaction scheme, is based on species which are now quite well known. E.m.f. measurements (15,16,17,18, 19,20) give $\Delta F_f^0 298.15 = -22.735$; assuming an uncertainty of 1.0 mv. in E° , this leads to $\Delta F_f^0 298.15 = -22.02 \pm 0.03$ when combined with the statistical entropies. The equilibria of Lewis (625-692°K) give $\Delta F_f^0 298.15 = -22.20 \pm 0.44$ (second law) and -22.30 ± 0.04 (third law).

1. P. D. Rossini, J. Res. N.B.S. 9, 679 (1932).
2. D. H. Wagman, private communication, National Bureau of Standards, June 26, 1964.
3. W. H. Johnson, J. R. Ambrose, J. Res. N.B.S. 67A, 427 (1963).
4. J. R. Eickman, P. D. Rossini, *ibid.*, 3, 537 (1953).
5. W. H. Johnson, S. Sumner, *Acta Chem. Scand.*, 17, 1917 (1963).
6. W. H. Johnson, S. Sumner, *ibid.*, 17, 1917 (1963).
7. C. E. Vanderzee, J. A. Swanson, J. Phys. Chem., 67, 2808 (1963).
8. C. E. Vanderzee, J. D. Nutter, *ibid.*, 2521 (1963).
9. C. S. R. Gunn, L. G. Green, J. Chem. Eng. Data 8, 180 (1963).
10. J. R. Lacher, J. J. McKiney, C. M. Snow, L. Michel, G. Nelson, J. D. Park, J. Am. Chem. Soc. 71, 1331 (1949).
11. A. Roth, H. Richter, *Phys. Z.*, 33, 354 (1932).
12. A. Roth, H. Richter, *Phys. Z.*, 33, 354 (1932).
13. H. V. Wartenberg, K. Hanisch, *ibid.*, 161, 173 (1935); 164, 144 (1935).
14. H. V. Wartenberg, K. Hanisch, *ibid.*, 161, 173 (1935); 164, 144 (1935).
15. R. G. Bates, V. E. Bower, J. Res. N.B.S. 53A, 283 (1954).
16. H. S. Harned, T. R. Paxton, J. Phys. Chem. 57, 531 (1953).
17. J. G. Aston, F. L. Oittier, J. Am. Chem. Soc. 77, 3173 (1955).
18. N. Kneke, H. V. Wartenberg, *ibid.*, 77, 3173 (1955).
19. N. Kneke, H. V. Wartenberg, *ibid.*, 77, 3173 (1955).
20. S. R. Gupta, G. J. Hille, D. J. G. Ives, *Trans. Faraday Soc.* 59, 1874 (1963).
21. O. N. Lewis, J. Am. Chem. Soc. 28, 1380 (1906).
22. W. A. Roth, Z. Elektrochem. 50, 107 (1944).

Heat Capacity and Entropy

Spectroscopic constants for HCl³⁵ and HCl³⁷ were selected from the work of E. K. Flyler, E. D. Tidwell, Z. Elektrochem. 64, 717 (1960) and C. Haeuveler, P. Barchewitz, Compt. rend. 246, 3040 (1958). The values were adjusted to 75.5% HCl³⁵.

C1H

Hypochlorous Acid (HClO)

(Ideal Gas) Mol. Wt. = 52.465

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	7.954	0.000	INFINITE	INFINITE	2.440	21.294	21.294	INFINITE	
100	7.954	47.566	47.566	47.566	1.445	21.294	21.294	21.294	
200	8.258	57.237	57.237	57.237	1.445	21.294	21.294	21.294	
298	8.584	58.136	58.136	58.136	1.445	21.294	21.294	21.294	
300	8.697	58.601	58.601	58.601	1.445	21.294	21.294	21.294	
400	9.553	59.253	59.253	59.253	1.445	21.294	21.294	21.294	
500	10.090	61.445	61.445	61.445	1.445	21.294	21.294	21.294	
600	10.509	63.323	63.323	63.323	1.445	21.294	21.294	21.294	
700	10.844	64.949	64.949	64.949	1.445	21.294	21.294	21.294	
800	11.125	66.436	66.436	66.436	1.445	21.294	21.294	21.294	
900	11.370	67.781	67.781	67.781	1.445	21.294	21.294	21.294	
1000	11.589	68.970	68.970	68.970	1.445	21.294	21.294	21.294	
1100	11.787	70.084	70.084	70.084	1.445	21.294	21.294	21.294	
1200	11.967	71.118	71.118	71.118	1.445	21.294	21.294	21.294	
1300	12.131	72.082	72.082	72.082	1.445	21.294	21.294	21.294	
1400	12.279	72.987	72.987	72.987	1.445	21.294	21.294	21.294	
1500	12.413	73.839	73.839	73.839	1.445	21.294	21.294	21.294	
1600	12.534	74.644	74.644	74.644	1.445	21.294	21.294	21.294	
1700	12.643	75.407	75.407	75.407	1.445	21.294	21.294	21.294	
1800	12.742	76.132	76.132	76.132	1.445	21.294	21.294	21.294	
1900	12.831	76.824	76.824	76.824	1.445	21.294	21.294	21.294	
2000	12.911	77.484	77.484	77.484	1.445	21.294	21.294	21.294	
2100	12.983	78.116	78.116	78.116	1.445	21.294	21.294	21.294	
2200	13.048	78.721	78.721	78.721	1.445	21.294	21.294	21.294	
2300	13.108	79.303	79.303	79.303	1.445	21.294	21.294	21.294	
2400	13.162	79.862	79.862	79.862	1.445	21.294	21.294	21.294	
2500	13.211	80.400	80.400	80.400	1.445	21.294	21.294	21.294	
2600	13.256	80.919	80.919	80.919	1.445	21.294	21.294	21.294	
2700	13.296	81.420	81.420	81.420	1.445	21.294	21.294	21.294	
2800	13.334	81.904	81.904	81.904	1.445	21.294	21.294	21.294	
2900	13.368	82.373	82.373	82.373	1.445	21.294	21.294	21.294	
3000	13.399	82.826	82.826	82.826	1.445	21.294	21.294	21.294	
3100	13.428	83.264	83.264	83.264	1.445	21.294	21.294	21.294	
3200	13.456	83.693	83.693	83.693	1.445	21.294	21.294	21.294	
3300	13.479	84.107	84.107	84.107	1.445	21.294	21.294	21.294	
3400	13.502	84.510	84.510	84.510	1.445	21.294	21.294	21.294	
3500	13.523	84.902	84.902	84.902	1.445	21.294	21.294	21.294	
3600	13.542	85.283	85.283	85.283	1.445	21.294	21.294	21.294	
3700	13.559	85.654	85.654	85.654	1.445	21.294	21.294	21.294	
3800	13.577	86.016	86.016	86.016	1.445	21.294	21.294	21.294	
3900	13.593	86.369	86.369	86.369	1.445	21.294	21.294	21.294	
4000	13.607	86.713	86.713	86.713	1.445	21.294	21.294	21.294	
4100	13.621	87.050	87.050	87.050	1.445	21.294	21.294	21.294	
4200	13.634	87.378	87.378	87.378	1.445	21.294	21.294	21.294	
4300	13.646	87.699	87.699	87.699	1.445	21.294	21.294	21.294	
4400	13.657	88.013	88.013	88.013	1.445	21.294	21.294	21.294	
4500	13.667	88.320	88.320	88.320	1.445	21.294	21.294	21.294	
4600	13.677	88.620	88.620	88.620	1.445	21.294	21.294	21.294	
4700	13.687	88.914	88.914	88.914	1.445	21.294	21.294	21.294	
4800	13.695	89.203	89.203	89.203	1.445	21.294	21.294	21.294	
4900	13.704	89.485	89.485	89.485	1.445	21.294	21.294	21.294	
5000	13.711	89.762	89.762	89.762	1.445	21.294	21.294	21.294	
5100	13.719	90.034	90.034	90.034	1.445	21.294	21.294	21.294	
5200	13.726	90.300	90.300	90.300	1.445	21.294	21.294	21.294	
5300	13.732	90.562	90.562	90.562	1.445	21.294	21.294	21.294	
5400	13.739	90.818	90.818	90.818	1.445	21.294	21.294	21.294	
5500	13.745	91.071	91.071	91.071	1.445	21.294	21.294	21.294	
5600	13.750	91.318	91.318	91.318	1.445	21.294	21.294	21.294	
5700	13.754	91.560	91.560	91.560	1.445	21.294	21.294	21.294	
5800	13.758	91.800	91.800	91.800	1.445	21.294	21.294	21.294	
5900	13.762	92.036	92.036	92.036	1.445	21.294	21.294	21.294	
6000	13.770	92.268	92.268	92.268	1.445	21.294	21.294	21.294	

C1H0

MOL. WT. = 52.465

(IDEAL GAS)

HYPOCHLOROUS ACID (HClO)

$\Delta H_f^0 = [-22] \pm 3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = [-22] \pm 3 \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 56.546 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Point Group C_s

Vibrational Levels and Multiplicities

(μ , cm.⁻¹)

759 (1)
 1242 (1)
 3626 (1)

O-H distance = $0.98 \pm 0.01 \text{ \AA}$ O-Cl distance = $1.72 \pm 0.04 \text{ \AA}$ H-O-Cl angle = $104^\circ \pm 3^\circ$ $\sigma = 1$

Product of moments of inertia = $4.54 \times 10^{-117} \text{ g. cm.}^2$

Heat of Formation

I. E. Fils, K. P. Mikhchenko, and N. V. Pakhomova, Zhur. Neorg. Khim. 3, 1772, 1761 (1958), report the following heats of reaction:

$\text{ClO}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{HCl}(\text{aq})$

$\Delta H_f^0 298.15 = -5.64 \pm 0.03 \text{ kcal.}$

$\Delta H_f^0 298.15 = -56.93 \pm 0.05 \text{ kcal.}$

If the following auxiliary heats of formation are used:

$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

$\Delta H_f^0 298.15 = -40.02 \text{ kcal. mole}^{-1}$ (National Bureau of Standards Circ. 500, 1952)

$\Delta H_f^0 298.15 = -66.32 \text{ kcal. mole}^{-1}$ (National Bureau of Standards Circ. 500, 1952)

$\Delta H_f^0 298.15 = -45.70 \pm 0.02 \text{ kcal. mole}^{-1}$ (P. A. Giguère, B. G. Morissette, A. W. Olmos, and O. Knop, Can. J. Chem. 33, 804 (1955), consistent with $\Delta H_f^0 298.15$ of $\text{H}_2\text{O}_2(\text{g})$ in this compilation)

$\Delta H_f^0 298.15$ for $\text{HCl}(\text{aq})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is found to be $-31.35 \text{ kcal. mole}^{-1}$. From the heats of solution in water of other weak acids, $\Delta H_{\text{solution}}$ for HClO is estimated to be $-8 \pm 3 \text{ kcal. mole}^{-1}$. These heats yield $-23 \pm 3 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$. By averaging the heats of formation of $\text{H}_2\text{O}(\text{g})$ and $\text{Cl}_2\text{O}(\text{g})$, $\Delta H_f^0 298.15$ of $\text{HClO}(\text{g})$ is estimated to be $-20 \pm 5 \text{ kcal. mole}^{-1}$. The value $-23 \pm 3 \text{ kcal. mole}^{-1}$ is adopted here.

$\Delta H_f^0 298.15$ of $\$

INTERIM TABLE

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
100	8.020	49.000	INFINITE	- 2.733	- 45.884	- 45.884	INFINITE	
200	9.438	55.559	40.918	- 1.072	- 44.263	- 44.263	40.369	
298	12.199	59.865	59.865	- 1.000	- 46.000	- 46.000	31.249	
300	12.245	59.860	59.865	1.023	- 46.013	- 46.000	31.032	
400	14.205	64.703	64.703	1.023	- 46.037	- 46.000	22.235	
500	14.296	64.233	61.425	2.904	- 49.121	- 38.654	16.695	
600	17.691	70.328	62.655	4.604	- 49.479	- 36.525	13.304	
700	19.860	73.147	63.931	6.434	- 49.731	- 34.364	10.722	
800	20.871	75.734	65.268	8.373	- 49.895	- 32.005	9.778	
900	21.584	77.184	66.582	10.423	- 49.982	- 30.582	9.042	
1000	21.984	78.341	67.833	12.508	- 50.037	- 29.673	8.406	
1100	21.957	82.407	69.066	14.676	- 50.039	- 25.436	5.033	
1200	22.437	84.339	70.259	16.896	- 50.008	- 23.200	4.225	
1300	22.939	86.181	71.412	19.160	- 49.953	- 20.768	3.525	
1400	23.468	87.936	72.536	21.471	- 49.874	- 18.741	2.946	
1500	23.668	89.466	73.603	23.795	- 49.800	- 16.519	2.407	
1600	23.714	90.988	74.642	26.154	- 49.713	- 14.304	1.944	
1700	23.726	92.433	75.647	28.536	- 49.615	- 11.984	1.541	
1800	23.710	93.805	76.616	30.939	- 49.508	- 9.065	1.101	
1900	23.666	95.112	77.553	33.364	- 49.393	- 6.142	0.634	
2000	23.606	96.362	78.466	35.791	- 49.268	- 3.242	0.154	
2100	24.527	97.555	79.347	38.238	- 49.136	- 0.343	- 0.36	
2200	24.634	98.699	80.201	40.696	- 48.990	2.550	- 2.23	
2300	24.729	99.799	81.029	43.164	- 48.830	5.320	- 4.79	
2400	24.818	100.856	81.820	45.640	- 48.656	8.134	- 7.16	
2500	24.888	101.865	82.614	48.126	- 48.469	11.194	- 9.78	
2600	24.955	102.842	83.374	50.619	- 48.265	14.065	- 1.192	
2700	25.016	103.785	84.112	53.117	- 48.033	16.930	- 1.370	
2800	25.070	104.696	84.831	55.622	- 47.784	19.789	- 1.545	
2900	25.118	105.578	85.531	58.134	- 47.518	22.642	- 1.717	
3000	25.165	106.429	86.214	60.645	- 47.236	25.500	- 1.936	
3100	25.205	107.255	86.879	63.164	- 46.930	28.349	- 1.999	
3200	25.242	108.056	87.529	65.686	- 46.606	31.198	- 2.131	
3300	25.277	108.833	88.162	68.212	- 46.264	34.043	- 2.234	
3400	25.309	109.586	88.781	70.743	- 45.904	36.881	- 2.311	
3500	25.336	110.322	89.387	73.274	- 45.528	39.716	- 2.400	
3600	25.363	111.036	89.978	75.809	- 45.139	42.549	- 2.612	
3700	25.387	111.731	90.557	78.346	- 44.736	45.380	- 2.865	
3800	25.410	112.409	91.123	80.886	- 44.319	48.208	- 3.105	
3900	25.431	113.069	91.679	83.429	- 43.889	51.026	- 3.322	
4000	25.450	113.713	92.220	85.972	- 43.446	53.836	- 3.546	
4100	25.468	114.342	92.752	88.510	- 42.990	56.636	- 3.793	
4200	25.485	114.956	93.273	91.046	- 42.522	59.426	- 4.060	
4300	25.501	115.556	93.785	93.615	- 42.042	62.206	- 4.344	
4400	25.516	116.141	94.281	96.178	- 41.549	64.976	- 4.642	
4500	25.529	116.716	94.778	98.718	- 41.044	67.736	- 4.946	
4600	25.542	117.277	95.261	101.272	- 40.527	70.486	- 5.224	
4700	25.554	117.826	95.735	103.827	- 39.998	73.226	- 5.481	
4800	25.566	118.364	96.201	106.383	- 39.456	75.956	- 5.705	
4900	25.576	118.892	96.659	108.939	- 38.901	78.676	- 5.906	
5000	25.586	119.408	97.109	111.496	- 38.332	81.386	- 6.085	
5100	25.596	119.915	97.551	114.057	- 37.749	84.086	- 6.245	
5200	25.605	120.412	97.986	116.617	- 37.152	86.776	- 6.385	
5300	25.613	120.900	98.414	119.178	- 36.542	89.456	- 6.503	
5400	25.620	121.379	98.831	121.739	- 35.919	92.126	- 6.606	
5500	25.626	121.849	99.249	124.302	- 35.284	94.786	- 6.692	
5600	25.636	122.311	99.656	126.866	- 34.636	97.436	- 6.765	
5700	25.643	122.764	100.056	129.429	- 33.976	100.076	- 6.825	
5800	25.649	123.213	100.453	131.994	- 33.304	102.706	- 6.875	
5900	25.654	123.653	100.843	134.554	- 32.622	105.326	- 6.915	
6000	25.661	124.081	101.223	137.125	- 31.930	107.936	- 6.937	

December 31, 1960.

Chlorosilane (H₃SiCl)

(Ideal Gas)

Mol. Wt. = 66.571

ΔH_f^o 298.15 = [-40 ± 15] kcal. mole⁻¹

S_{298.15} = 59.9 ± 2 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

$\omega_{cm.}^{-1}$

2201 (1)

949 (1)

551 (1)

2195 (2)

954.4(2)

664 (2)

Moments of Inertia: I_A = .9784 X 10⁻³⁹ g. cm.² I_B = 12.6749 X 10⁻³⁹ g. cm.² I_C = 12.6749 X 10⁻³⁹ g. cm.² ζ = 3

Heat of Formation. ΔH_f^o 298.15 was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data," January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were found in C. B. Henderson and R. S. Scheffee, Atlantic Res. Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960. Moments of inertia were calculated using the constants found in C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

CH₃Si

Ammonium Chloride (NH₄Cl)

(Crystal) Mol. wt. = 53.49158

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	-5.423	-74.424	-	INFINITE
100	9.400	5.400	59.116	-3.328	-74.538	-66.082	144.416
200	16.040	14.281	24.653	-2.074	-75.202	-57.336	62.651
298	20.650	22.672	22.672	-0.000	-75.180	-48.563	35.566
300	20.780	22.800	22.672	0.038	-75.182	-48.598	35.268
400	24.610	29.512	23.432	5.407	-73.940	-30.279	21.699
500	21.630	30.647	23.432	5.407	-73.940	-30.704	13.420
600	24.300	40.826	27.653	7.904	-73.834	-22.062	8.036
700	26.960	44.772	29.619	10.467	-73.478	-13.457	4.201
800	29.610	48.545	31.926	13.266	-72.876	-4.923	1.345
900	32.260	52.189	33.976	16.382	-72.078	1.161	0.000
1000	34.950	55.710	35.974	19.735	-70.995	11.861	2.592
1100	36.500	59.096	37.923	23.290	-69.694	20.084	3.990
1200	38.200	62.351	39.824	27.033	-68.270	28.186	5.133
1300	39.000	65.433	41.677	30.984	-66.764	36.162	6.079
1400	40.870	68.397	43.480	34.983	-65.135	44.081	6.841
1500	42.000	71.259	45.237	39.035	-63.385	51.757	7.341

AMMONIUM CHLORIDE (NH₄Cl)

(CRYSTAL)

MOL. WT. = 53.49158



$S_{298.15}^0 = 22.7 \pm 1.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_2 = 242.6^\circ \text{K.}$
 $T_1 = 457.7^\circ \text{K.}$
 $T_m = 795.2^\circ \text{K.}$
 $T_d = 612^\circ \text{K.}$

Heat of Formation.

The equilibrium pressures for the reaction $\text{NH}_4\text{Cl}(c) = \text{NH}_3(g) + \text{HCl}(g)$, at $320\text{--}625^\circ \text{K.}$, have been measured by many investigators. A. Smith and W. de Lange, *J. Chem. Soc.*, 2944 (1928), using the densi-tensimeter, determined the vapor pressure of $\text{NH}_4\text{Cl}(c)$ and the density of the saturated vapor simultaneously. The results obtained indicate that within the pressure $597\text{--}626^\circ \text{K.}$ the saturated vapor completely dissociates into gaseous NH_3 and HCl . Based on this conclusion, the reported vapor pressure data were employed to evaluate the heat of dissociation of $\text{NH}_4\text{Cl}(c)$ by both the second and third law methods. The results are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	Drift, e.u.
Smith and Calvert (1)	521.6-619.1	43.18 ± 0.08	42.11	-2.0 ± 0.2
Smith and Lange (2)	527.9-625.6	42.15 ± 0.22	42.14	-0.2 ± 0.4
Braune and Knoke (3)	525.4-615.0	42.05 ± 0.08	42.05	-0.5 ± 0.2
Rodebush and Michalek (4)	471.3-557.0	42.43 ± 0.38	42.08	-0.3 ± 0.2
Wagner and Neumann (5)	535.0-632.4	42.83 ± 0.38	42.17	-4.9 ± 1.1
Markowitz and Boryta (6)	503.4-611.4	41.27 ± 0.39	42.12	1.3 ± 0.8

- (1) A. Smith and R. P. Calvert, *J. Am. Chem. Soc.*, 35, 1363 (1914), using isoteniscopes.
- (2) A. Smith and W. D. Lange, *J. Chem. Soc.*, 2944 (1928), using densi-tensimeter.
- (3) H. Braune and S. Knoke, *Z. phys. Chem.*, 135, 748 (1929), gases diaphragm manometer.
- (4) W. H. Rodebush and J. C. Michalek, *J. Am. Chem. Soc.*, 51, 1961 (1929), torsion-effusion method.
- (5) H. Wagner and K. Neumann, *Z. phys. Chem.*, 28, 51 (1961), torsion-effusion method.
- (6) M. M. Markowitz and D. A. Boryta, *J. Phys. Chem.*, 66, 1477 (1962), differential thermal analysis.

The value of ΔH_f^0 298.15 adopted is $42.15 \pm 0.10 \text{ kcal. mole}^{-1}$, yielding ΔH_f^0 298.15 ($\text{NH}_4\text{Cl}, c$) = $-75.8 \pm 0.20 \text{ kcal. mole}^{-1}$. The corresponding ΔH_f^0 298.15 value evaluated from solution data, selected by V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NSRDS-NBS2, National Bureau of Standards, is $42.06 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The heat capacities ($20.1\text{--}523.2^\circ \text{K.}$) of $\text{NH}_4\text{Cl}(c)$ have been measured by the following investigators: (1) R. Ewell, *Ann. Physik*, 45, 1213 (1914), $138\text{--}301^\circ \text{K.}$; (2) P. Simon, *ibid.*, 69, 241 (1922), $20.1\text{--}290.8^\circ \text{K.}$; (3) R. Klinkhardt, *ibid.*, 84, 167 (1927), $323.2\text{--}523.2^\circ \text{K.}$; (4) P. Simon, C. v. Simon and M. Neumann, *Z. phys. Chem.*, 129, 339 (1927), $204.5\text{--}275.8^\circ \text{K.}$; (5) W. T. Ziegler and C. E. Messer, *J. Am. Chem. Soc.*, 63, 2694 (1941), $107.2\text{--}320.2^\circ \text{K.}$; (6) R. Extermann and J. Weigle, *Helv. Phys. Acta*, 15, 455 (1942), $228.2\text{--}248.2^\circ \text{K.}$; and (7) M. M. Popov and G. L. Galchenko, *J. Gen. Chem.*, USSR, 21, 2489 (1951), $373.2\text{--}523.2^\circ \text{K.}$. These C_p data were plotted and a smooth C_p curve was drawn and adopted. The C_p values above 523°K. were obtained by graphical extrapolation of the previous C_p curve. $S_{298.15}^0$ was derived from the adopted low temperature data, based on $S_{20.1}^0 = 0.114 \text{ e.u.}$

Transition Data.

There are two transitions reported in the literature. The low temperature transition data (T_2 and ΔH_f^0) were derived based on the heat capacity ($107\text{--}320^\circ \text{K.}$) data reported by W. T. Ziegler and C. E. Messer, *loc. cit.*, in which the other T_2 values given by previous investigators were reviewed. The high temperature transition data (T_1 and ΔH_f^0) were taken from R. Klinkhardt, *loc. cit.*. However, ΔH_f^0 = 1030 and ΔH_f^0 463.5 = $1059.1 \pm 8.0 \text{ cal. mole}^{-1}$ were reported by E. C. Scheffer, *Proc. Acad. Sci. Amsterdam*, 24, 1513 (1915/16), and M. M. Popov and G. L. Galchenko, *loc. cit.*, respectively. M. M. Markowitz and D. A. Boryta, *loc. cit.* determined T_1 to be $459.5 \pm 0.5^\circ \text{K.}$

Melting Temperature.

T_m was obtained from H. Rassow, *Z. anorg. Chem.*, 114, 117 (1920), determined under pressure.

Decomposition Temperature.

The value of T_d was calculated as the temperature at which the vapor pressure of the decomposition products (NH_3 and HCl) equals 1 atm. By differential thermal analysis, T_d for $\text{NH}_4\text{Cl}(c)$ was determined to be 611.4°K. by M. M. Markowitz and D. A. Boryta, *loc. cit.*



T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
100	19.000	17.422	67.672	- 66.301	- 66.301	INFINITE
200	25.030	32.844	46.054	- 70.036	- 37.389	21.673
298	30.610	44.020	44.020	- 70.690	- 21.217	15.552
300	30.700	44.210	44.021	- 70.699	- 20.911	15.233
400	40.500	57.154	47.823	- 70.699	- 20.911	15.233
500	46.380	67.154	71.164	- 70.803	- 12.201	5.229

600	47.220	74.739	51.542	- 67.750	28.592	- 10.414
700	52.060	82.381	55.407	- 66.549	44.561	- 13.912
800	56.900	89.649	59.236	- 64.923	60.324	- 16.479
900	61.740	96.640	63.026	- 62.866	75.866	- 18.600
1000	66.580	103.388	66.708	- 60.376	91.118	- 19.920
1100	71.599	109.972	70.343	43.592	106.161	- 21.091
1200	76.000	116.395	73.914	50.977	120.889	- 22.016
1300	80.984	122.632	77.423	58.772	135.318	- 22.748
1400	85.500	128.688	80.868	66.978	149.489	- 23.329
1500	89.500	134.477	84.250	75.341	163.484	- 23.789

S_{298.15} = 44.02 ± 0.04 cal. deg.⁻¹ mole⁻¹
ΔH_f° = 2.3 ± 0.2 kcal. mole⁻¹

ΔH_f° 298.15 = -70.69 ± 0.30 kcal. mole⁻¹
T_f = 513.15°K
T_d = [513]°K.

Heat of Formation.

A. A. Gilliland and W. H. Johnson, J. Research Natl. Bur. Standards 65A, 67 (1961), and M. M. Birky and L. O. Hepler, J. Phys. Chem. 64, 686 (1960), have derived the heat of formation for NH₄ClO₄(c) from solution-calorimetric measurements. Their values are -70.74 ± 0.32 and -70.63 kcal. mole⁻¹, respectively. The mean of these is adopted here.

Heat Capacity and Entropy.

B. H. Justice and E. F. Westrum, private communication, April 1961, have measured the heat capacity from 5° to 350°K. The C_p values above 350°K were extrapolated. From the partial molar entropies of NH₄⁺(aq) and ClO₄⁻(aq) and the entropy of solution, Birky and Hepler, loc. cit., calculated a value of 43.6 cal. deg.⁻¹ mole⁻¹ for S_{298.15}. The fair agreement of this value with that derived from C_p suggests that there is no residual entropy at 0°K, as there would be if the NH₄⁺ ion had a random orientation.

Transition and Decomposition Data.

T_f and ΔH_f° were obtained (under a pressure of NH₃) by M. M. Markowitz, Foote Mineral Company, Exton, Pennsylvania (private communication, September 20, 1962). T_d was estimated from the report by M. M. Markowitz, loc. cit.

Mercury Monochloride (HgCl)

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 236.067

MERCURY MONOCHLORIDE (HgCl)

(IDEAL GAS)

MOL. WT. = 236.067

ClHg

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔG° _f	Log K _p
0	7.000	8.000	INFINITE	2.353	19.727	INFINITE	
100	6.523	6.523	2.164	1.644	19.727	17.211	-16.269
200	6.046	6.046	1.961	1.441	19.727	15.695	-14.753
298	6.073	6.073	1.900	1.384	19.727	15.595	-14.655
300	6.079	6.079	1.899	1.383	19.727	15.583	-14.651
400	6.049	6.049	1.848	1.332	19.727	15.483	-14.551
500	6.028	6.028	1.784	1.268	19.727	15.383	-14.451
600	6.011	6.011	1.708	1.192	19.727	15.283	-14.351
700	6.001	6.001	1.622	1.106	19.727	15.183	-14.251
800	6.000	6.000	1.528	1.012	19.727	15.083	-14.151
900	6.003	6.003	1.428	0.912	19.727	14.983	-14.051
1000	6.010	6.010	1.323	0.807	19.727	14.883	-13.951
1100	6.023	6.023	1.214	0.698	19.727	14.783	-13.851
1200	6.041	6.041	1.101	0.585	19.727	14.683	-13.751
1300	6.064	6.064	0.975	0.468	19.727	14.583	-13.651
1400	6.091	6.091	0.838	0.348	19.727	14.483	-13.551
1500	6.122	6.122	0.692	0.225	19.727	14.383	-13.451
1600	6.157	6.157	0.538	0.100	19.727	14.283	-13.351
1700	6.204	6.204	0.378	-0.025	19.727	14.183	-13.251
1800	6.261	6.261	0.215	-0.148	19.727	14.083	-13.151
1900	6.328	6.328	0.051	-0.272	19.727	13.983	-13.051
2000	6.404	6.404	-0.114	-0.396	19.727	13.883	-12.951
2100	6.489	6.489	-0.281	-0.519	19.727	13.783	-12.851
2200	6.582	6.582	-0.451	-0.642	19.727	13.683	-12.751
2300	6.682	6.682	-0.624	-0.765	19.727	13.583	-12.651
2400	6.787	6.787	-0.800	-0.888	19.727	13.483	-12.551
2500	6.897	6.897	-0.978	-1.011	19.727	13.383	-12.451
2600	6.999	6.999	-1.149	-1.134	19.727	13.283	-12.351
2700	7.099	7.099	-1.314	-1.247	19.727	13.183	-12.251
2800	7.199	7.199	-1.473	-1.360	19.727	13.083	-12.151
2900	7.299	7.299	-1.627	-1.473	19.727	12.983	-12.051
3000	7.399	7.399	-1.777	-1.586	19.727	12.883	-11.951
3100	7.499	7.499	-1.922	-1.699	19.727	12.783	-11.851
3200	7.599	7.599	-2.062	-1.812	19.727	12.683	-11.751
3300	7.699	7.699	-2.197	-1.925	19.727	12.583	-11.651
3400	7.799	7.799	-2.327	-2.038	19.727	12.483	-11.551
3500	7.899	7.899	-2.452	-2.151	19.727	12.383	-11.451
3600	7.999	7.999	-2.572	-2.264	19.727	12.283	-11.351
3700	8.099	8.099	-2.687	-2.377	19.727	12.183	-11.251
3800	8.199	8.199	-2.797	-2.490	19.727	12.083	-11.151
3900	8.299	8.299	-2.902	-2.603	19.727	11.983	-11.051
4000	8.399	8.399	-3.002	-2.716	19.727	11.883	-10.951
4100	8.499	8.499	-3.097	-2.829	19.727	11.783	-10.851
4200	8.599	8.599	-3.187	-2.942	19.727	11.683	-10.751
4300	8.699	8.699	-3.272	-3.055	19.727	11.583	-10.651
4400	8.799	8.799	-3.352	-3.168	19.727	11.483	-10.551
4500	8.899	8.899	-3.427	-3.281	19.727	11.383	-10.451
4600	8.999	8.999	-3.497	-3.394	19.727	11.283	-10.351
4700	9.099	9.099	-3.562	-3.507	19.727	11.183	-10.251
4800	9.199	9.199	-3.622	-3.620	19.727	11.083	-10.151
4900	9.299	9.299	-3.677	-3.733	19.727	10.983	-10.051
5000	9.399	9.399	-3.727	-3.846	19.727	10.883	-9.951
5100	9.499	9.499	-3.772	-3.959	19.727	10.783	-9.851
5200	9.599	9.599	-3.812	-4.072	19.727	10.683	-9.751
5300	9.699	9.699	-3.847	-4.185	19.727	10.583	-9.651
5400	9.799	9.799	-3.877	-4.298	19.727	10.483	-9.551
5500	9.899	9.899	-3.902	-4.411	19.727	10.383	-9.451
5600	9.999	9.999	-3.922	-4.524	19.727	10.283	-9.351
5700	10.099	10.099	-3.937	-4.637	19.727	10.183	-9.251
5800	10.199	10.199	-3.947	-4.750	19.727	10.083	-9.151
5900	10.299	10.299	-3.952	-4.863	19.727	9.983	-9.051
6000	10.399	10.399	-3.952	-4.976	19.727	9.883	-8.951

December 31, 1961

Ground State Configuration 2p⁴S_{298.15} = 62.105 cal deg⁻¹ mole⁻¹ΔH_f 298.15 = 18.75 ± 2.3 kcal mole⁻¹

Electronic Levels and Multiplicities

$$\frac{g_i}{2}$$

$$\frac{g_i}{2}$$

σ = 1

ω_ex_e = 1.5844 cm⁻¹ω_e = 290.94 cm⁻¹r_e = 2.23 Åα_e = [0.0007] cm⁻¹B_e = [0.1121] cm⁻¹

Heat of Formation

A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London 1953, gives 23 ± 2.3 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from K. Wieland Zeits. f. Elektrochemie 54, 761 (1960) were weighted according to their natural isotopic abundances. Rotational constants were estimated using equation III, 123 p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. Bond length given by G. Herzberg (loc. cit.).

ClHg

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _f
0	0.000	0.000	0.000	INFINITE	2.907	8.699	8.699	INFINITE
100	9.619	10.921	34.181	2.326	8.693	8.693	8.693	15.119
200	11.840	18.406	24.571	1.233	8.690	8.690	8.690	5.557
298	13.200	23.405	23.405	0.000	8.666	8.666	3.362	2.464
300	13.223	23.487	23.405	0.024	8.661	8.661	3.330	2.426
400	14.387	27.253	23.636	1.406	10.081	10.081	1.597	0.872
500	15.387	30.773	24.982	2.866	14.779	14.779	0.961	0.420
600	16.287	33.659	26.102	4.480	14.077	14.077	4.044	1.473
700	17.086	36.150	27.446	6.150	13.296	13.296	7.004	2.187
800	17.785	38.550	28.746	7.746	12.446	12.446	9.846	2.690
900	18.383	40.690	29.908	9.703	11.567	11.567	12.528	3.094
1000	18.880	42.653	31.086	11.086	10.569	10.569	15.200	3.523

Mar. 31, 1962; Sept. 30, 1963; Sept. 30, 1965

IODINE MONOCHLORIDE (CI)

(CRYSTAL)

MOL. WT. = 162.3574

$\Delta H_f^0 = -8.699 \pm 0.025$ kcal. mole ⁻¹
$\Delta H_f^{298.15} = -8.466 \pm 0.025$ kcal. mole ⁻¹
$\Delta H_m^0 = 2.773 \pm 0.002$ kcal. mole ⁻¹
$\Delta H_m^{298.15} = 12.450$ kcal. mole ⁻¹

 $S_{298.15}^{298.15} = 23.405$ cal. mole⁻¹ deg.⁻¹ $T_m = 300.53^\circ\text{K.}$

Heat of Formation.

The heat of formation is that adopted by O. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2445 (1965) from an analysis of the equilibrium data of J. McMorris and D. M. Yost, J. Am. Chem. Soc. 53, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 7, 44 (1939). This yielded a heat of formation of ICl(g), from which the heat of formation of ICl(c) was calculated by using the heat of vaporization determined by Calder and Giauque loc. cit.

Heat Capacity and Entropy.

The heat capacity has been measured by Calder and Giauque loc. cit. from 17-322°K. The entropy was calculated based on $S_{15} = 0.592$ cal. mole⁻¹ deg.⁻¹ Above 300° the heat capacity data was extrapolated smoothly.

Melting Data.

All data were measured by Calder and Giauque loc. cit.

Iodine Monochloride (ICl)

(Liquid) Mol. Wt. = 162.3574

CII

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	keal. mole ⁻¹	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0								
298	24.560	32.544	32.544	-	0.000	- 5.720	- 3.341	2.449
300	24.582	32.696	32.544	-	0.065	- 5.694	- 3.326	2.423
400	23.500	39.649	33.501	-	2.459	- 6.281	- 2.676	1.462
500	22.500	44.785	35.267	-	4.759	- 10.169	- 1.436	.627
600	21.500	48.799	37.200	-	6.959	- 8.852	- 1.185	.067
800	20.500	52.798	39.096	-	11.059	- 7.641	- 1.594	.498
900	19.500	54.715	40.715	-	12.954	- 6.454	- 1.954	.875
1000	18.500	56.849	42.850	-	12.959	- 5.531	- 3.947	.958
1000	17.500	58.847	44.088	-	14.759	- 4.631	- 4.950	1.082

IODINE MONOCHLORIDE (CII)

(LIQUID)

MOL. WT. = 162.3574

S_{298.15}° = 32.544 cal. mole⁻¹ deg.⁻¹
T_m° = 300.53°K.

ΔH_f° 298.15 = -5.72 ± 0.03 kcal. mole⁻¹
ΔH_m° = 2.773 ± 0.002 kcal. mole⁻¹

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m° and the difference between H_{300.53}-H_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity from 300.53 to 317.76°K. has been measured by G. V. Calder and W. P. Giauque, J. Phys. Chem. 69, 2443 (1965). Above 318°K. it was extrapolated in a smooth manner. The entropy was obtained in a manner analogous to the heat of formation.

(Ideal Gas) Mol. Wt. = 162.3574

MOL. WT. = 162.3574

(IDEAL GAS)

IODINE MONOCHLORIDE (ICl)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	-	2.284	4.574	4.574	INFINITE
100	7.476	50.831	50.831	1.816	4.537	4.537	- 5.453
200	8.273	59.312	59.312	.816	4.437	4.437	- 5.543
298	8.497	59.145	59.145	.000	4.184	- 1.368	- 14.003
300	8.502	59.198	59.145	.016	4.180	- 1.402	- 14.022
400	8.700	61.674	59.482	.877	2.040	- 3.164	- 14.729
500	8.808	63.628	60.122	1.755	3.272	- 3.959	- 15.731
600	8.873	65.240	60.845	2.637	3.270	- 4.097	- 14.992
700	8.918	66.611	61.573	3.527	3.269	- 4.235	- 14.322
800	8.952	67.805	62.279	4.420	3.269	- 4.374	- 14.195
900	8.978	68.860	62.953	5.317	3.270	- 4.511	- 14.095
1000	9.000	69.808	63.592	6.216	3.270	- 4.650	- 14.016
1100	9.019	70.666	64.196	7.117	3.271	- 4.788	- 14.951
1200	9.036	71.452	64.769	8.020	3.273	- 4.926	- 14.897
1300	9.052	72.176	65.311	8.924	3.274	- 5.064	- 14.851
1400	9.066	72.847	65.826	9.830	3.276	- 5.200	- 14.812
1500	9.080	73.473	66.315	10.737	3.278	- 5.339	- 14.778
1600	9.094	74.059	66.781	11.646	3.281	- 5.474	- 14.748
1700	9.106	74.611	67.225	12.556	3.283	- 5.611	- 14.721
1800	9.119	75.132	67.650	13.467	3.286	- 5.749	- 14.698
1900	9.131	75.625	68.057	14.380	3.289	- 5.884	- 14.677
2000	9.143	76.094	68.447	15.293	3.293	- 6.023	- 14.658
2100	9.155	76.540	68.822	16.208	3.296	- 6.158	- 14.641
2200	9.167	76.967	69.183	17.124	3.300	- 6.296	- 14.625
2300	9.178	77.374	69.530	18.042	3.304	- 6.430	- 14.611
2400	9.190	77.765	69.865	18.960	3.309	- 6.566	- 14.598
2500	9.201	78.141	70.189	19.880	3.315	- 6.704	- 14.586
2600	9.212	78.502	70.502	20.800	3.321	- 6.839	- 14.575
2700	9.223	78.849	70.804	21.722	3.328	- 6.972	- 14.564
2800	9.234	79.185	71.098	22.645	3.336	- 7.106	- 14.555
2900	9.246	79.509	71.382	23.569	3.345	- 7.241	- 14.546
3000	9.257	79.823	71.658	24.494	3.354	- 7.377	- 14.537
3100	9.268	80.127	71.927	25.420	3.365	- 7.512	- 14.530
3200	9.279	80.421	72.188	26.348	3.377	- 7.644	- 14.522
3300	9.290	80.707	72.441	27.276	3.390	- 7.777	- 14.515
3400	9.300	80.984	72.689	28.205	3.404	- 7.909	- 14.508
3500	9.311	81.254	72.929	29.136	3.418	- 8.042	- 14.502
3600	9.322	81.516	73.164	30.068	3.434	- 8.172	- 14.496
3700	9.333	81.772	73.394	31.000	3.451	- 8.305	- 14.491
3800	9.344	82.021	73.617	31.934	3.468	- 8.437	- 14.485
3900	9.355	82.264	73.836	32.869	3.487	- 8.567	- 14.480
4000	9.366	82.501	74.050	33.805	3.506	- 8.698	- 14.475
4100	9.376	82.732	74.259	34.742	3.526	- 8.825	- 14.470
4200	9.387	82.958	74.463	35.681	3.546	- 8.954	- 14.466
4300	9.398	83.179	74.663	36.620	3.567	- 9.084	- 14.462
4400	9.409	83.396	74.859	37.560	3.589	- 9.214	- 14.458
4500	9.419	83.607	75.051	38.502	3.611	- 9.339	- 14.454
4600	9.430	83.814	75.240	39.444	3.633	- 9.465	- 14.450
4700	9.441	84.017	75.424	40.388	3.654	- 9.593	- 14.446
4800	9.452	84.216	75.605	41.332	3.677	- 9.720	- 14.443
4900	9.462	84.411	75.783	42.278	3.699	- 9.844	- 14.439
5000	9.473	84.602	75.957	43.225	3.721	- 9.969	- 14.436
5100	9.484	84.790	76.129	44.173	3.742	- 10.095	- 14.433
5200	9.495	84.974	76.297	45.121	3.765	- 10.218	- 14.429
5300	9.505	85.155	76.463	46.071	3.786	- 10.342	- 14.426
5400	9.516	85.333	76.625	47.022	3.808	- 10.466	- 14.424
5500	9.527	85.508	76.785	47.975	3.828	- 10.591	- 14.421
5600	9.537	85.680	76.942	48.928	3.849	- 10.718	- 14.418
5700	9.548	85.848	77.097	49.882	3.870	- 10.835	- 14.415
5800	9.559	86.015	77.249	50.837	3.890	- 10.960	- 14.413
5900	9.570	86.178	77.399	51.794	3.909	- 11.081	- 14.410
6000	9.580	86.339	77.547	52.751	3.929	- 11.201	- 14.408

Mar. 31, 1962; Sept. 30, 1963; Dec. 31, 1963; Sept. 30, 1965

$\Delta H_f^{\circ} 0 = 4.574 \pm 0.025 \text{ kcal. mole}^{-1}$

$\Delta H_f^{\circ} 298.15 = 4.184 \pm 0.025 \text{ kcal. mole}^{-1}$

$S_{298.15}^{\circ} = 59.145 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$

Ground State Configuration $1 \Sigma^{+}$

Electronic Levels and Quantum Weight

$\epsilon_1, \text{ cm.}^{-1} \frac{g_1}{1}$

$\omega_e x_e = 1.450 \text{ cm.}^{-1}$

$\omega_e = 382.18 \text{ cm.}^{-1}$

$\sigma_e = 2.327 \text{ \AA}$

Heat of Formation.

The dissociation energy from spectroscopic measurements of ICl(g) has been summarized by W. H. Evans, T. R. Munson and D. D. Wegman, J. Res. Natl. Bur. Standards, 55, 147 (1955) from which they adopt $D_0^{\circ} = 49.64 \text{ kcal. mole}^{-1}$. J. McMorris and D. M. Yost, J. Am. Chem. Soc. 54, 2247 (1932) and C. M. Beeson and D. M. Yost, J. Chem. Phys. 1, 44 (1939) studied the equilibria $\text{NOCl} = \text{NO} + 1/2 \text{ Cl}_2$ and $\text{NO} + \text{ICl} = \text{NOCl} + 1/2 \text{ I}_2(\text{g})$ from which the equilibrium constant of $\text{ICl} = 1/2 \text{ Cl}_2 + 1/2 \text{ I}_2(\text{g})$ can be obtained. G. V. Calder and W. F. Giauque, J. Phys. Chem. 69, 2443 (1965) have used 3rd law analysis to obtain $D_0^{\circ} = 49.578 \pm 0.025 \text{ kcal. mole}^{-1}$. This value was adopted yielding $\Delta H_f^{\circ} 298 = 4.184 \pm 0.025 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The molecular and vibrational constants were obtained from G. Herzberg "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York 1950. The values were then adjusted for the normal isotopic abundance of chlorine.

Potassium Chloride (KCl)

Mol. Wt. = 74.555

CIK

MOL. WT. = 74.555

(CRYSTAL)

POTASSIUM CHLORIDE (KCl)

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	2.717	-104.297	-104.297	-104.297	INFINITE	
100	9.369	7.594	2.249	-104.297	-104.297	-104.297	INFINITE	
200	11.577	14.969	20.833	-1.173	-104.498	-99.919	109.186	
298	12.258	19.731	0.000	-104.370	-97.700	71.616		
300	12.268	19.807	0.023	-104.368	-97.659	71.144		
400	12.700	23.598	20.218	1.272	-104.848	-95.329	52.085	
500	13.086	26.274	21.151	2.261	-104.728	-92.963	40.634	
600	13.460	28.693	22.212	3.889	-104.561	-90.624	33.010	
700	13.863	30.797	23.291	5.254	-104.350	-88.317	27.574	
800	14.359	32.679	24.349	6.564	-104.095	-86.044	23.506	
900	14.906	34.437	25.377	8.132	-103.784	-83.805	20.351	
1000	15.006	36.038	26.292	9.942	-103.422	-81.600	17.835	
1100	17.200	37.622	27.310	11.343	-121.827	-78.425	15.582	
1200	18.200	39.163	28.234	13.115	-121.002	-74.515	13.571	
1300	19.000	40.652	29.132	14.977	-120.088	-70.677	11.882	
1400	19.600	42.084	30.006	16.908	-119.106	-66.913	10.446	
1500	20.000	43.451	30.857	18.890	-118.074	-63.221	9.211	

$S_{298}^{\circ} = 19.73 \pm 0.04$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{\circ} = -104.37 \pm 0.06$ kcal. mole⁻¹
 $\Delta H_m^{\circ} = 6.282$ kcal. mole⁻¹
 $T_m = 1044^{\circ}\text{K.}$

Heat of Formation.

The heat of formation was calculated from the heat of hydrolysis of K(c), the heats of solution of HCl(g) and KCl(c), and the standard heat of neutralization of a strong acid and strong base. Extensive measurements are available for all these quantities. Values used in the calculation, in addition to the heat of formation for HCl(g), are summarized below.

Source	Reaction	ΔH_f° 298.15 (kcal.)
1,2,3,4	$\text{K(c)} + \text{H}_2\text{O(l)} \rightarrow \text{KOH}(\infty \text{H}_2\text{O}) + 1/2 \text{H}_2(\text{g})$	-46.966 ± 0.05
5,2,6	$\text{HCl(g)} \rightarrow \text{HCl}(\infty \text{H}_2\text{O})$	-17.86 ± 0.015
7	$\text{KCl}(\infty \text{H}_2\text{O}) \rightarrow \text{KCl(c)}$	-4.115 ± 0.010
7	$\text{KOH}(\infty \text{H}_2\text{O}) + \text{HCl}(\infty \text{H}_2\text{O}) \rightarrow \text{KCl}(\infty \text{H}_2\text{O}) + \text{H}_2\text{O(l)}$	-13.345 ± 0.025

- S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.* 80, 4782 (1957).
- S. R. Gunn, *UCRL-7932*, Livermore, Calif., Jul. 1964.
- C. E. Messer, L. G. Fasolino, and C. E. Thalmayer, *J. Am. Chem. Soc.* 77, 4524 (1955).
- E. E. Ketchen and W. E. Wallace, *J. Am. Chem. Soc.* 75, 2521 (1953).
- C. E. Vandervee and J. D. Nutter, *J. Phys. Chem.* 67, 2521 (1963).
- S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.* 80, 4780 (1958).
- S. R. Parker, *Thermodynamic Properties of Aqueous Uni-univalent Electrolytes*, NBS-RS-NBS2, U. S. Government Printing Office, Washington, D.C., 1965.

Heat Capacity and Entropy.

Low temperature heat capacities were obtained from the data (2.8-275°K.) of W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* A242, 467 (1957). Previous measurements scatter around the selected values and are in good agreement. These include P. G. Strelkov, E. S. Itskevich, V. N. Kostyukov, and G. G. Mirskaya (12-298°K.), *Zhur. Fiz. Khim.* 29, 845 (1954); K. Clausen, J. Goldmann, and A. Perlick (10-275°K.), *Z. Naturforsch.* 4a, 429 (1949); and J. C. Southard and R. A. Nelson (17-285°K.), *J. Am. Chem. Soc.* 55, 4865 (1933). For other less extensive data see the review by K. K. Kelley and E. G. King, *USNB Bulletin* 592, 1961. The entropy is based on the extrapolation $S_{2.8}^{\circ} = 0.0006$ cal./deg.-mole.

High temperature values are based on enthalpy data (373-1038°K.) from T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. These values join smoothly with the low temperature values and are in excellent agreement with the enthalpy data (675-933°K.) of S. M. Skuratov and S. A. Lapushkin, *J. Gen. Chem. (USSR)* 21, 2465 (1951) and the adiabatic heat capacities (334-721°K.) of A. Mustajoki, *Ann. Acad. Scient. Fennicae, Series A, I*, 38, 7 (1951).

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of $T_m = 1043^{\circ}$ and 1045°K. have been reported by E. Aukrust, B. Ejlorge, H. Flood, and T. Forland, *Ann. New York Acad. Sci.* 79, 830 (1960) and J. W. Johnson and M. A. Bredig, *J. Phys. Chem.* 62, 604 (1958), respectively. The heat of melting is confirmed by $\Delta H_m^{\circ} = 6.34$ kcal./mole obtained from enthalpy data by A. S. Dvorkin and M. A. Bredig, *J. Phys. Chem.* 64, 269 (1960) and $\Delta H_m^{\circ} = 6.4$ and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

CIK

T, °K	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H _{298^o)/T}	H ^o -H _{298^o}	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100								
200								
298	17.590	20.714	20.714	•000	- 100.810	- 94.433		69.221
300	17.590	20.823	20.714	•033	- 100.798	- 94.394		68.766
400	17.590	25.883	21.404	1.702	- 100.768	- 92.244		50.400
500	17.590	29.808	22.707	3.551	- 100.178	- 90.180		39.418
600	17.590	32.015	24.166	5.310	- 99.580	- 88.236		32.160
700	17.590	32.727	25.626	7.069	- 98.976	- 86.304		26.573
800	17.590	38.076	27.041	8.828	- 98.372	- 84.639		23.122
900	17.590	40.147	28.385	10.587	- 97.770	- 82.957		20.145
1000	17.590	42.001	29.655	12.346	- 97.179	- 81.344		17.778
1100	17.590	43.571	30.885	14.092	- 96.589	- 79.760		15.449
1200	17.590	45.208	32.085	15.828	- 95.993	- 78.200		13.142
1300	17.590	46.616	33.060	17.623	- 95.388	- 76.669		10.879
1400	17.590	47.919	34.075	19.382	- 94.772	- 75.169		8.588
1500	17.590	49.133	35.039	21.161	- 94.145	- 73.693		6.208
1600	17.590	50.268	35.954	22.900	- 93.500	- 72.225		3.975
1700	17.590	51.334	36.829	24.659	- 92.843	- 70.775		1.806
1800	17.590	52.340	37.663	26.418	- 92.173	- 69.349		0.208
1900	17.590	53.291	38.461	28.177	- 91.490	- 67.937		5.584
2000	17.590	54.193	39.225	29.936	- 90.796	- 66.546		

POTASSIUM CHLORIDE (KCl)

(LIQUID)

MOL. WT. = 74.555

$S_{298.15}^o = 20.71$ cal. deg. ⁻¹ mole ⁻¹
 $T_m = 1044^oK.$
 $T_b = 1710^oK.$ (to equilibrium vapor)
 $T_b = [1750^oK.]$ (to monomer only)
 $\Delta H_f^{298.15} = -100.81$ kcal. mole ⁻¹
 $\Delta H_m^o = 6.282$ kcal. mole ⁻¹
 $\Delta H_v^o = 29.7$ kcal. mole ⁻¹ (equilibrium vapor)
 $\Delta H_v^o = [37.14]$ kcal. mole ⁻¹ (monomer)

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m^o and the difference between ($H_{1044}^o - H_{298}^o$) for the crystal and liquid.

Heat Capacity and Entropy.

The constant heat capacity, 17.59 cal./deg.-mole, was derived from enthalpy data (1053-1173°K.) of T. B. Douglas, private communication, U. S. Natl. Bur. Std., May 23, 1961. This value was extrapolated above and below the experimental range. A lower value of 16.7 cal./deg.-mole was derived by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964, from enthalpy data (1050-1110°K.) obtained in a heat of melting study. The entropy of the liquid was obtained in a manner analogous to the heat of formation.

Melting Data.

The melting point and heat of melting are from Douglas, loc. cit. Values of $T_m = 1043^o$ and $1045^oK.$ have been reported by E. Aukrust, B. Bjorge, H. Flood, and T. Forland, Ann. New York Acad. Sci. 79, 830 (1960) and J. W. Johnson and M. A. Bredig, J. Phys. Chem. 62, 804 (1958), respectively. The heat of melting is confirmed by $\Delta H_m^o = 6.34$ kcal./mole obtained from enthalpy data by A. S. Dworkin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960) and $\Delta H_m^o = 6.4$ and 6.5 kcal./mole based on enthalpy and phase diagram studies of Aukrust et al., loc. cit., respectively.

Vaporization Data.

T_b (to equilibrium vapor) is the temperature resulting in unit total pressure based on the calculated partial pressures of KCl(g) and K₂Cl₂(g). This value may be compared with boiling points of 1698° and 1690°K. observed respectively by O. Ruff and S. Magdan, Z. anorg. allgem. Chem. 117, 147 (1921), and H. von Wartenburg and F. Albrecht, Z. Elektrochem. 27, 162 (1921). ΔH_v^o (equilibrium vapor) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 22.3 mole percent of dimer. According to the selected functions, the amount of dimer at lower temperatures increases gradually to about 32 mole percent at the melting point then decreases rapidly over the crystal. T_b (to monomer only) is taken as the temperature at which the calculated free energy change is zero for KCl(l) → KCl(g), while ΔH_v^o (monomer) is the corresponding heat of reaction.

Data on vapor pressures and dimer-monomer equilibrium are reviewed on the tables for KCl(g) and K₂Cl₂(g), respectively.

Potassium Chloride (KCl)

(Ideal Gas) Mol. Wt. = 74.555

C/K

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o kcal. mole ⁻¹	Log K _p
0	∞	INFINITE	-2.362	-50.882	INFINITE
100	7.576	48.122	6.639	-52.638	115.040
200	8.430	53.687	57.907	-51.109	59.307
298	8.723	57.116	57.116	-51.310	40.893
300	8.726	57.117	57.117	-51.314	40.861
400	8.857	59.701	57.461	-52.163	31.234
500	8.930	61.685	58.114	-52.443	25.520
600	8.979	63.318	58.850	-52.708	21.690
700	9.016	64.686	59.386	-52.941	18.941
800	9.046	65.915	59.864	-53.148	16.758
900	9.072	66.978	60.089	-53.467	15.250
1000	9.097	67.935	61.637	-53.726	13.949
1100	9.119	68.803	62.249	-53.901	12.676
1200	9.142	69.598	62.838	-54.058	11.468
1300	9.166	70.330	63.407	-54.198	10.314
1400	9.182	71.010	63.959	-54.309	9.210
1500	9.202	71.644	64.495	-54.400	8.160
1600	9.221	72.238	64.967	-54.462	7.165
1700	9.239	72.797	65.377	-54.507	6.228
1800	9.255	73.327	65.728	-54.537	5.350
1900	9.278	73.828	66.160	-54.559	4.527
2000	9.297	74.304	66.555	-54.576	3.766
2100	9.316	74.758	66.935	-54.588	3.063
2200	9.333	75.197	67.299	-54.596	2.416
2300	9.353	75.607	67.649	-54.600	1.824
2400	9.372	76.006	67.992	-54.601	1.286
2500	9.390	76.389	68.321	-54.600	0.801
2600	9.408	76.758	68.638	-54.596	0.369
2700	9.425	77.113	68.945	-54.589	0.000
2800	9.445	77.455	69.232	-54.578	-0.384
2900	9.463	77.788	69.532	-54.563	-0.761
3000	9.482	78.109	69.813	-54.544	-1.129
3100	9.500	78.420	70.085	-54.520	-1.487
3200	9.518	78.712	70.351	-54.492	-1.834
3300	9.536	79.001	70.608	-54.460	-2.170
3400	9.555	79.300	70.866	-54.424	-2.496
3500	9.573	79.577	71.105	-54.384	-2.812
3600	9.591	79.847	71.345	-54.340	-3.119
3700	9.609	80.167	71.578	-54.292	-3.416
3800	9.627	80.467	71.799	-54.240	-3.703
3900	9.646	80.617	72.029	-54.184	-3.980
4000	9.664	80.862	72.246	-54.124	-4.248
4100	9.682	81.101	72.459	-54.061	-4.507
4200	9.699	81.334	72.668	-54.000	-4.757
4300	9.716	81.566	72.872	-53.932	-5.000
4400	9.736	81.786	73.072	-53.860	-5.236
4500	9.755	82.005	73.268	-53.784	-5.466
4600	9.773	82.220	73.461	-53.704	-5.691
4700	9.792	82.430	73.649	-53.620	-5.912
4800	9.809	82.637	73.833	-53.532	-6.129
4900	9.827	82.839	74.016	-53.440	-6.342
5000	9.845	83.038	74.194	-53.344	-6.551
5100	9.863	83.233	74.370	-53.244	-6.756
5200	9.880	83.424	74.542	-53.140	-6.957
5300	9.898	83.613	74.718	-53.032	-7.154
5400	9.918	83.798	74.878	-52.920	-7.347
5500	9.936	83.980	75.042	-52.804	-7.536
5600	9.954	84.159	75.203	-52.684	-7.721
5700	9.972	84.336	75.362	-52.560	-7.902
5800	9.990	84.510	75.518	-52.432	-8.079
5900	10.008	84.680	75.672	-52.300	-8.252
6000	10.026	84.849	75.823	-52.164	-8.421

Dec. 31, 1961 Mar. 31, 1966

POTASSIUM CHLORIDE (KCl) (IDEAL GAS) MOL. WT. = 74.555

Ground State Configuration $1s^2 2s^2 2p^6 3s^2 3p^4$
 $S^{\circ}_{298.15} = 57.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_f 0 = -50.88 \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = -51.31 \pm 0.1 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weights

$\omega_e = 278.6 \text{ cm.}^{-1}$
 $\omega_e x_e = 1.157 \text{ cm.}^{-1}$
 $\sigma = 1$
 $B_e = 0.127536 \text{ cm.}^{-1}$
 $\alpha_e = 0.0007799$
 $r_e = 2.6667 \text{ \AA}$

Heat of Formation.

The heat of formation was calculated from that of the liquid based on $\Delta H^{\circ}_{298.15} = 49.5 \text{ kcal./mole}$ as selected from vapor pressure analyses summarized below. Partial pressures for the monomer were obtained from data of the first four sources by combination of total vapor pressures with PVT data or with transpiration data. Mass spectrometric values (source 5) are based on temperature variation of ion intensity. These same five studies were used in selection of $\Delta H^{\circ}_{298.15} = 45.0 \text{ kcal./mole}$ for the dimer-monomer equilibrium (see K_2Cl_2).

The resulting tables were tested by comparison with total pressure data over the range 819-1691°K. Dimer-monomer ratios calculated from the tables were used to convert observed total pressures to the monomer pressures which are analyzed below (sources 6-11). The results are consistent except near the boiling point where the observed pressures (sources 10 and 11) are 6-18 percent larger than those calculated. Knudsen effusion and transpiration studies over the crystal were not analyzed since they are in essential agreement with the torion effusion data of source 6.

Source	Method	No. of Points	Temp. °K.	ΔH°_{vap} 298 kcal./mole	Drift eu
1. Datz (1960)	PVT + Vap. Press. (a)	15	1310-1404	51.940-40	-1.050-4
2. Schrier (1957)	Trans. + Vap. Press. (b)	15	1261-1372	50.2650-77	-0.850-6
3. C. Beunen, OHNL-2523, Oak Ridge, Tenn., Jun 1957 (1959), 60, 1413 (1956).	Trans. + Vap. Press. (b)	7	1250-1473	49.670-66	-0.150-5
4. Barton et al. (1959)	Mass Spectrometry	137	774-1016	49.6-1.8	0.06
5. Milne et al. (1960)	Total Vap. Press.	9	819-945	49.5	1.050-6
6. Pugh et al. (1956)	Total Vap. Press.	9	847-956	49.0	-0.850-6
7. Dietz (1956)	Total Vap. Press.	9	1170-1466	51.0	-0.250-2
8. P. Dietz, J. Chem. Phys. 4, 575 (1936).	Total Vap. Press.	7	1393-1688	53.6	-2.750-4
9. E. F. Mook and W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).	Total Vap. Press.	16	1389-1691	50.2	-0.850-5
10. O. Ruff and S. Mugdan, Z. anorg. allgem. Chem. 111, 49 (1920).	Total Vap. Press.	16	1389-1691	50.2	-0.850-5
11. Wartenburg et al. (1921)	Total Vap. Press.	16	1389-1691	50.2	-0.850-5

(a) Total vapor pressure from sources 2, 3 and 8.

(b) 1235°K. was omitted.

1. S. Datz, OHNL-2523, Oak Ridge, Tenn., May 1960.

2. E. E. Schrier, Ph.D. Thesis, Rensselaer Polytechnic Inst., Troy, N.Y., Jun 1961.

3. C. Beunen, OHNL-2523, Oak Ridge, Tenn., Jun 1957 (1959), 60, 1413 (1956).

4. A. Barton and R. E. Bloom, J. Am. Chem. Soc. 81, 5657 (1959), 81, 5657 (1959).

5. T. A. Milne and R. E. Milne, J. Am. Chem. Soc. 82, 5657 (1960), 82, 5657 (1960).

6. A. C. P. Pugh and R. P. Burrow, Trans. Faraday Soc. 54, 671 (1958).

7. V. Dietz, J. Chem. Phys. 4, 575 (1936).

8. E. F. Mook and W. H. Rodebush, J. Am. Chem. Soc. 48, 2522 (1926).

9. O. I. Novikov and O. O. Polyachenok, Russ. J. Inorg. Chem. 6, 996 (1961).

10. O. Ruff and S. Mugdan, Z. anorg. allgem. Chem. 111, 49 (1920).

11. H. von Wartenburg and P. Albrecht, Z. elektrochem. 27, 162 (1921).

Heat Capacity and Entropy.

Rotational and vibrational constants are based on the microwave studies of P. L. Clouser and W. Gordy, Phys. Rev. 134, 4863 (1964). Earlier microwave data of A. Honig, M. Mandel, M. L. Storch, and C. H. Townes, Phys. Rev. 95, 629 (1954) and electric resonance data of C. A. Lee, B. P. Fabre, R. O. Carlson, and I. I. Rabi, Phys. Rev. 92, 1395 (1953) are in excellent agreement. Infrared spectra of S. A. Rice and W. Klemperer, J. Chem. Phys. 21, 573 (1957) yield $\omega_e = 281.6 \text{ cm.}^{-1}$ which is also in good agreement. The constants were adjusted to a natural isotopic composition of 24.47% ^{37}Cl and 6.8% ^{41}K .

C/K

ΔH_f°	$-100.9 \text{ kcal. mole}^{-1}$
ΔH_f°	$-102.6 \pm 1.0 \text{ kcal. mole}^{-1}$
ΔH_f°	$3.29 \text{ kcal. mole}^{-1}$
ΔH_f°	Unknown
T_m	798°K.
T_b	572.7°K.
T_g	$361 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Heat of Formation.

The heat of decomposition of $\text{KClO}_4(c)$ to $\text{KCl}(c)$ and $\text{O}_2(g)$ was measured by W. H. Johnson and A. A. Gilliland, J. Res. Natl. Bur. Std., 63 (1961), yielding $\Delta H^\circ_{298.15} = -103.22 \pm 0.15 \text{ kcal. mole}^{-1}$. K. A. Hofmann and F. H. Marin, Stöber, preuss. Akad. Wiss. Physik. Math. Kl. 448 (1932), burned a mixture of persulfur and potassium perchlorate and obtained $\Delta E_{298.15} = -1.73 \text{ kcal. mole}^{-1}$ for the constant volume process corresponding to the reaction: $\text{KClO}_4(c) = \text{KCl}(c) + 2\text{O}_2(g)$. Correction of their value for ΔP° gives $\Delta H^\circ_{298.15} = -0.55 \text{ kcal. mole}^{-1}$ which agrees reasonably well to the corresponding value, $-0.96 \pm 0.10 \text{ kcal. mole}^{-1}$, reported by W. H. Johnson and A. A. Gilliland, loc. cit. However, for the same reaction, $\Delta H^\circ_{298.15} = -2.55 \pm 0.18 \text{ kcal. mole}^{-1}$ was determined by S. M. Skuratov, A. F. Vorob'ev and N. M. Privolova, Russ. J. Inorg. Chem. 17, 342 (1962). They measured this quantity by two different methods which gave results differing by 0.2 kcal. mole⁻¹. They measured $\pm 0.2 \text{ kcal. mole}^{-1}$. The value used here is the average of these four results. $\Delta H^\circ_{298.15}$ reported was $-101.9 \text{ kcal. mole}^{-1}$. The value used here is the average of these four results. M. Berthelot and P. Vieille, the heat of explosion of ammonium picrate between the heat of explosion of potassium picrate and that of an ammonium picrate-potassium perchlorate mixture, and also the difference between the heat of explosion of potassium picrate and that of a potassium picrate-potassium perchlorate mixture. They obtained $\Delta H^\circ_{298.15} = 7.5 \text{ kcal. mole}^{-1}$ for the reaction $\text{KClO}_4(c) = \text{KCl}(c) + 2\text{O}_2(g)$. From that the value of $\Delta H^\circ_{298.15}$ was calculated to be $-111.9 \text{ kcal. mole}^{-1}$. This value was not used.

Heat Capacity and Entropy.

The low temperature heat capacities ($12.53-298.0^{\circ}\text{K}$.) were measured by W. M. Latimer and J. E. Ahlberg, *J. Am. Chem. Soc.* **52**, 549 (1930). The heat capacities above 298°K . were estimated by comparison with those of $\text{NiCl}_2(\text{c})$. $S_{298.15}^{\circ}$ was reported by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961), based on the low temperature heat capacities measured by W. M. Latimer and J. E. Ahlberg, loc. cit., using $S_{12.59}^{\circ}$ (extrap.) 0.14 cal. deg.⁻¹ mole⁻¹.

Transition Data.

T_c and ΔH_c° were obtained from the National Bureau of Standards, Circ. 500, "Selected Values of Chemical Thermodynamic Properties," by F. D. Rossini, et al., 1952.

Temperature of Melting.

^mT was taken from Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use," June 1949.

Lithium Chloride (LiCl)

(Crystal) Mol. Wt. = 42.397

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	8.679	3.000	INFINITE	2.263	97.400	97.400	INFINITE
100	10.361	3.247	23.576	2.233	97.400	97.400	26.215
200	11.361	9.610	15.191	1.076	97.722	91.720	102.408
298	11.479	14.173	14.173	1.000	97.578	91.766	67.278
300	11.495	14.244	14.173	1.021	97.575	91.751	66.837
400	12.162	17.652	14.633	1.207	97.423	89.674	36.408
500	12.749	20.432	15.523	2.454	98.023	87.674	36.408
600	13.287	22.604	16.544	3.756	97.668	85.857	31.272
700	13.780	24.111	17.652	5.111	97.652	83.673	26.165
800	14.325	26.769	18.622	6.518	97.658	81.673	22.330
900	14.833	28.686	19.624	7.976	97.658	80.068	19.379
1000	15.337	30.075	20.590	9.485	96.687	78.134	17.075
1100	15.839	31.540	21.521	11.043	96.265	76.299	15.156
1200	16.338	32.960	22.421	12.632	95.794	74.505	13.569
1300	16.836	34.287	23.276	14.260	95.272	72.822	12.230
1400	17.336	35.553	24.111	15.928	94.700	71.250	11.107
1500	17.831	36.766	24.914	17.778	94.078	69.372	10.107
1600	18.323	37.933	25.692	19.586	93.405	67.746	9.253
1700	18.811	39.066	26.475	21.443	92.730	66.036	8.335
1800	19.295	40.168	27.261	23.348	92.058	64.182	7.426
1900	19.805	41.205	27.987	25.305	91.387	62.173	6.619
2000	20.298	42.234	28.679	27.310	90.723	60.180	5.898

LITHIUM CHLORIDE (LiCl)

(CRYSTAL)

MOL. WT. = 42.397

$$\Delta H_f^{\circ} 298.15 = -97.578 \pm 0.273 \text{ kcal mole}^{-1}$$

$$S^{\circ} 298.15 = 14.173 \pm 0.015 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$T_m = 883 \pm 2^{\circ}\text{K}$$

Heat of Formation

The heat of formation was obtained as follows:

- (1) $\text{LiOH} \cdot 100\text{H}_2\text{O} + \text{HCl} \cdot 100\text{H}_2\text{O} \rightarrow \text{LiCl} \cdot 201\text{H}_2\text{O}$
T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.*, **44**, 684 (1922).
- (2) $\text{Li}(c) + 100\text{H}_2\text{O}(l) + \text{LiOH} \cdot 100\text{H}_2\text{O} + 1/2 \text{H}_2(g)$
S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.*, **80**, 4782 (1958).
- (3) $\text{LiOH} \cdot 100\text{H}_2\text{O} + \text{LiOH} \cdot 100\text{H}_2\text{O} + 900\text{H}_2\text{O}(l)$
T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.*, **43**, 770 (1921).
- (4) $1/2 \text{H}_2(g) + 1/2 \text{Cl}_2(g) \rightarrow \text{HCl}(g)$
JANAF Tables.
- (5) $\text{HCl}(g) + 100\text{H}_2\text{O}(l) \rightarrow \text{HCl} \cdot 100\text{H}_2\text{O}$
C. H. Slansky, *J. Am. Chem. Soc.*, **62**, 2430 (1940), and
J. H. Sturtevant, *J. Am. Chem. Soc.*, **62**, 3265 (1940).
- (6) $\text{LiCl} \cdot 201\text{H}_2\text{O} + \text{LiCl}(c) + 201\text{H}_2\text{O}(l)$
E. Lange and F. Dürr, *Z. phys. Chem.*, **121**, 361 (1926).

$$(1) + (2) + (3) + (4) + (5) + (6) \text{ gives Li}(c) + 1/2 \text{Cl}_2(g) \rightarrow \text{LiCl}(c)$$

A direct calorimetric determination by H. Siemensen and U. Siemensen, *Z. Electrochem.*, **56**, 643 (1952) gave -94.8 ± 0.6 kcal mole⁻¹. However, the solution route was thought to be inherently more accurate and was adopted.

Heat Capacity and Entropy

The heat capacity between 15° and 325°K has been measured by D. A. Shirley, *J. Am. Chem. Soc.*, **82**, 3861 (1960) and by F. L. Oetting, W. E. Hutton and G. C. Sinke, unpublished work, Thermal Laboratory, Dow Chemical Company. The two sets of data are in substantial agreement and were plotted together and used to evaluate the entropy at 298°. The extrapolation to 0°K was done assuming a T³ law and yielded S₁₅ = 0.019 e.u. Above 298° T. B. Douglas, J. L. Dever and A. W. Harman, quoted in Natl. Bur. Standards Report 6297, have made enthalpy measurements to 1200°K. E. N. Rodigina, K. Z. Gornelski, and V. F. Luginina, *Zhur. Neorg. Khim.*, **4**, 975 (1959) also made enthalpy determinations to 1100°K. These two sets of measurements were averaged and joined smoothly to the low temperature values.

Melting and Transition Data

The melting point has been reported as follows: 880°K., Douglas et al., loc. cit.; 883°K., Rodigina et al., loc. cit.; 883°K., H. M. Haendler, P. S. Bennett, and C. M. Wheeler, *J. Electrochem. Soc.*, **106**, 264 (1959); 879°K., H. Flood, O. Fyke, and S. Urnes, *Z. Electrochem.*, **59**, 364 (1955); 879°K., H. von Martenberg and H. Schulz, *Z. Electrochem.*, **27**, 566 (1921). The highest value of 883°K. was taken as representing the most pure samples. At this temperature the enthalpy equations of Douglas et al. yield a heat of fusion of 4.718 kcal mole⁻¹, those of Rodigina et al., 4.669 kcal mole⁻¹. A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **64**, 263 (1960) report a value of 4.76 ± 0.10 kcal mole⁻¹ and quote 4.83 kcal mole⁻¹ from a private communication from D. F. Smith. The average value ΔH_m = 4.74 ± 0.10 kcal mole⁻¹ was adopted.

A transition at 838°K has been reported by Kislova and Bergman, *Russ. J. Inorg. Chem.*, **5**, 1210 (1960) but is not supported by the enthalpy measurements quoted above.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100	11,479	19,745	0.000	93.394	-86.945	65.210
200	11,495	19,816	1.051	93.391	-86.938	64.788
300	11,512	19,887	2.102	93.388	-86.931	64.366
400	11,529	19,958	3.153	93.385	-86.924	63.944
500	11,546	20,029	4.204	93.382	-86.917	63.522
600	11,563	20,100	5.255	93.379	-86.910	63.100
700	11,580	20,171	6.306	93.376	-86.903	62.678
800	11,597	20,242	7.357	93.373	-86.896	62.256
900	11,614	20,313	8.408	93.370	-86.889	61.834
1000	11,631	20,384	9.459	93.367	-86.882	61.412
1100	11,648	20,455	10.510	93.364	-86.875	60.990
1200	11,665	20,526	11.561	93.361	-86.868	60.568
1300	11,682	20,597	12.612	93.358	-86.861	60.146
1400	11,699	20,668	13.663	93.355	-86.854	59.724
1500	11,716	20,739	14.714	93.352	-86.847	59.302
1600	11,733	20,810	15.765	93.349	-86.840	58.880
1700	11,750	20,881	16.816	93.346	-86.833	58.458
1800	11,767	20,952	17.867	93.343	-86.826	58.036
1900	11,784	21,023	18.918	93.340	-86.819	57.614
2000	11,801	21,094	19.969	93.337	-86.812	57.192

LITHIUM CHLORIDE (LiCl)

(LIQUID)

MOL. WT. = 42.397

$$\Delta H_f^o 298.15 = -93.394 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 16.745 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^o = 4.74 \pm 0.10 \text{ kcal. mole}^{-1}$$

$$T_m = 883 \pm 2^\circ \text{K}$$

$$T_b(\text{monomeric gas}) = 1701^\circ \text{K}$$

$$T_b(\text{equilibrium mixture}) = 1656^\circ \text{K}$$

Heat of Formation.

Obtained from that of the crystal by adding ΔH_m and $H_{883}^o - H_{298}^o(c)$ and subtracting $H_{883}^o - H_{298}^o(l)$.

Heat Capacity and Entropy.

The heat capacity from the melting point to 1100°K and 1200°K has been reported by E. N. Rodigins, K. Z. Gornitski, and V. F. Luginska, Zhur. Neorg. Khim. **4**, 975 (1959) and T. B. Douglas, J. L. Dever, and A. W. Harman, quoted in Natl. Bur. of Standards Report 6297. The equation given by the former authors for the enthalpy of the liquid does not agree with their measurements and has been replaced by $H_m - H_{298.15} = 18.000T - 1.5 \times 10^{-5}T^2 - 2279 \text{ cal. mole}^{-1}$, which fits to $\pm 0.5\%$. The two sets of results were averaged and the equations were assumed to hold up to the normal boiling point. The entropy was calculated from that of the crystal in a manner analogous to the heat of formation.

Melting.

See table for crystal.

Boiling.

The equilibrium boiling point was taken from H. von Wertenburg and H. Schultz, Z. Electrochem. **27**, 568 (1921) and the boiling point of the monomeric gas is defined as the temperature at which it reaches 1 atm. pressure. This was obtained from the free energy crossover between liquid and monomeric gas. The heat of vaporization to the monomeric gas was found from the tables to be 39.8 kcal. mole⁻¹.

June 30, 1962

CILI

CILI

Lithium Chloride (LiCl)

(Ideal Gas) Mol. Wt. = 42.397

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	2.146	-	-46.742	-46.742	INFINITE
100	6.978	42.859	57.562	-	-46.516	-46.516	105.700
200	7.412	47.860	51.575	-	-46.601	-50.197	54.850
298	7.946	50.864	50.864	0.000	-46.778	-51.926	38.061
300	7.984	50.913	50.864	0.015	-46.782	-51.958	37.850
400	8.312	53.255	51.181	1.829	-47.003	-51.651	29.312
500	8.534	55.135	51.790	1.673	-48.004	-55.208	24.130
600	8.677	56.705	52.462	2.534	-48.291	-56.920	20.623
700	8.775	58.050	53.104	3.407	-48.557	-57.988	18.104
800	8.840	59.181	53.697	4.280	-48.800	-58.827	16.179
900	8.901	60.272	54.252	5.175	-49.053	-60.317	14.719
1000	8.945	61.212	55.145	6.068	-49.304	-61.589	13.525
1100	8.981	62.067	55.736	6.964	-49.544	-63.135	12.543
1200	9.012	62.869	56.296	7.864	-49.782	-64.361	11.721
1300	9.040	63.572	56.858	8.766	-50.016	-65.356	11.022
1400	9.066	64.197	57.411	9.666	-50.246	-66.152	10.426
1500	9.087	64.869	57.816	10.576	-50.477	-67.023	9.866
1600	9.108	65.456	58.275	11.489	-50.702	-67.980	9.435
1700	9.129	66.009	58.714	12.401	-50.976	-68.993	9.056
1800	9.145	66.537	59.137	13.310	-51.248	-69.968	8.722
1900	9.155	67.036	59.537	14.230	-51.516	-70.908	8.426
2000	9.162	67.497	59.923	15.148	-51.786	-71.812	8.157
2100	9.169	67.945	60.294	16.067	-52.053	-72.686	7.912
2200	9.175	68.373	60.652	16.987	-52.318	-73.532	7.682
2300	9.180	68.787	61.000	17.900	-52.580	-74.352	7.466
2400	9.185	69.177	61.329	18.811	-52.839	-75.148	7.262
2500	9.193	69.554	61.651	19.759	-53.096	-75.922	7.068
2600	9.198	69.918	61.962	20.686	-53.350	-76.672	6.884
2700	9.204	70.268	62.263	21.615	-53.605	-77.400	6.712
2800	9.209	70.607	62.555	22.545	-53.861	-78.107	6.550
2900	9.214	70.937	62.838	23.474	-54.117	-78.794	6.398
3000	9.218	71.250	63.113	24.410	-54.374	-79.462	6.256
3100	9.223	71.556	63.381	25.344	-54.631	-80.112	6.124
3200	9.228	71.854	63.641	26.280	-54.888	-80.744	6.000
3300	9.232	72.142	63.894	27.216	-55.145	-81.359	5.884
3400	9.236	72.421	64.141	28.151	-55.402	-81.957	5.776
3500	9.241	72.685	64.382	29.087	-55.659	-82.538	5.674
3600	9.245	72.940	64.616	30.039	-55.916	-83.101	5.576
3700	9.249	73.219	64.865	30.992	-56.173	-83.646	5.482
3800	9.253	73.491	65.107	31.946	-56.430	-84.174	5.392
3900	9.258	73.771	65.350	32.897	-56.687	-84.686	5.306
4000	9.262	74.046	65.591	33.850	-56.944	-85.181	5.224
4100	9.266	74.319	65.826	34.803	-57.201	-85.660	5.146
4200	9.270	74.590	66.055	35.756	-57.458	-86.124	5.072
4300	9.274	74.859	66.279	36.709	-57.715	-86.573	4.999
4400	9.278	75.126	66.500	37.662	-57.972	-87.007	4.928
4500	9.282	75.391	66.716	38.615	-58.229	-87.426	4.858
4600	9.286	75.655	66.928	39.568	-58.486	-87.831	4.788
4700	9.290	75.918	67.136	40.521	-58.743	-88.222	4.718
4800	9.294	76.179	67.341	41.474	-59.000	-88.599	4.648
4900	9.298	76.439	67.543	42.427	-59.257	-88.963	4.578
5000	9.302	76.698	67.741	43.380	-59.514	-89.314	4.508
5100	9.306	76.956	67.936	44.333	-59.771	-89.661	4.438
5200	9.310	77.213	68.128	45.286	-60.028	-90.000	4.368
5300	9.314	77.469	68.317	46.239	-60.285	-90.331	4.298
5400	9.318	77.724	68.503	47.192	-60.542	-90.657	4.228
5500	9.322	77.978	68.686	48.145	-60.799	-90.978	4.158
5600	9.326	78.231	68.867	49.098	-61.056	-91.294	4.088
5700	9.330	78.484	69.046	50.051	-61.313	-91.606	4.018
5800	9.334	78.736	69.222	51.004	-61.570	-91.913	3.948
5900	9.338	78.988	69.396	51.957	-61.827	-92.216	3.878
6000	9.342	79.239	69.568	52.910	-62.084	-92.514	3.808

LITHIUM CHLORIDE (LiCl)

(IDEAL GAS)

MOL. WT. = 42.397

Cili

$$\Delta H_f^\circ = -46.742 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.742 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -46.778 \pm 3.0 \text{ kcal. mole}^{-1}$$
</

INTERIM TABLE

T, °K.	C_p^0	S^0	$\text{cal. mole}^{-1}\text{deg.}^{-1}$	$-(F^0-H_{298}^0)/T$	$H^0-H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
100	6.000	51.090	INFINITE	-7.794	-2.755	-2.755	-	INFINITE
200	9.061	57.615	61.166	-9.50	-3.076	-3.076	-3.457	4.340
298	10.266	61.264	61.264	-9.00	-3.400	-3.400	-4.342	3.163
300	10.286	61.326	61.264	-9.04	-3.406	-3.406	-4.348	3.167
400	11.415	67.010	67.495	-2.256	-4.768	-4.768	-4.727	2.066
500	12.367	69.227	69.436	3.474	-5.077	-5.077	-4.689	1.706
600	12.720	71.163	71.603	4.731	-5.349	-5.349	-4.603	1.437
700	12.960	72.876	73.359	6.035	-5.598	-5.598	-4.480	1.226
800	13.120	74.344	74.864	7.384	-5.824	-5.824	-4.324	1.054
1000	13.270	75.406	76.165	9.681	-6.066	-6.066	-4.155	.906
1100	13.372	77.076	78.009	9.973	-6.280	-6.280	-3.942	.783
1200	13.453	78.243	78.814	11.315	-6.511	-6.511	-3.719	.677
1300	13.517	79.361	80.361	12.663	-6.768	-6.768	-3.477	.585
1400	13.570	80.435	81.723	14.025	-7.042	-7.042	-3.216	.505
1500	13.610	81.264	82.913	15.377	-7.337	-7.337	-2.947	.429
1600	13.645	82.143	84.023	16.740	-7.658	-7.658	-2.658	.363
1700	13.675	82.971	85.121	18.106	-8.005	-8.005	-2.342	.312
1800	13.700	83.745	86.205	19.475	-8.378	-8.378	-2.000	.264
1900	13.718	84.465	87.265	20.845	-8.778	-8.778	-1.630	.226
2000	13.738	85.139	88.309	22.216	-9.205	-9.205	-1.240	.196
2100	13.754	85.760	89.335	23.593	-9.658	-9.658	-8.771	.170
2200	13.768	86.330	90.345	24.969	-10.137	-10.137	-8.227	.145
2300	13.780	86.852	91.335	26.345	-10.642	-10.642	-7.602	.120
2400	13.790	87.326	92.305	27.725	-11.175	-11.175	-6.900	.095
2500	13.800	87.752	93.255	29.104	-11.737	-11.737	-6.120	.070
2600	13.808	88.134	94.185	30.485	-12.328	-12.328	-5.270	.045
2700	13.815	88.465	95.095	31.866	-12.948	-12.948	-4.350	.020
2800	13.822	88.752	95.985	33.247	-13.598	-13.598	-3.370	.005
2900	13.828	89.000	96.855	34.628	-14.278	-14.278	-2.330	.000
3000	13.833	89.210	97.705	36.013	-14.988	-14.988	-1.230	.000
3100	13.838	89.425	98.535	37.397	-15.728	-15.728	-.070	.000
3200	13.842	89.605	99.345	38.781	-16.498	-16.498	.130	.000
3300	13.845	89.755	100.125	40.165	-17.298	-17.298	.330	.000
3400	13.848	89.885	100.875	41.550	-18.128	-18.128	.530	.000
3500	13.854	89.925	101.605	42.935	-18.988	-18.988	.730	.000
3600	13.857	89.935	102.305	44.321	-19.878	-19.878	.930	.000
3700	13.860	89.995	102.985	45.707	-20.798	-20.798	1.130	.000
3800	13.862	90.065	103.645	47.092	-21.748	-21.748	1.330	.000
3900	13.865	90.125	104.285	48.477	-22.728	-22.728	1.530	.000
4000	13.867	90.176	104.905	49.866	-23.738	-23.738	1.730	.000
4100	13.869	90.119	105.505	51.253	-24.778	-24.778	1.930	.000
4200	13.871	90.133	106.085	52.640	-25.848	-25.848	2.130	.000
4300	13.873	90.196	106.645	54.027	-26.948	-26.948	2.330	.000
4400	13.876	90.240	107.185	55.412	-28.078	-28.078	2.530	.000
4500	13.876	90.276	107.705	56.797	-29.238	-29.238	2.730	.000
4600	13.878	90.275	108.205	58.182	-30.428	-30.428	2.930	.000
4700	13.879	90.244	108.685	59.567	-31.648	-31.648	3.130	.000
4800	13.880	90.195	109.145	60.952	-32.898	-32.898	3.330	.000
4900	13.881	90.130	109.585	62.337	-34.178	-34.178	3.530	.000
5000	13.883	90.042	110.005	63.721	-35.488	-35.488	3.730	.000
5100	13.884	90.147	110.405	65.106	-36.828	-36.828	3.930	.000
5200	13.885	90.417	110.785	66.491	-38.198	-38.198	4.130	.000
5300	13.887	90.802	111.145	67.876	-39.608	-39.608	4.330	.000
5400	13.888	91.196	111.485	69.261	-41.048	-41.048	4.530	.000
5500	13.888	91.600	111.805	70.646	-42.518	-42.518	4.730	.000
5600	13.888	92.014	112.105	72.031	-44.018	-44.018	4.930	.000
5700	13.889	92.438	112.385	73.416	-45.538	-45.538	5.130	.000
5800	13.890	92.872	112.645	74.801	-47.078	-47.078	5.330	.000
5900	13.890	93.316	112.885	76.186	-48.648	-48.648	5.530	.000
6000	13.891	93.770	113.105	77.571	-50.248	-50.248	5.730	.000

December 31, 1960.

LITHIUM HYPOCHLORITE (LiClO) (Ideal Gas)

Mol. Wt. = 58.397

 ΔH_f^0 298.15 = [-3.4 ± 20] kcal. mole⁻¹ ΔG_f^0 298.15 = [61.264] cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

$$\frac{\omega_{cm.}^{-1}}{\left[\frac{1150}{500}\right](1), \left[\frac{700}{1}\right](1)}$$

Li-O-Cl angle 115°, Li-O dist. 1.82 Å, O-Cl dist. 1.75 Å σ = 1.

Data from D. L. Hildenbrand, Aeronutronic Division of Ford Motor Company, Newport Beach, Calif., "Tables of Thermodynamic Data for Performance Calculations", September, 1959.

Lithium Perchlorate (LiClO₄)
(Crystal) Mol. Wt. = 106.397

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100								
200								
298								
300	25.100	30.000	30.000	0.000	0.000	-91.000	-60.706	44.497
300	25.200	30.156	30.000	0.047	0.047	-90.958	-60.519	44.086
400	31.000	38.181	31.056	2.850	2.850	-90.652	-50.398	27.535
500	34.300	45.699	33.728	6.136	6.136	-90.673	-40.336	17.630
600	36.500	51.466	35.566	13.450	13.450	-88.752	-20.455	1.054
700	38.333	57.733	38.566	21.369	21.369	-87.453	-10.863	2.968
800	39.800	62.952	41.277	25.563	25.563	-84.885	-8.011	1.751
900	41.150	67.719	43.054	29.845	29.845	-83.417	-17.229	3.423
1000	42.300	72.116	46.453	34.223	34.223	-81.731	-26.311	4.792
1100	43.325	76.197	49.065	38.650	38.650	-80.257	-35.261	5.928
1200	44.200	80.005	51.086	43.251	43.251	-78.561	-44.084	6.881
1300	45.140	83.580	53.619	47.904	47.904	-76.786	-52.783	7.690
1400	46.073	86.960	56.066					
1500	47.000	90.170	58.234					

LiClO₄

MOL. WT. = 106.397

(CRYSTAL)

LITHIUM PERCHLORATE (LiClO₄)

ΔH_f^o = Unknown

S_{298.15} = [30 ± 1] cal. deg⁻¹ mole⁻¹

ΔH_f^o 298.15 = -91.0 ± 0.7 kcal. mole⁻¹

ΔH_m^o = [7] kcal. mole⁻¹

T_m = 509°K.

Heat of Formation.

The heats of reaction (ΔH_f^o) involving LiClO₄(c) has been determined by several investigators as follows:

Investigator	Chemical Reaction	ΔH _f ^o 298.15, kcal. mole ⁻¹	ΔH _f ^o 298.15, kcal. mole ⁻¹
Gilliland and Johnson (1)	LiClO ₄ (c) + KCl(c) → LiCl(c) + KClO ₄ (c)	-5.86 ± 0.06	-90.34
Markowitz, et al. (2)	LiOH(225H ₂ O) + HClO ₄ (225H ₂ O) → LiClO ₄ (451H ₂ O) + H ₂ O(l)	-13.54 ± 0.09	-91.7
Birky and Hepler (3)	LiClO ₄ (c) → Li ⁺ (aq.) + ClO ₄ ⁻ (aq.)	-6.31 ± 0.13	-91.11

(1) A. A. Gilliland and W. H. Johnson, J. Res. Natl. Bur. Std. 65A, 67 (1961).

(2) M. M. Markowitz, R. F. Harris and H. Stewart, Jr., J. Phys. Chem. 63, 1325 (1959).

(3) M. M. Birky and L. G. Hepler, J. Phys. Chem. 64, 686 (1960).

The adopted value, ΔH_f^o 298.15 = -91.0 kcal. mole⁻¹, for LiClO₄(c) is the weighted average of the three values listed.

Heat Capacity and Entropy:

Heat capacities and S_{298.15} were estimated by comparison with those of KClO₄(c).

Melting Data.

T_m was obtained from T. W. Richards and H. H. Willard, J. Am. Chem. Soc., 32, 4 (1910). The value of ΔH_m^o 509 was estimated by comparison with the value, ΔH_m^o 528 = 5.4 kcal. mole⁻¹, for NaClO₃(c) reported by K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, XIII. High-Temperature Heat-Content, Heat-Capacity and Entropy Data for the Elements and Inorganic Compounds, U. S. Bur. Mines Bull. 584 (1960).

LiClO₄

LITHIUM PERCHLORATE (LiClO₄) (LIQUID) MOL. WT. = 106.397

T, °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _P	
0								
100								
200								
298	38.500	39.245	39.245	-	0.00	- 85.684	- 58.146	42.620
300	38.500	39.483	39.246	+0.71	- 85.657	- 57.976	- 42.234	
400	38.500	40.559	40.786	3.921	- 86.965	- 46.962	- 26.740	
500	38.500	59.150	43.607	7.771	- 83.722	- 40.210	- 17.575	
600	38.500	66.169	46.801	11.621	- 82.429	- 31.620	- 11.517	
700	38.500	72.504	50.002	15.471	- 81.374	- 23.228	- 7.252	
800	38.500	78.185	53.245	19.311	- 79.765	- 15.908	- 4.056	
900	38.500	81.780	56.034	23.171	- 78.169	- 1.068	- 1.677	
1000	38.500	85.836	58.815	27.021	- 76.110	- 1.065	- .293	
1100	38.500	89.506	61.441	30.871	- 77.075	6.931	- 1.774	
1200	38.500	92.655	63.921	34.721	- 76.050	16.705	- 3.042	
1300	38.500	95.937	66.267	38.571	- 75.060	24.505	- 4.101	
1400	38.500	98.770	68.489	42.421	- 74.075	32.308	- 4.986	
1500	38.500	101.447	70.599	46.271	- 73.103	39.535	- 5.762	

$S_{298.15}^{\circ} = [39.245]$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{\circ} 298.15 = [-85.574]$ cal. deg.⁻¹ mole⁻¹
 $\Delta F_f^{\circ} = [7]$ kcal. mole⁻¹
 $T_m = 509^{\circ}\text{K}.$

Heat of Formation.

$\Delta H_f^{\circ} 298.15(1)$ was obtained from $\Delta H_f^{\circ} 298.15(c)$ by adding ΔH_m° and the difference between $H_{370.6}^{\circ}$ and $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

C_p for LiClO₄(l) was estimated by comparison with that for NaClO₃(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting temperature (T_m) was obtained from T. W. Richards and H. H. Willard, J. Am. Chem. Soc., 32, 4 (1910). The value of $\Delta H_m^{\circ} 509$ was estimated by comparison with the value, $\Delta H_m^{\circ} 528 = 5.4$ kcal. mole⁻¹, for NaClO₃(c) reported by K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, XIII. High-Temperature Heat-Content, Heat-Capacity and Entropy Data for the Elements and Inorganic Compounds, U. S. Bur. Mines Bull. 584 (1960).

Magnesium Monochloride (MgCl)

(Ideal Gas) Mol. Wt. = 59.765

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T kcal. mole ⁻¹	H° - H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	7.077	47.399	2.237	-10.344	IMFINITE
200	7.830	52.531	1.840	-10.152	27.111
298	8.324	55.760	1.795	-10.129	16.078
300	8.330	55.812	1.790	-10.129	12.279
400	8.587	58.247	1.601	-10.103	12.232
500	8.730	60.180	1.429	-10.085	10.533
600	8.819	61.780	1.286	-10.078	9.156
700	8.878	63.145	1.166	-10.078	8.363
800	8.915	64.306	1.066	-10.078	7.784
900	8.936	65.306	1.000	-10.078	7.340
1000	8.953	66.331	0.958	-10.078	6.984
1100	9.007	67.188	0.939	-10.078	6.653
1200	9.027	67.973	0.932	-10.078	6.365
1300	9.043	68.700	0.935	-10.078	6.130
1400	9.053	69.387	0.940	-10.078	5.906
1500	9.079	69.993	0.946	-10.078	5.696
1600	9.094	70.580	0.953	-10.078	5.492
1700	9.108	71.151	0.960	-10.078	5.291
1800	9.121	71.706	0.967	-10.078	5.097
1900	9.136	72.246	0.974	-10.078	4.910
2000	9.150	72.615	0.981	-10.078	4.731
2100	9.163	73.002	0.988	-10.078	4.561
2200	9.175	73.408	0.994	-10.078	4.401
2300	9.187	73.834	0.999	-10.078	4.251
2400	9.200	74.288	1.005	-10.078	4.111
2500	9.212	74.664	1.010	-10.078	3.981
2600	9.225	75.055	1.015	-10.078	3.861
2700	9.237	75.473	1.020	-10.078	3.751
2800	9.250	75.918	1.025	-10.078	3.651
2900	9.261	76.334	1.030	-10.078	3.561
3000	9.272	76.734	1.035	-10.078	3.481
3100	9.284	77.152	1.040	-10.078	3.411
3200	9.296	77.588	1.045	-10.078	3.351
3300	9.308	78.044	1.050	-10.078	3.291
3400	9.319	78.512	1.055	-10.078	3.241
3500	9.331	78.994	1.060	-10.078	3.191
3600	9.343	79.494	1.065	-10.078	3.151
3700	9.354	79.994	1.070	-10.078	3.111
3800	9.366	80.512	1.075	-10.078	3.071
3900	9.377	81.044	1.080	-10.078	3.031
4000	9.389	81.588	1.085	-10.078	3.001
4100	9.400	82.144	1.090	-10.078	2.971
4200	9.412	82.712	1.095	-10.078	2.941
4300	9.424	83.294	1.100	-10.078	2.911
4400	9.436	83.888	1.105	-10.078	2.881
4500	9.448	84.494	1.110	-10.078	2.851
4600	9.457	85.112	1.115	-10.078	2.821
4700	9.469	85.744	1.120	-10.078	2.791
4800	9.480	86.388	1.125	-10.078	2.761
4900	9.492	87.044	1.130	-10.078	2.731
5000	9.503	87.712	1.135	-10.078	2.701
5100	9.515	88.394	1.140	-10.078	2.671
5200	9.526	89.088	1.145	-10.078	2.641
5300	9.538	89.794	1.150	-10.078	2.611
5400	9.549	90.512	1.155	-10.078	2.581
5500	9.560	91.244	1.160	-10.078	2.551
5600	9.571	91.988	1.165	-10.078	2.521
5700	9.582	92.744	1.170	-10.078	2.491
5800	9.593	93.512	1.175	-10.078	2.461
5900	9.604	94.294	1.180	-10.078	2.431
6000	9.617	95.088	1.185	-10.078	2.401

Dec. 31, 1960 Mar. 31, 1966

CIMG

MOL. WT. = 59.765

(IDEAL GAS)

MAGNESIUM MONOCHLORIDE (MgCl)

Ground State Configuration $2\sum$ $\Delta H_f^0 = -10.34 \pm 10$ kcal. mole⁻¹
 $S_{298.15}^0 = 55.760$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^0 = -10.4 \pm 10$ kcal. mole⁻¹
 $S_{298.15}^0 = 55.760$ cal. deg.⁻¹ mole⁻¹ $\Delta H_f^0 = -10.4 \pm 10$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

ϵ_1 , cm. ⁻¹	$\frac{g_1}{2}$
0	1

$\omega_e = 462.4$ cm.⁻¹ $\sigma = 1$
 $\alpha_e = [0.0014]$ cm.⁻¹ $r_e = 2.199$ Å

Heat of Formation.

The heat of formation is calculated from $D_0^0 = 3.2$ e.v. reported by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York, 1950. $D_0^0 = 2.7 \pm 0.7$ e.v. reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London, 1953, yields ΔH_f^0 298 (MgCl, g) = 1.0 ± 16 kcal. mole⁻¹.

Heat Capacity and Entropy.

Spectroscopic constants were reported by Herzberg loc. cit. and adjusted for natural isotopic abundance. The bond length was reported by E. Morgan and R. P. Barrow, Nature 192, 1182, (1961). B_e and α_e were estimated by the method suggested by Herzberg loc. cit. The moment of inertia (I) is 11.578×10^{-59} g. cm.²

CIMG

(IDEAL GAS)

Ground State Configuration {¹Σ}

$S_{298.15}^{\circ} = [54.6 \pm 2] \text{ gibbs/mol}$

$\Delta H_f^{\circ} = 156 \pm 20 \text{ kcal/mol}$

$\Delta H_f^{\circ}_{298.15} = 156 \pm 20 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

State	$\epsilon_i, \text{cm}^{-1}$	g_i
$1\Sigma^+$	0	1
$3\Sigma_u^-$	[9000]	6
$1\Pi_u$	[11000]	2
$3\Sigma_g^-$	[20000]	3
1Δ	[25000]	2
$1\Sigma^+$	[30000]	1

$\omega_e x_e = [2] \text{ cm}^{-1}$ $\sigma = 1$

$B_e = [0.2415] \text{ cm}^{-1}$ $r_e = [2.2] \text{ \AA}$

Heat of Formation

The ionization potential of MgCl(g) was reported to be $7.2, 7.5 \pm 0.5$, and $7 \pm 1 \text{ eV}$ by Krasnov (1), Hildenbrand (2), and Beckett (2), respectively. The corresponding heats of formation at 298°K for MgCl(g) are derived as 156, 163, and 151 kcal/mol, using $\Delta H_f^{\circ}(\text{MgCl}, g) = -10.34 \text{ kcal/mol}$ from the JANAF MgCl(g) table (March 31, 1966). The value of $\Delta H_f^{\circ}_{298}$ for MgCl⁺(g) is tentatively selected as $156 \pm 20 \text{ kcal/mol}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as NaCl(g) which is isoelectronic with MgCl⁺(g). The six electronic states are obtained from Fougere (3). The corresponding electronic levels are estimated by comparison with the isoelectronic molecules BeS (4), BaO (5, 6), and HgO (5, 7). The bond distance is estimated by the method suggested by Krasnov (8). The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for MgCl(g) and NaCl(g). B_e and α_e are calculated by the method recommended by Herzberg (5). The moment of inertia is $1.159 \times 10^{-38} \text{ g cm}^2$. The enthalpy at 0°K is -2.27 kcal/mol .

References

1. K. S. Krasnov, *Teplotfiz. Vysokikh Temperatur*, Akad. Nauk SSSR **3**, 927 (1965).
2. C. W. Beckett and E. C. Cassidy, *Natl. Bur. Std. Rept.* 8628, 1 January 1965.
3. P. F. Fougere and R. K. Nesbet, *J. Chem. Phys.* **44**, 285 (1965).
4. G. Verhaegen and W. G. Richards, *Proc. Phys. Soc. (London)* **50**, 579 (1967).
5. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
6. G. Verhaegen and W. G. Richards, *J. Chem. Phys.* **45**, 1828 (1966).
7. L. Brewer and S. Trajmar, *J. Chem. Phys.* **36**, 1585 (1962).
8. K. S. Krasnov, *Zh. Strukt. Khim.* **1**, 209 (1960).
9. D. L. Hildenbrand, McDonnell Douglas Corporation, private communication, July 24, 1968.

June 30, 1968

Nitrosyl Chloride (NOCl)

(Ideal Gas) Mol. Wt. = 65.4591

CINO

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	Log K _p
0	-0.09	INFINITE	-	2.713	12.828	INFINITE	
100	8.357	52.217	1.947	-1.913	15.598	-29.716	
200	9.731	58.445	67.095	-	11.529	-15.055	
298	10.680	62.527	70.000	-	12.370	-11.561	
300	10.684	62.593	70.000	-	12.369	-11.525	
400	11.770	68.334	65.781	2.277	12.384	-7.925	
500	12.196	70.521	64.776	3.477	12.396	-7.023	
600	12.535	72.427	65.693	4.714	12.426	-6.377	
800	12.826	74.120	66.642	7.282	12.496	-5.890	
1000	13.073	75.599	67.600	10.000	12.580	-5.512	
1100	13.273	77.033	68.438	8.595	12.629	-5.204	
1200	13.446	78.306	69.278	9.931	12.703	-4.953	
1300	13.597	79.483	70.080	11.283	12.781	-4.742	
1400	13.726	80.578	70.846	12.649	12.862	-4.562	
1500	13.843	82.557	72.278	15.417	13.033	-4.272	
1600	14.035	83.459	72.949	16.816	13.121	-4.153	
1700	14.120	84.313	73.593	18.224	13.212	-4.047	
1800	14.195	85.122	74.211	19.640	13.303	-3.953	
1900	14.263	85.893	74.803	21.063	13.396	-3.868	
2000	14.325	86.625	75.379	22.493	13.490	-3.790	
2100	14.386	87.326	75.931	23.929	13.585	-3.719	
2200	14.458	87.997	76.464	25.372	13.680	-3.655	
2300	14.515	88.661	76.980	26.821	13.777	-3.596	
2400	14.568	89.318	77.481	28.275	13.874	-3.542	
2500	14.623	89.856	77.962	29.735	13.970	-3.490	
2600	14.675	90.430	78.430	31.200	14.068	-3.443	
2700	14.724	90.995	78.885	32.670	14.166	-3.399	
2800	14.770	91.544	79.328	34.144	14.263	-3.358	
2900	14.810	92.041	79.756	35.621	14.359	-3.320	
3000	14.856	92.544	80.174	37.108	14.458	-3.283	
3100	14.910	93.032	80.581	38.597	14.556	-3.249	
3200	14.957	93.506	80.978	40.090	14.653	-3.217	
3300	14.997	93.967	81.364	41.588	14.751	-3.187	
3400	15.039	94.416	81.740	43.089	14.849	-3.158	
3500	15.083	94.852	82.110	44.597	14.947	-3.130	
3600	15.126	95.277	82.470	46.107	15.044	-3.105	
3700	15.169	95.692	82.822	47.622	15.143	-3.080	
3800	15.211	96.098	83.166	49.141	15.243	-3.056	
3900	15.251	96.496	83.503	50.663	15.343	-3.032	
4000	15.292	96.880	83.832	52.191	15.443	-3.012	
4100	15.333	97.258	84.155	53.722	15.545	-2.991	
4200	15.371	97.628	84.471	55.257	15.648	-2.972	
4300	15.411	97.990	84.782	56.796	15.752	-2.953	
4400	15.451	98.346	85.088	58.338	15.856	-2.937	
4500	15.491	98.693	85.384	59.887	15.964	-2.917	
4600	15.530	99.033	85.677	61.438	16.074	-2.900	
4700	15.570	99.368	85.965	62.993	16.184	-2.884	
4800	15.608	99.698	86.246	64.552	16.297	-2.868	
4900	15.647	100.016	86.521	66.117	16.412	-2.853	
5000	15.688	100.335	86.789	67.681	16.529	-2.838	
5100	15.721	100.646	87.067	69.252	16.648	-2.824	
5200	15.766	100.952	87.331	70.826	16.771	-2.810	
5300	15.808	101.252	87.591	72.404	16.895	-2.797	
5400	15.850	101.548	87.842	73.982	17.019	-2.784	
5500	15.878	101.839	88.098	75.572	17.152	-2.771	
5600	15.911	102.125	88.346	77.161	17.283	-2.759	
5700	15.951	102.407	88.591	78.754	17.418	-2.747	
5800	15.990	102.685	88.831	80.351	17.557	-2.736	
5900	16.027	102.959	89.068	81.952	17.696	-2.726	
6000	16.066	103.228	89.302	83.558	17.841	-2.713	

June 30, 1961, Dec. 31, 1965

NITROSYL CHLORIDE (NOCl)

(IDEAL GAS)

MOL. WT. = 65.4591

Point Group C_∞ $\Delta H_f^o = 12.83 \pm 0.2$ kcal. mole⁻¹ $\Delta H_f^o = 298.15 \pm 0.2$ kcal. mole⁻¹ $S_{298.15}^o = 62.53$ cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies & Degeneracies

 ω , cm.⁻¹

1800 (1)

594.9 (1)

331.5 (1)

Bond Distance: N-Cl = 1.95 ± 0.06 ÅBond Angle: Cl-N-O = $114 \pm 3^\circ$ Product of the Moments of Inertia: $I_A I_B I_C = 2.278778 \times 10^{-115}$ g.³ cm.⁶ $\sigma = 1$

Heat of Formation.

The equilibrium constants for the reaction $2\text{NOCl}(g) = 2\text{NO}(g) + \text{Cl}_2(g)$ have been measured in the temperature range from 372° to 491° K. by C. M. Beeson and D. M. Yost, J. Chem. Phys. **2**, 44 (1938). Using the reported equilibrium constants, the heat of reaction (ΔH_r^o) has been calculated by both the second and the third law methods, as 16.33 ± 0.1 kcal. mole⁻¹ and 18.42 ± 0.1 kcal. mole⁻¹, respectively. The third law value is adopted to calculate the heat of formation of nitrosyl chloride (g) as $\Delta H_f^o = 12.37 \pm 0.2$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The selected bond distances and angle were obtained from the microwave measurements by J. D. Rogers and D. Williams, J. Chem. Phys. **34**, 2195 (1961). J. A. A. Ketelaar and K. J. Palmer, J. Am. Chem. Soc. **59**, 2629 (1937), reported the bond distance N-Cl = 1.95 Å and the angle O-N-Cl = 116° by the electron diffraction method. These two are in good agreement. The three principal moments of inertia are $I_A = 0.995 \times 10^{-59}$, $I_B = 14.6885 \times 10^{-59}$ and $I_C = 15.6780 \times 10^{-59}$ g. cm.². The selected vibrational frequencies which were obtained from the infrared spectrum by L. Landau and W. H. Fletcher, J. Mol. Spectry. **4**, 276 (1960), have been modified to natural isotopic mixture. W. G. Burns and J. J. Bernstein, J. Chem. Phys. **18**, 1669 (1950), reported the vibrational frequencies as 1799, 592 and 332 cm.⁻¹.

J. S. Gordon, J. Chem. Eng. Data **7**, 82 (1962), has calculated the thermodynamic functions from 298.15° to 6000° K. by the method of R. E. Fennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from Landau and Fletcher, loc. cit., and J. D. Rogers, W. J. Pietenpol and D. Williams, Phys. Rev. **85**, 431 (1951). These calculated functions have been adopted in the tabulation. Below 298° K. the rigid-rotator harmonic oscillator method was used to calculate the functions.

CINO

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _f
0	-0.00	0.00	INFINITE	-2.916	4.102	4.102	INFINITE	
100	8.441	53.818	74.938	-2.112	3.590	6.525	-14.261	
200	10.744	60.355	66.133	-1.156	3.154	9.644	-10.538	
298	12.712	65.030	65.030	-0.000	2.900	12.889	-9.447	
300	12.744	65.108	65.030	0.024	2.897	12.951	-9.434	
400	14.408	72.312	66.577	1.847	2.475	15.415	-7.545	
500	15.408	75.332	66.577	2.863	2.452	17.716	-6.617	
600	16.291	75.193	67.777	4.450	2.794	23.106	-5.416	
700	16.966	77.757	69.023	6.134	2.877	26.485	-4.269	
800	17.485	80.058	70.261	7.838	2.988	29.849	-3.154	
900	17.881	82.116	71.467	9.540	3.077	33.141	-2.061	
1000	18.250	84.043	72.651	11.242	3.263	36.534	-0.984	
1100	18.448	85.790	73.749	13.245	3.414	39.853	-0.918	
1200	18.648	87.404	74.820	15.100	3.571	43.159	-0.860	
1300	18.809	88.903	75.847	16.873	3.731	46.452	-0.809	
1400	18.942	90.311	76.821	18.582	3.894	49.745	-0.762	
1500	19.052	91.613	77.772	20.261	4.053	53.000	-0.712	
1600	19.144	92.845	78.676	22.671	4.214	56.259	-0.664	
1700	19.222	94.008	79.544	24.589	4.375	59.508	-0.650	
1800	19.286	95.109	80.378	26.251	4.531	62.747	-0.618	
1900	19.339	96.147	81.167	27.805	4.681	65.978	-0.585	
2000	19.394	97.147	81.955	30.383	4.836	69.197	-0.561	
2100	19.436	98.094	82.701	32.325	4.984	72.412	-0.536	
2200	19.474	98.999	83.422	34.270	5.125	75.619	-0.512	
2300	19.506	99.865	84.118	36.220	5.265	78.811	-0.489	
2400	19.533	100.694	84.782	38.172	5.402	81.990	-0.467	
2500	19.561	101.494	85.444	40.126	5.526	85.205	-0.448	
2600	19.584	102.262	86.076	42.084	5.650	88.390	-0.429	
2700	19.604	103.001	86.689	44.043	5.768	91.571	-0.412	
2800	19.622	103.715	87.284	46.004	5.880	94.745	-0.395	
2900	19.639	104.404	87.867	47.967	5.988	97.911	-0.379	
3000	19.654	105.070	88.426	49.932	6.089	101.086	-0.364	
3100	19.668	105.714	88.973	51.898	6.186	104.253	-0.349	
3200	19.680	106.334	89.506	53.866	6.276	107.412	-0.336	
3300	19.691	106.945	90.025	55.834	6.361	110.570	-0.322	
3400	19.700	107.534	90.529	57.804	6.441	113.728	-0.309	
3500	19.711	108.104	91.025	59.774	6.516	116.880	-0.298	
3600	19.720	108.659	91.508	61.746	6.587	120.037	-0.287	
3700	19.728	109.200	91.978	63.718	6.652	123.185	-0.276	
3800	19.735	109.726	92.439	65.692	6.713	126.335	-0.266	
3900	19.741	110.241	92.890	67.664	6.770	129.480	-0.256	
4000	19.748	110.738	93.329	69.640	6.822	132.628	-0.246	
4100	19.754	111.226	93.759	71.615	6.870	135.772	-0.237	
4200	19.760	111.702	94.181	73.591	6.915	138.914	-0.228	
4300	19.765	112.167	94.594	75.567	6.957	142.050	-0.219	
4400	19.770	112.623	94.996	77.544	6.997	145.182	-0.210	
4500	19.774	113.066	95.395	79.521	7.028	148.339	-0.204	
4600	19.778	113.501	95.784	81.499	7.061	151.482	-0.197	
4700	19.782	113.926	96.165	83.477	7.089	154.622	-0.190	
4800	19.786	114.343	96.540	85.455	7.116	157.762	-0.183	
4900	19.789	114.751	96.911	87.433	7.143	160.902	-0.176	
5000	19.793	115.151	97.268	89.413	7.169	164.029	-0.169	
5100	19.796	115.542	97.622	91.392	7.182	167.174	-0.164	
5200	19.799	115.927	97.971	93.372	7.201	170.306	-0.157	
5300	19.802	116.304	98.313	95.352	7.217	173.459	-0.152	
5400	19.804	116.674	98.644	97.332	7.232	176.612	-0.146	
5500	19.807	117.038	98.981	99.313	7.246	179.718	-0.141	
5600	19.809	117.395	99.306	101.294	7.257	182.848	-0.136	
5700	19.811	117.745	99.627	103.275	7.268	185.985	-0.131	
5800	19.813	118.090	99.942	105.256	7.277	189.125	-0.126	
5900	19.815	118.431	100.256	107.236	7.285	192.265	-0.121	
6000	19.817	118.762	100.558	109.210	7.292	195.392	-0.117	

Dec. 31, 1962; Dec. 31, 1985

Point Group C_{2v} $\Delta H_f^\circ = 4.20 \pm 0.4 \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ = 298.15 = 2.90 \pm 0.4 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = 65.0 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
1293 (1)	1085 (1)
794 (1)	411 (1)
367 (1)	651 (1)

Bond Distances: N-Cl = 1.83 Å N-O = 1.21 Å

Bond Angles: O-N-O = 129.5° O-N-Cl = 115.25°

Product of Moments of Inertia: $I_A I_B I_C = 2.36688 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The selected heat of formation was obtained from the recalculation of the heat of reaction $\text{ClNO}_2 + \text{NO} = \text{ClNO} + \text{NO}_2$ which has been measured calorimetrically as $-9.27 \text{ kcal. mole}^{-1}$ by J. Ray and R. Ogg, Jr., J. Chem. Phys. **33**, 168 (1959). Not only the thermal effects of $2\text{NO}_2 = \text{N}_2\text{O}_4$ but also $\text{NO} + \text{NO}_2 = \text{N}_2\text{O}_3$ (a minor one) have been considered in calculation. Using all JANAF auxiliary data for ClNO , NO , NO_2 , N_2O_3 and N_2O_4 , the recalculation gives $\Delta H_f^\circ = 2.90 \pm 0.4 \text{ kcal. mole}^{-1}$ for $\text{NO}_2\text{Cl(g)}$. For the reaction $\text{ClNO} + \text{H}_2\text{O}_2 = \text{ClNO}_2 + 2\text{NO}_2$ also measured by Ray and Ogg, loc. cit., the recalculation gives $\Delta H_f^\circ = 2.56 \pm 0.4 \text{ kcal. mole}^{-1}$.

H. Martin and E. Koshlein, Z. physik. Chem. **17**, 375 (1958), have determined kinetically the heat of reaction, $\Delta H_f^\circ = 2.75 \pm 0.1 \text{ kcal. mole}^{-1}$, for the reaction $\text{NO}_2 + \text{NOCl} = \text{NO} + \text{NO}_2\text{Cl}$ which gives $\Delta H_f^\circ = 1.90 \pm 1 \text{ kcal. mole}^{-1}$ for $\text{NO}_2\text{Cl(g)}$. H. Cordes and H. Johnston, J. Am. Chem. Soc., **76**, 4264 (1954), have also determined kinetically the $\Delta H_f^\circ = 29.5 \text{ kcal. mole}^{-1}$ for the reaction $\text{NO}_2\text{Cl} = \text{NO}_2 + \text{Cl}$ which gives $\Delta H_f^\circ = 6.3 \pm 0.3 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The selected bond distances and bond angles were obtained from microwave spectrum studies by L. Clayton, Q. Williams and T. L. Weatherly, J. Chem. Phys. **30**, 1328 (1959). D. J. Millen and K. M. Simmott, J. Chem. Soc. **350** (1958), reported bond distance N-Cl = 1.840 Å, N-O = 1.202 Å and angle ONO = 130° 35' from the microwave measurement. These two are in good agreement.

The selected vibrational frequencies were obtained from infrared and Raman spectrum measurements by R. Ryanon and M. K. Wilson, J. Chem. Phys. **22**, 2000 (1954). However, the assignment of the fundamental frequencies has been revised by R. E. Dodd, J. A. Rolfe and L. A. Woodward, Trans. Faraday Soc. **52**, 145 (1956), and Y. Morino and T. Tanaka, J. Mol. Spectry. **15**, 179 (1965). Morino and Tanaka's assignment was adopted. The three principal moments of inertia are $I_A = 6.3568 \times 10^{-39}$, $I_B = 16.3809 \times 10^{-39}$ and $I_C = 22.7267 \times 10^{-39} \text{ g. cm.}^2$.

Sodium Chloride (NaCl)

(Crystal) Mol. Wt. = 58.448

CINA

MOL. WT. = 58.448

(CRYSTAL)

SODIUM CHLORIDE (NaCl)

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	8.349	4.000	INFINITE	-2.536	-98.158	-98.158	INFINITE
100	8.349	5.670	27.281	-2.161	-98.454	-96.192	210.218
200	11.203	12.573	18.319	-1.469	-98.369	-93.043	102.051
298	12.072	17.236	17.236	0.000	-98.260	-91.788	67.279
300	12.080	17.311	17.236	0.022	-98.257	-91.748	66.835
400	12.512	20.648	17.716	1.253	-98.786	-89.546	48.923
500	12.692	23.681	18.635	2.523	-98.683	-87.246	38.133
600	13.259	26.064	19.679	3.631	-98.531	-84.972	30.950
700	13.672	28.338	20.743	5.777	-98.353	-82.700	21.906
800	14.059	30.539	21.829	8.015	-97.764	-78.339	15.022
900	14.478	31.699	22.793	9.015	-97.388	-76.200	10.653
1000	15.503	33.293	23.764	9.529	-97.388	-76.200	10.653
1100	16.330	34.809	24.700	11.420	-96.941	-74.104	14.722
1200	17.200	36.268	25.604	12.457	-119.652	-71.051	11.969
1300	18.250	37.689	26.483	13.527	-117.966	-63.714	9.946
1400	18.530	39.029	27.327	16.382	-117.966	-63.714	9.946
1500	18.940	40.322	28.151	18.257	-117.041	-59.870	8.723

$$\Delta H_f^0 = -98.16 \pm 0.08 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{298.15} = -98.26 \pm 0.08 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 6.73 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 17.24 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1073.8 \pm 1.0^\circ\text{K.}$$

Heat of Formation.

The heat of formation is based on $\Delta H_f^{298.15} = -57.39$ and $-39.95 \text{ kcal. mole}^{-1}$ for $\text{Na}^+(\infty \text{H}_2\text{O})$ and $\text{Cl}^-(\infty \text{H}_2\text{O})$, respectively, and on the heat of solution $\Delta H_{\text{sol}}^{298.15} = 0.922 \text{ kcal. mole}^{-1}$ for NaCl. These values were reported in a private communication from D. D. Wagman, National Bureau of Standards, June, 1964.

Heat Capacity and Entropy.

The low temperature values are based on the heat capacities (3-266°K) reported by T. H. K. Barron, A. J. Leadbetter, J. A. Morrison, Proc. Roy. Soc. (London) A279 (1376), 62 (1964). The earlier work of K. Clusius, J. Goldman, A. Perlick, Z. Naturforsch. 48, 424 (1949), results in a slightly higher entropy ($S_{298.15}^0 = 17.35 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$) but a lower heat capacity at room temperature ($C_p^{298.15} = 11.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$). The high temperature values have been obtained by reanalysis of the enthalpies (672 - 1279°K) of R. Dawson, E. B. Brackett, T. E. Brackett, J. Phys. Chem. 67, 1669 (1963), using the new value for $C_p^{298.15}$. The resulting tables agree within $\pm 0.1 \text{ kcal.}$ with the enthalpies (312 - 1058°K) of W. A. Roth, W. Bertram, Z. Elektrochem. 35, 38 (1929). The enthalpies (540 - 1037°K) of A. Magnus, Physik. Zeitschr. 14, 5 (1913), agree well at the lower temperatures but are about 0.3 kcal. smaller near the melting point.

Melting Data.

The melting temperature was taken from Dawson, Brackett and Brackett, loc. cit., and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of $T_m = 1073^\circ\text{K.}$ and $\Delta H_m^0 = 6.69 \pm 0.06 \text{ kcal. mole}^{-1}$ were reported by A. S. Dworkin, M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

Heat of Sublimation.

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details see the tables for NaCl gases).

CINA

Sodium Chloride (NaCl)

CINa

(Liquid) Mol. Wt. = 58.448

SODIUM CHLORIDE (NaCl)

(LIQUID)

MOL. WT. = 58.448

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
cal. mole ⁻¹ deg. ⁻¹ kcal. mole ⁻¹							
100							
200							
298	12.072	22.719	22.719	0.000	- 92.237	- 87.400	64.063
300	12.080	22.704	22.719	+0.22	- 92.234	- 87.370	63.646
400	12.512	26.331	23.199	1.253	- 92.763	- 85.716	46.831
500	12.892	29.164	24.118	2.523	- 92.660	- 83.964	36.699
600	13.259	31.947	25.162	3.831	- 92.508	- 82.239	29.954
700	13.522	34.671	26.228	5.177	- 92.303	- 79.879	21.548
800	13.740	37.349	27.368	6.568	- 91.979	- 77.273	18.763
900	13.920	39.980	28.501	8.377	- 91.579	- 74.460	16.552
1000	14.070	42.570	29.627	10.140	- 91.100	- 71.400	14.755
1100	14.190	45.120	30.754	11.843	- 90.550	- 68.100	13.260
1200	14.290	47.640	31.881	13.497	- 90.000	- 64.600	11.960
1300	14.370	50.130	33.008	15.102	- 89.400	- 60.900	10.760
1400	14.440	52.590	34.135	16.657	- 88.750	- 57.100	9.660
1500	14.500	55.020	35.262	18.162	- 88.050	- 53.200	8.660
1600	14.550	57.430	36.389	19.617	- 87.300	- 49.200	7.760
1700	14.600	59.810	37.516	21.022	- 86.500	- 45.100	6.960
1800	14.640	62.160	38.643	22.377	- 85.650	- 40.900	6.260
1900	14.680	64.490	39.770	23.682	- 84.750	- 36.600	5.660
2000	14.710	66.800	40.897	24.937	- 83.800	- 32.200	5.160
2100	14.740	69.090	42.024	26.142	- 82.800	- 27.700	4.760
2200	14.770	71.360	43.151	27.297	- 81.750	- 23.100	4.460
2300	14.800	73.610	44.278	28.402	- 80.650	- 18.400	4.260
2400	14.820	75.840	45.405	29.457	- 79.500	- 13.600	4.160
2500	14.840	78.060	46.532	30.462	- 78.300	- 8.700	4.160

Heat of Formation.

ΔH_f^o(l) was obtained from ΔH_f^o(c) by addition of ΔH_m^o and the difference between (H_{1073.8}^o - H_{298.15}^o) for the crystal and liquid.

Heat Capacity and Entropy.

These were obtained by analysis of the enthalpies (1076 - 1279°K) of R. Dawson, E. B. Brackett, T. E. Brackett, J. Phys. Chem. 67, 1669 (1963). The heat capacity was extrapolated to a constant value of 16.0 at the higher temperatures. A glass transition was assumed at 600°K. and below this temperature C_p was taken equal to that of the crystal.

Melting Data.

The melting temperature was taken from Dawson, Brackett and Brackett, loc. cit., and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of T_m = 1073°K. and ΔH_m^o = 6.69 ± 0.06 kcal. mole⁻¹ were reported by A. S. Dworkin, M. A. Bregie, J. Phys. Chem. 64, 269 (1960).

Heat of Sublimation.

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details see the tables for NaCl gases).

CINa

(Ideal Gas) Mol. Wt. = 58.448

T, °K.	C _p (cal. mole ⁻¹ deg. ⁻¹)	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ (kcal. mole ⁻¹)	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+0.00	INFINITE	-2.208	-43.020	-43.020	INFINITE
100	7.258	46.193	-2.208	-43.020	-43.020	97.869
200	8.258	52.193	-2.208	-43.020	-43.020	97.869
300	8.553	54.657	-2.208	-43.020	-43.020	97.869
400	8.558	54.950	-2.208	-43.020	-43.020	97.869
500	8.479	57.441	-2.208	-43.020	-43.020	97.869
600	8.484	59.406	-2.208	-43.020	-43.020	97.869
700	8.491	61.026	-2.208	-43.020	-43.020	97.869
800	8.496	62.405	-2.208	-43.020	-43.020	97.869
900	8.496	63.605	-2.208	-43.020	-43.020	97.869
1000	8.496	64.668	-2.208	-43.020	-43.020	97.869
1100	8.496	65.622	-2.208	-43.020	-43.020	97.869
1200	8.496	66.487	-2.208	-43.020	-43.020	97.869
1300	8.496	67.278	-2.208	-43.020	-43.020	97.869
1400	8.496	68.008	-2.208	-43.020	-43.020	97.869
1500	8.496	68.686	-2.208	-43.020	-43.020	97.869
1600	8.496	69.318	-2.208	-43.020	-43.020	97.869
1700	8.496	69.910	-2.208	-43.020	-43.020	97.869
1800	8.496	70.468	-2.208	-43.020	-43.020	97.869
1900	8.496	71.005	-2.208	-43.020	-43.020	97.869
2000	8.496	71.525	-2.208	-43.020	-43.020	97.869
2100	8.496	72.031	-2.208	-43.020	-43.020	97.869
2200	8.496	72.525	-2.208	-43.020	-43.020	97.869
2300	8.496	73.008	-2.208	-43.020	-43.020	97.869
2400	8.496	73.481	-2.208	-43.020	-43.020	97.869
2500	8.496	73.945	-2.208	-43.020	-43.020	97.869
2600	8.496	74.400	-2.208	-43.020	-43.020	97.869
2700	8.496	74.846	-2.208	-43.020	-43.020	97.869
2800	8.496	75.284	-2.208	-43.020	-43.020	97.869
2900	8.496	75.714	-2.208	-43.020	-43.020	97.869
3000	8.496	76.137	-2.208	-43.020	-43.020	97.869
3100	8.496	76.553	-2.208	-43.020	-43.020	97.869
3200	8.496	76.962	-2.208	-43.020	-43.020	97.869
3300	8.496	77.364	-2.208	-43.020	-43.020	97.869
3400	8.496	77.759	-2.208	-43.020	-43.020	97.869
3500	8.496	78.147	-2.208	-43.020	-43.020	97.869
3600	8.496	78.528	-2.208	-43.020	-43.020	97.869
3700	8.496	78.902	-2.208	-43.020	-43.020	97.869
3800	8.496	79.270	-2.208	-43.020	-43.020	97.869
3900	8.496	79.632	-2.208	-43.020	-43.020	97.869
4000	8.496	79.989	-2.208	-43.020	-43.020	97.869
4100	8.496	80.341	-2.208	-43.020	-43.020	97.869
4200	8.496	80.688	-2.208	-43.020	-43.020	97.869
4300	8.496	81.031	-2.208	-43.020	-43.020	97.869
4400	8.496	81.370	-2.208	-43.020	-43.020	97.869
4500	8.496	81.705	-2.208	-43.020	-43.020	97.869
4600	8.496	82.036	-2.208	-43.020	-43.020	97.869
4700	8.496	82.363	-2.208	-43.020	-43.020	97.869
4800	8.496	82.686	-2.208	-43.020	-43.020	97.869
4900	8.496	83.006	-2.208	-43.020	-43.020	97.869
5000	8.496	83.322	-2.208	-43.020	-43.020	97.869
5100	8.496	83.635	-2.208	-43.020	-43.020	97.869
5200	8.496	83.945	-2.208	-43.020	-43.020	97.869
5300	8.496	84.252	-2.208	-43.020	-43.020	97.869
5400	8.496	84.556	-2.208	-43.020	-43.020	97.869
5500	8.496	84.857	-2.208	-43.020	-43.020	97.869
5600	8.496	85.155	-2.208	-43.020	-43.020	97.869
5700	8.496	85.450	-2.208	-43.020	-43.020	97.869
5800	8.496	85.742	-2.208	-43.020	-43.020	97.869
5900	8.496	86.031	-2.208	-43.020	-43.020	97.869
6000	8.496	86.317	-2.208	-43.020	-43.020	97.869

MOL. WT. = 58.448

(IDEAL GAS)

Ground State Configuration $1s^2 2s^2 2p^6 3s^2 3p^6$
 $\Delta H_f^0 = -43.02 \pm 0.5$ kcal. mole⁻¹
 $\Delta H_f^0 = -43.36 \pm 0.5$ kcal. mole⁻¹
 $\Delta H_f^0 = -43.36 \pm 0.5$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

$$\frac{E_i}{0} = \frac{E_i}{1}$$

$\sigma = 1$

$r_e = 2.3606 \text{ \AA}$

Heat of Formation

The heat of formation is based on a heat of sublimation $\Delta H_g^0 = 54.9$ kcal. mole⁻¹ obtained from the more consistent sets of vapor pressure data by correction for the presence of dimer. Observed vapor pressures were converted to monomer pressures by use of dimer-monomer ratios calculated from JANAF free energy functions and $\Delta H_f^0 = 48.6$ kcal. for the reaction $(NaCl)_2(g) \rightarrow 2NaCl(g)$. Higher polymeric species were neglected. Analyses of the resulting monomer pressures are summarized below.

Heat of Sublimation
 $\Delta H_g^0 = 54.9$ kcal. mole⁻¹

Temperature Range (°K)

2nd Law

3rd Law

743 - 948*
55.35
54.94
760 - 897*
55.15
54.91
890 - 944*
49.6
55.37
893 - 973*
52.6
55.03
1340 - 1540**
56.67
54.68
1250 - 1428**
56.85
54.98
1429 - 1720**
60.0
54.45
1433 - 1723**
59.5
54.44

**total pressures over liquid

*Knudsen effusion measurements over crystal

1) A. N. Nemeyanov, L. A. Sazonov, Zhur. Neorg. Khim. **2**, 946 (1957).

2) B. H. Zimm, J. E. Mayer, J. Chem. Phys. **12**, 362 (1944).

3) J. E. Mayer, J. H. Mintner, J. Chem. Phys. **5**, 301 (1935).

4) K. Nawa, J. Fac. Sci., Hokkaido Univ., Ser. III, **2**, 201 (1935).

5) J. L. Barton, H. Bloom, J. Phys. Chem. **60**, 1413 (1956).

6) E. F. Flock, M. H. Rodebush, J. Am. Chem. Soc. **48**, 2522 (1926).

7) H. von Martenberg, P. Albrecht, Z. Elektrochem. **27**, 162 (1921).

8) O. Ruff, S. Mugdan, Z. anorg. allgem. Chem. **117**, 147 (1921).

Heat Capacity and Entropy

The molecular constants are based on molecular beam studies of the rotational spectra by Clouser and Gordy, Bull. Am. Phys. Soc. **9**, 326 (1963) and on microwave studies by Honig, Mandel, Stinch and Townes, Phys. Rev. **96**, 629 (1954). The infrared spectra of Rice and Kempner, J. Chem. Phys. **21**, 573 (1957) give a frequency in close agreement (366 cm⁻¹).

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100	26,600	34,000	+000	- 91.480	- 60.785	44.555
200	26,700	34,001	+009	- 91.476	- 60.595	44.161
300	26,700	34,001	+009	- 91.476	- 60.595	44.161
400	32,500	42,622	35,115	- 91.704	- 50.300	27.482
500	35,900	50,256	37,395	- 90.905	- 40.034	17.498
600	38,300	62,774	40,207	- 86.515	- 30.065	10.951
700	40,207	74,959	43,948	- 85.285	- 20.752	6.479
800	41,800	86,800	47,600	- 84.000	- 11.400	3.000
900	43,400	98,350	50,600	- 82.396	- 2.680	1.651
1000	44,700	109,991	53,782	- 80.782	- 6.092	1.331
1100	45,900	121,727	56,727	- 79.073	- 14.694	2.919
1200	47,000	133,559	59,529	- 77.346	- 23.506	4.298
1300	48,000	145,400	62,200	- 75.598	- 32.318	5.677
1400	49,000	157,253	64,756	- 73.830	- 41.130	7.056
1500	50,000	169,110	67,204	- 72.042	- 49.942	8.435

Heat Capacity and Entropy.

Heat capacities and S°_{298.15} were estimated by comparison with those for NaClO₃(c) and KClO₄(c), respectively.

Transition Data.

T_c was reported in the National Bureau of Standards, Circ. 500, loc. cit. ΔH_c was estimated from that for KClO₄(c).

Temperature of Melting.

T_m was obtained from Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use," June 1949.

ΔH_f^o = Unknown

S°_{298.15} = [34] cal. deg.⁻¹ mole⁻¹

T_c = 581°K.

ΔH_c^o = [3.34] kcal. mole⁻¹

T_m = 755°K.

ΔH_m^o = Unknown

Heat of Formation.

A. A. Gilliland and W. H. Johnson, J. Res. Natl. Bur. Std. 65A, 67 (1961) measured the heat of solution of NaClO₄(c) and gave ΔH_f^o 298.15 = -91.48 ± 0.22 kcal. mole⁻¹ for NaClO₄(c). The heat of dilution of NaClO₄(c) was measured by C. E. Vanderveer and J. A. Swenson, J. Phys. Chem. 67, 285 (1963). The data led to ΔH_f^o 298.15 = -91.464 kcal. mole⁻¹ which agrees very well with the data reported by A. A. Gilliland and W. H. Johnson, loc. cit. The value of ΔH_f^o 298.15 was reported to be -92.18 kcal. mole⁻¹ in the National Bureau of Standards Circ. 500, "Selected Values of Chemical Thermodynamic Properties," 1952, based upon the data prior to 1950. A. P. Vorob'ev, et al., Proc. Acad. Sci. USSR, 135, 1439 (1960) measured the heat of decomposition of NaClO₄(c) into NaCl(c) and O₂(g) and gave ΔH_f^o 298.15 = -90.68 ± 0.3 kcal. mole⁻¹ for NaClO₄(c). The value reported by A. A. Gilliland and W. H. Johnson, loc. cit. was used.

Chlorine Monoxide (ClO)

(Ideal Gas) Mol. Wt. = 51.457

CHLORINE MONOXIDE (ClO)

(IDEAL GAS)

MOL. WT. = 51.457

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	6.959	46.371	2.115	24.211	INFINITE
200	7.125	46.371	1.420	23.968	52.226
298	7.300	46.371	1.000	23.690	1.077
300	7.308	46.371	1.000	23.690	1.077
400	7.508	54.191	0.14	24.192	16.968
500	7.942	54.446	1.769	24.197	12.562
600	8.259	58.224	1.599	24.214	9.917
700	8.429	59.743	2.432	24.236	8.153
800	8.571	61.054	3.263	24.258	6.891
900	8.676	62.205	4.145	24.279	5.944
1000	8.754	63.232	5.017	24.296	5.207
1100	8.816	64.156	5.865	24.316	4.616
1200	8.865	65.000	6.780	24.333	4.133
1300	8.906	65.773	7.668	24.347	3.730
1400	8.941	66.488	8.561	24.360	3.389
1500	8.971	67.151	9.456	24.372	3.096
1600	8.998	67.771	10.355	24.382	2.843
1700	9.022	68.353	11.256	24.390	2.621
1800	9.044	68.900	12.159	24.398	2.425
1900	9.063	69.409	13.065	24.404	2.250
2000	9.100	70.375	14.861	24.409	2.094
2100	9.117	70.819	15.782	24.410	1.954
2200	9.133	71.244	16.702	24.407	1.827
2300	9.146	71.650	17.619	24.404	1.711
2400	9.163	72.040	18.534	24.398	1.606
2500	9.178	72.414	19.451	24.389	1.510
2600	9.192	72.774	20.370	24.379	1.421
2700	9.206	73.122	21.290	24.366	1.339
2800	9.219	73.457	22.211	24.350	1.263
2900	9.232	73.780	23.133	24.332	1.192
3000	9.245	74.094	24.057	24.312	1.127
3100	9.258	74.397	24.982	24.289	1.066
3200	9.271	74.691	25.909	24.263	1.009
3300	9.283	74.976	26.836	24.235	0.955
3400	9.295	75.254	27.765	24.205	0.905
3500	9.308	75.523	28.696	24.173	0.858
3600	9.320	75.786	29.627	24.139	0.813
3700	9.332	76.041	30.559	24.102	0.772
3800	9.344	76.290	31.493	24.065	0.732
3900	9.356	76.533	32.428	24.025	0.695
4000	9.368	76.770	33.364	23.983	0.661
4100	9.379	77.002	34.302	23.941	0.625
4200	9.391	77.228	35.240	23.897	0.593
4300	9.403	77.449	36.180	23.852	0.563
4400	9.415	77.665	37.121	23.806	0.534
4500	9.426	77.877	38.063	23.759	0.507
4600	9.438	78.084	39.006	23.712	0.480
4700	9.449	78.287	39.950	23.664	0.455
4800	9.461	78.486	40.896	23.616	0.432
4900	9.472	78.682	41.843	23.568	0.409
5000	9.484	78.873	42.790	23.519	0.387
5100	9.495	79.061	43.739	23.471	0.366
5200	9.506	79.245	44.689	23.423	0.346
5300	9.518	79.427	45.641	23.376	0.326
5400	9.529	79.605	46.593	23.328	0.308
5500	9.541	79.780	47.546	23.281	0.290
5600	9.552	79.952	48.501	23.235	0.273
5700	9.563	80.121	49.457	23.188	0.256
5800	9.574	80.287	50.414	23.143	0.240
5900	9.586	80.451	51.372	23.098	0.225
6000	9.597	80.612	52.331	23.054	0.210

June 30, 1961

$D_0 = 63.35 \pm 0.03$ kcal. mole⁻¹
 $\Delta H_f^\circ 298.15 = 24.19 \pm 0.05$ kcal. mole⁻¹
 $S^\circ 298.15 = 54.145$ cal. deg.⁻¹ mole⁻¹
 Ground State Configuration $2\Pi_{3/2}$

Electronic Level and Multiplicity

$$\frac{E_i}{0} \quad \frac{E_i}{4}$$

$\omega_e x_e = 7.5$ cm.⁻¹
 $\omega_e = 866 \pm 26$ cm.⁻¹
 $B_e = 0.645(3)$
 $\alpha_e = [0.0069]$ cm.⁻¹
 $D_e = 2(2) \times 10^{-6}$ cm.⁻¹
 $r_e = 1.546 \text{ \AA}$
 $\sigma = 1$

Heat of Formation

R. A. Durie and D. A. Ramsay, Can. J. Phys. 35, 35 (1958) and G. Herzberg and D. A. Ramsay, Disc. Faraday Soc. 9, 80 (1950) report $D_0 = 22152 \pm 10$ cm.⁻¹ and $D_0 = 22141$ cm.⁻¹ respectively, and these values have been averaged.

Heat Capacity and Entropy

The spectroscopic constants are for the natural mixture of isotopes and are based on measurements by Durie and Ramsay, loc. cit., and by G. Porter, Disc. Faraday Soc. 9, 60 (1950). α_e has been estimated by the method given by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Company, Inc., New York, 1950, p. 108.

Titanium Oxide Chloride (TiOCl)

(Ideal Gas) Mol. Wt. = 99.357

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	0.000	INFINITE	INFINITE	-	2.902	- 57.998	INFINITE
100	6.756	51.462	73.018	-	2.156	- 56.707	128.208
200	11.049	36.318	64.084	-	1.513	- 56.248	64.755
298	12.346	62.992	62.992	-	+0.00	- 56.360	43.779
300	12.345	63.049	62.992	-	-0.23	- 56.382	43.515
400	13.170	66.744	63.688	-	1.303	- 56.493	32.673
500	13.671	69.742	64.449	-	2.647	- 56.590	26.476
600	13.993	72.266	65.547	-	4.031	- 56.690	22.205
700	14.208	74.440	66.666	-	5.442	- 56.802	19.149
800	14.357	76.247	67.759	-	6.871	- 56.925	16.832
900	14.453	77.700	68.811	-	8.319	- 57.058	14.801
1000	14.543	79.573	69.811	-	9.762	- 57.211	13.625
1100	14.602	80.962	70.762	-	11.220	- 57.375	12.448
1200	14.649	82.235	71.666	-	12.682	- 57.507	11.456
1300	14.675	83.409	72.519	-	14.149	- 57.607	10.676
1400	14.684	84.484	73.319	-	15.619	- 57.687	9.976
1500	14.738	85.514	74.019	-	17.092	- 57.741	9.243
1600	14.758	86.466	74.562	-	18.567	- 57.776	8.685
1700	14.774	87.361	75.043	-	20.043	- 57.799	8.191
1800	14.786	88.200	75.466	-	21.501	- 57.811	7.755
1900	14.800	89.006	75.833	-	22.941	- 57.819	7.368
2000	14.810	89.765	77.124	-	24.361	- 57.822	6.987
2100	14.819	90.488	78.125	-	25.663	- 57.826	6.642
2200	14.826	91.178	78.702	-	26.945	- 57.831	6.328
2300	14.833	91.833	79.257	-	28.207	- 57.836	6.041
2400	14.838	92.459	79.793	-	29.452	- 57.841	5.776
2500	14.844	93.074	80.310	-	30.686	- 57.846	5.531
2600	14.848	93.656	80.818	-	31.906	- 57.851	5.305
2700	14.852	94.217	81.304	-	33.113	- 57.856	5.094
2800	14.856	94.758	81.769	-	34.307	- 57.861	4.895
2900	14.859	95.278	82.213	-	35.487	- 57.866	4.715
3000	14.862	95.782	82.675	-	36.653	- 57.871	4.543
3100	14.865	96.269	83.105	-	37.806	- 57.876	4.382
3200	14.867	96.741	83.524	-	38.946	- 57.881	4.230
3300	14.869	97.198	83.924	-	40.073	- 57.886	4.087
3400	14.871	97.643	84.323	-	41.187	- 57.891	3.952
3500	14.873	98.074	84.715	-	42.289	- 57.896	3.824
3600	14.875	98.493	85.092	-	43.379	- 57.901	3.615
3700	14.877	98.901	85.460	-	44.457	- 57.906	3.532
3800	14.879	99.298	85.818	-	45.524	- 57.911	3.450
3900	14.881	99.684	86.169	-	46.579	- 57.916	3.368
4000	14.881	100.061	86.512	-	47.623	- 57.921	3.287
4100	14.882	100.428	86.847	-	48.654	- 57.926	3.207
4200	14.883	100.787	87.174	-	49.673	- 57.931	3.128
4300	14.884	101.137	87.493	-	50.681	- 57.936	3.050
4400	14.885	101.479	87.805	-	51.678	- 57.941	2.973
4500	14.886	101.814	88.116	-	52.664	- 57.946	2.897
4600	14.886	102.141	88.418	-	53.639	- 57.951	2.822
4700	14.887	102.461	88.713	-	54.603	- 57.956	2.748
4800	14.888	102.774	89.003	-	55.556	- 57.961	2.675
4900	14.889	103.082	89.286	-	56.500	- 57.966	2.602
5000	14.890	103.382	89.566	-	57.435	- 57.971	2.530
5100	14.890	103.677	89.840	-	58.360	- 57.976	2.459
5200	14.890	103.966	90.109	-	59.276	- 57.981	2.389
5300	14.891	104.250	90.373	-	60.183	- 57.986	2.320
5400	14.891	104.529	90.632	-	61.081	- 57.991	2.252
5500	14.892	104.801	90.887	-	61.970	- 57.996	2.185
5600	14.892	105.070	91.138	-	62.851	- 58.001	2.119
5700	14.893	105.333	91.485	-	63.724	- 58.006	2.054
5800	14.893	105.594	91.827	-	64.590	- 58.011	1.989
5900	14.893	105.847	92.164	-	65.448	- 58.016	1.925
6000	14.894	106.097	92.492	-	66.300	- 58.021	1.862

Sept. 30, 1963

TITANIUM OXIDE CHLORIDE (TiOCl)

(IDEAL GAS)

MOL. WT. = 99.357

Point Group [C_{2v}]ΔH°_f 0 = [-59.0] kcal. mole⁻¹S°_{298.15} = [62.992] cal. deg.⁻¹ mole⁻¹ΔH°_f 298.15 = [-58.4] kcal. mole⁻¹

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹
[880] (1)
[230] (2)
[490] (1)

Bond Distances: O-Ti = [1.62] Å Ti-F = [2.17] Å

Bond Angles: O-Ti-Cl = [180°] C = 1

Rotational Constant: B₀ = [0.09225] cm.⁻¹

Heat of Formation.

ΔH°_f 0 was estimated as -58 kcal. mole⁻¹ by J. S. Gordon, Astronautics, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH°_f 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moments were: I_A = I_C = 30.34 X 10⁻³⁹ g. cm.²

CIOTI

CIOTI

Chlorine Dioxide (ClO₂)

(Ideal Gas) Mol. Wt. = 67.457

CHLORINE DIOXIDE (ClO₂) (IDEAL GAS) MOL. WT. = 67.457

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	2.582	25.500	INFINITE	INFINITE
100	5.000	51.621	1.034	25.500	25.500	25.500
200	9.997	51.621	1.034	25.500	25.500	25.500
298	10.017	51.621	1.034	25.500	25.500	25.500
300	10.057	61.515	1.019	24.988	29.259	21.314
400	11.011	64.584	1.074	24.968	30.691	16.768
500	11.744	67.094	2.213	24.969	32.135	14.046
600	12.279	69.275	3.416	24.922	33.580	12.231
700	12.669	71.199	4.664	24.933	35.020	10.933
800	12.957	72.910	5.967	24.955	36.455	9.958
900	13.176	74.435	7.325	24.985	37.885	9.199
1000	13.346	75.837	8.750	25.025	39.310	8.591
1100	13.480	77.125	10.106	25.148	40.728	8.091
1200	13.590	78.303	11.397	25.204	42.142	7.675
1300	13.681	79.395	12.639	25.259	43.552	7.321
1400	13.756	80.411	13.840	25.314	44.956	7.018
1500	13.824	81.363	15.003	25.369	46.357	6.754
1600	13.882	82.257	16.144	25.423	47.755	6.523
1700	13.933	83.100	17.261	25.477	49.150	6.318
1800	13.979	83.898	18.356	25.527	50.540	6.136
1900	14.021	84.655	19.432	25.575	51.929	5.973
2000	14.059	85.375	20.486	25.621	53.313	5.826
2100	14.095	86.062	21.521	25.665	54.698	5.692
2200	14.128	86.718	22.537	25.705	56.079	5.571
2300	14.159	87.347	23.535	25.744	57.458	5.460
2400	14.189	87.950	24.517	25.779	58.836	5.358
2500	14.217	88.530	25.483	25.809	60.213	5.264
2600	14.244	89.088	26.436	25.838	61.589	5.177
2700	14.270	89.626	27.376	25.863	62.965	5.096
2800	14.295	90.146	28.304	25.885	64.338	5.022
2900	14.320	90.648	29.221	25.904	65.711	4.952
3000	14.344	91.134	30.128	25.919	67.084	4.887
3100	14.367	91.604	31.023	25.932	68.457	4.826
3200	14.389	92.061	31.905	25.942	69.828	4.769
3300	14.411	92.504	32.776	25.949	71.198	4.715
3400	14.433	92.934	33.636	25.953	72.569	4.664
3500	14.454	93.353	34.486	25.956	73.939	4.617
3600	14.475	93.761	35.326	25.955	75.311	4.572
3700	14.496	94.157	36.156	25.953	76.682	4.529
3800	14.517	94.544	36.976	25.948	78.055	4.489
3900	14.537	94.922	37.786	25.943	79.423	4.451
4000	14.557	95.290	38.586	25.934	80.794	4.414
4100	14.577	95.650	39.376	25.924	82.164	4.380
4200	14.600	96.001	40.156	25.913	83.539	4.347
4300	14.616	96.345	40.926	25.901	84.912	4.315
4400	14.636	96.681	41.686	25.887	86.283	4.285
4500	14.655	97.010	42.436	25.872	87.655	4.257
4600	14.674	97.333	43.176	25.856	89.026	4.230
4700	14.693	97.648	43.906	25.839	90.396	4.204
4800	14.712	97.958	44.626	25.822	91.769	4.179
4900	14.731	98.262	45.336	25.805	93.140	4.154
5000	14.750	98.559	46.036	25.786	94.515	4.131
5100	14.768	98.852	46.726	25.767	95.891	4.109
5200	14.787	99.139	47.406	25.748	97.264	4.088
5300	14.806	99.420	48.076	25.729	98.635	4.068
5400	14.824	99.697	48.736	25.710	100.005	4.048
5500	14.843	99.969	49.386	25.691	101.377	4.029
5600	14.861	100.237	50.026	25.671	102.748	4.011
5700	14.879	100.500	50.656	25.652	104.117	3.993
5800	14.898	100.759	51.276	25.633	105.488	3.977
5900	14.916	101.014	51.886	25.615	106.859	3.960
6000	14.934	101.265	52.486	25.597	108.230	3.944

March 31, 1961

ΔH°_f = 25.6 ± 1.5 kcal. mole⁻¹
 ΔH°_f 298.15 = 25 ± 1.5 kcal. mole⁻¹
 S°_{298.15} = 61.453 cal. deg.⁻¹ mole⁻¹
 Point Group C_{2v}

Vibrational Levels and Multiplicities

(ω), cm. ⁻¹
945.3 (1)
447.4 (1)
1109 (1)

Electronic Level and Multiplicity

E ₁ , cm. ⁻¹	E ₂
0	2

No Ω₁ available.

σ = 2

Rotational constants: A₀₀₀ = 1.6006 cm.⁻¹, B₀₀₀ = 0.33283 cm.⁻¹, C₀₀₀ = 0.27553 cm.⁻¹
 X₁₁ = -4.4 cm.⁻¹
 X₃₃ = -2.0 cm.⁻¹
 X₁₂ = -3.0 cm.⁻¹
 X₃₁ = -14.4 cm.⁻¹

Heat of Formation

W. H. Evans, T. R. Munson, and D. D. Wagman, J. Research Natl. Bur. Standards **55**, 147 (1955), have evaluated the available data and chosen the above value.

Heat Capacity and Entropy

J. S. Gordon, private communication, February, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from J. B. Coon and E. Ortiz, J. Molec. Spectros. **1**, 61 (1957). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Phosphorus Monochloride (PCl)

(Ideal Gas) Mol. Wt. = 66.432

CIP

MOL. WT. = 66.432

(IDEAL GAS)

PHOSPHORUS MONOCHLORIDE (PCl)

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _p
0	∞	INFINITE	2.231	34.727	34.727	INFINITE
100	7.066	48.496	63.846	34.983	34.983	-71.117
200	7.799	57.575	7.93	35.046	35.046	-34.850
298	8.298	56.859	∞	35.000	27.625	-20.249
300	8.305	56.881	∞	34.990	27.580	-20.091
400	8.566	54.310	77.159	34.896	25.121	-13.775
500	8.712	61.238	57.789	34.763	22.592	-9.618
600	8.801	62.895	58.500	34.603	20.292	-7.391
800	8.951	64.317	4.495	34.575	17.921	-5.595
900	8.977	64.433	60.584	34.575	17.921	-5.595
1000	8.964	67.376	61.217	34.575	17.921	-5.595
1100	8.986	68.232	61.816	13.805	8.948	-1.778
1200	9.002	68.975	62.384	13.812	8.905	-1.569
1300	9.018	69.643	62.924	13.818	8.862	-1.369
1400	9.036	70.245	63.433	13.824	7.821	-1.180
1500	9.052	70.789	63.919	13.830	7.178	-1.046
1600	9.066	71.614	64.382	13.834	6.734	-0.920
1700	9.079	72.184	64.874	13.839	6.291	-0.809
1800	9.091	72.684	65.384	13.843	5.849	-0.709
1900	9.103	73.175	65.860	13.849	5.403	-0.621
2000	9.114	73.642	66.038	13.852	4.957	-0.542
2100	9.126	74.087	66.411	13.857	4.512	-0.470
2200	9.137	74.514	66.771	13.860	4.067	-0.404
2300	9.148	74.918	67.115	13.863	3.622	-0.344
2400	9.158	75.308	67.449	13.866	3.176	-0.289
2500	9.169	75.682	67.771	13.870	2.732	-0.239
2600	9.179	76.042	68.082	13.872	2.285	-0.192
2700	9.188	76.389	68.375	13.875	1.839	-0.149
2800	9.197	76.723	68.658	13.877	1.393	-0.109
2900	9.206	77.046	68.928	13.879	0.947	-0.071
3000	9.212	77.358	69.183	13.881	0.503	-0.037
3100	9.219	77.661	69.429	13.884	0.058	0.004
3200	9.225	77.957	69.666	13.887	0.390	0.055
3300	9.230	78.239	70.000	13.890	0.722	0.102
3400	9.235	78.505	70.258	13.893	1.054	0.148
3500	9.240	78.753	70.498	13.896	1.386	0.194
3600	9.245	79.045	70.732	13.899	1.718	0.240
3700	9.250	79.279	70.960	13.902	2.050	0.286
3800	9.255	79.505	71.180	13.905	2.382	0.332
3900	9.260	79.719	71.400	13.908	2.714	0.378
4000	9.265	79.925	71.613	13.911	3.046	0.424
4100	9.270	80.125	71.821	13.914	3.378	0.470
4200	9.275	80.295	72.024	13.917	3.710	0.516
4300	9.280	80.455	72.219	13.920	4.042	0.562
4400	9.285	80.605	72.419	13.923	4.374	0.608
4500	9.290	80.745	72.610	13.926	4.706	0.654
4600	9.295	80.875	72.797	13.929	5.038	0.700
4700	9.300	81.005	72.981	13.932	5.370	0.746
4800	9.305	81.125	73.158	13.935	5.702	0.792
4900	9.310	81.235	73.338	13.938	6.034	0.838
5000	9.315	81.345	73.512	13.941	6.366	0.884
5100	9.320	81.455	73.682	13.944	6.698	0.930
5200	9.325	81.565	73.850	13.947	7.030	0.976
5300	9.330	81.675	74.019	13.950	7.362	1.022
5400	9.335	81.785	74.176	13.953	7.694	1.068
5500	9.340	81.895	74.335	13.956	8.026	1.114
5600	9.345	81.995	74.492	13.959	8.358	1.160
5700	9.350	82.095	74.650	13.962	8.690	1.206
5800	9.355	82.195	74.809	13.965	9.022	1.252
5900	9.360	82.295	74.966	13.968	9.354	1.298
6000	9.365	82.395	75.123	13.971	9.686	1.344

June 30, 1963; Dec. 31, 1963

Ground State Configuration [$3\sum^-$]
 $\Delta H_f^0 = [34.7] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 298.15 = [56.8] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 298.15 = [35.0] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

ϵ_1 cm. ⁻¹	ϵ_2 [3]
0	

 $\omega_e = [472] \text{ cm.}^{-1}$ $\sigma = 1$ $\omega_e x_e = [1.89] \text{ cm.}^{-1}$ $x_e = [2.04] \text{ Å}$ $\alpha_e = [0.00098]$ $B_e = [0.2443]$

Heat of Formation.

The selected $\Delta H_f^0 298.15$ was calculated by assuming that the second and third bonds in $\text{PCl}_3(\text{g})$ are of equal strength, and that the first bond has a strength 20% greater than the other two. These assumptions were used by C. B. Henderson and R. S. Scheffee, Survey of Thermochemical Data, Atlantic Research Corporation, Alexandria, Virginia, January 1960. The selected $\Delta H_f^0 298.15$ was calculated using these bond strengths and auxiliary data from JANAP Tables.

A $\Delta H_f^0 298.15$, 40 kcal. mole⁻¹, estimated by C. J. O'Brien and J. R. Perrin, The Marquardt Corporation and J. Perrine, Olin Mathieson Chemical Corp., "Estimation of the Heats of Formation of Gaseous Combustion Product Molecules," WSC/CI Paper 58-4, October, 1959, when adjusted to the red V phosphorus reference state becomes [44.2] kcal. mole⁻¹.

A. A. Sandoval, H. C. Moser, and R. W. Kiser, J. Phys. Chem. 67, 124, (1963) have calculated a $\Delta H_f^0 298.15$ for PCl from an appearance potential. They selected the process $\text{PCl}_3 \rightarrow \text{Cl}^+ + \text{e}^- + \text{PCl} + \text{Cl}$ to explain this potential rather than the process $\text{PCl}_3 \rightarrow \text{Cl}^+ + \text{e}^- + \text{P} + \text{Cl}_2$. The reason for their selection was a calculated $\Delta H_f^0(\text{Cl})$, 10 kcal. lower than the literature value (See National Bureau of Standards "Selected Values of Chemical Thermodynamic Properties" Circular 500). Use of the JANAP $\Delta H_f^0 298.15$ for PCl_3 eliminates this difference.

Therefore, the process of the reported appearance potential would apparently be the second process which does not involve the neutral PCl radical.

Heat Capacity and Entropy.

The molecular constants were estimated by J. S. Gordon, Astrosystems International, Livingston, New Jersey, private communication, April 25, 1963.

CIP

INTERIM TABLE

Mol. Wt. = 242.67

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	-0.000	INFINITE	-2.340	3.901	3.901	INFINITE
100	7.440	53.389	69.716	1.633	1.636	-3.574
200	8.335	58.873	63.058	-	+0.97	-5.43
298	8.658	62.272	+0.000	3.900	-	1.637
300	8.662	62.325	+0.16	3.497	-2.543	1.852
400	8.854	65.213	+0.83	3.497	-2.543	1.852
500	8.981	66.813	1.775	3.089	-6.462	2.624
600	8.929	68.436	2.666	2.855	-8.349	3.041
700	8.964	69.816	3.560	1.441	-10.006	3.124
800	8.991	71.014	4.458	1.175	-11.624	3.175
900	9.014	72.054	5.358	+0.65	-13.204	3.204
1000	9.034	73.025	6.261	+0.65	-14.764	3.226
1100	9.054	73.887	7.165	+4.22	-16.295	3.237
1200	9.075	74.676	8.071	+1.87	-17.804	3.242
1300	9.098	75.403	8.980	+0.41	-19.294	3.243
1400	9.121	76.077	9.891	+0.41	-20.768	3.244
1500	9.144	76.709	10.805	+0.90	-22.222	3.246
1600	9.168	77.301	11.722	+0.714	-23.664	3.242
1700	9.222	77.859	12.643	+0.937	-25.090	3.225
1800	9.251	78.387	13.567	+1.162	-26.506	3.218
1900	9.278	78.887	14.494	+1.387	-27.906	3.211
2000	9.358	79.368	15.430	+1.614	-29.298	3.201
2100	9.408	79.826	16.368	-	-29.224	3.031
2200	9.459	80.265	17.311	-	-28.400	2.881
2300	9.515	80.687	18.260	-	-27.667	2.629
2400	9.576	81.094	19.213	-	-26.918	2.381
2500	9.618	81.484	20.173	-	-26.163	2.289
2600	9.671	81.862	21.137	-	-25.428	2.137
2700	9.723	82.228	22.107	-	-24.666	1.997
2800	9.775	82.583	23.082	-	-23.895	1.862
2900	9.827	82.927	24.061	-	-23.127	1.736
3000	9.871	83.261	25.047	-	-22.327	1.626
3100	9.917	83.585	26.036	-	-21.530	1.518
3200	9.961	83.901	27.030	-	-20.723	1.415
3300	10.003	84.208	28.028	-	-19.906	1.318
3400	10.044	84.507	29.029	-	-19.084	1.224
3500	10.080	84.799	30.037	-	-18.247	1.139
3600	10.115	85.083	31.046	-	-17.401	1.056
3700	10.148	85.361	32.060	-	-16.548	0.977
3800	10.178	85.632	33.076	-	-15.686	0.902
3900	10.207	85.897	34.093	-	-14.815	0.829
4000	10.235	86.155	35.118	-	-13.938	0.762
4100	10.261	86.408	36.143	-	-13.050	0.696
4200	10.284	86.656	37.170	-	-12.153	0.632
4300	10.305	86.898	38.199	-	-11.252	0.572
4400	10.324	87.135	39.224	-	-10.344	0.516
4500	10.344	87.368	40.264	-	-9.426	0.457
4600	10.361	87.595	41.300	-	-8.492	0.403
4700	10.377	87.818	42.336	-	-7.561	0.352
4800	10.391	88.037	43.373	-	-6.618	0.301
4900	10.404	88.251	44.410	-	-5.674	0.250
5000	10.416	88.461	45.456	-	-4.722	0.206
5100	10.427	88.668	46.501	-	-3.761	0.161
5200	10.438	88.870	47.541	-	-2.795	0.117
5300	10.446	89.069	48.585	-	-1.824	0.075
5400	10.452	89.265	49.634	-	-0.848	0.034
5500	10.464	89.457	50.676	-	+0.131	-0.005
5600	10.471	89.645	51.723	-	+1.117	-0.044
5700	10.478	89.831	52.771	-	+2.104	-0.081
5800	10.480	90.013	53.819	-	+3.088	-0.117
5900	10.484	90.192	54.868	-	+4.068	-0.152
6000	10.495	90.369	55.917	-	+5.048	-0.186

June 30, 1962

Lead Monochloride (PbCl) (Ideal Gas)

Mol. Wt. = 242.67

 $\Delta H_f^{298.15} = 3.5 \pm 7.2$ kcal. mole⁻¹ $S_{298.15}^{298.15} = 62.272$ cal. deg⁻¹ mole⁻¹Ground State Configuration 2π

Electronic Level and Multiplicity

ϵ , cm ⁻¹	E_1
0	2
[8266]	2

 $\omega_e = 303.6$ cm⁻¹ $\omega_e x_e = 0.88$ cm⁻¹ $\sigma = 1$
 $B_e = [0.1029]$ cm⁻¹ $\alpha_e = [0.00048]$ cm⁻¹

Heat of Formation. $\Delta H_f^{298.15}$ was calculated from the dissociation energy of PbCl(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e , and $\omega_e x_e$ were given by Herzberg, loc. cit. B_e , α_e , and ϵ were estimated by J. S. Gordon, Astrosystems, Inc., private communication, May, 1962.

Silicon Monochloride (SiCl)

SILICON MONOCHLORIDE (SiCl)

(IDEAL GAS)

GFW = 63.539

Ground State Configuration $2\pi_r$

$$\Delta H_f^\circ = 45.2 \pm 15 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 45.7 \pm 15 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 56.82 \text{ gibbs/mol}$$

$$GFW = 63.539$$

(Ideal Gas)

T, K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	7.000	47.000	INFINITE	-2.363	45.203	45.203	INFINITE
100	8.267	53.451	57.550	1.928	45.682	40.565	-1.651
200	8.582	56.815	56.815	.000	45.700	38.046	-2.786
300	8.556	56.868	56.815	.016	45.699	37.998	-27.682
400	8.611	57.332	57.353	1.756	45.641	37.999	-14.500
500	8.693	57.907	57.916	1.750	45.547	37.999	-14.500
600	8.866	62.918	58.518	2.440	45.428	30.380	-11.066
700	8.909	64.284	59.287	3.229	45.293	27.882	-8.705
800	8.941	65.480	59.954	4.421	45.143	25.404	-6.940
900	8.967	66.535	60.627	5.317	44.981	23.000	-5.252
1000	8.988	67.491	61.266	6.000	44.808	20.508	-4.462
1100	9.006	68.338	61.871	7.114	44.624	18.087	-3.593
1200	9.023	69.123	62.443	8.016	44.431	15.682	-2.656
1300	9.038	69.845	62.985	8.919	44.228	13.294	-2.235
1400	9.052	70.516	63.499	9.823	44.015	10.923	-1.705
1500	9.065	71.141	63.988	10.729	43.793	8.568	-1.248
1600	9.077	71.726	64.453	11.636	43.561	6.227	-.851
1700	9.089	72.277	64.898	12.545	43.327	4.007	-.515
1800	9.101	72.787	65.322	13.454	43.131	2.406	-.292
1900	9.113	73.259	65.729	14.365	42.936	.915	-.084
2000	9.124	73.707	66.116	15.277	42.740	-.764	.004
2100	9.135	74.202	66.483	16.189	42.545	-2.335	.243
2200	9.146	74.627	66.853	17.103	42.350	-3.697	.387
2300	9.156	75.034	67.200	18.019	42.156	-5.459	.519
2400	9.167	75.424	67.528	18.934	41.962	-7.462	.645
2500	9.177	75.798	67.838	19.852	41.767	-9.529	.766
2600	9.188	76.159	68.170	20.770	41.573	-10.556	.885
2700	9.199	76.506	68.472	21.690	41.378	-11.578	.937
2800	9.209	76.840	68.765	22.610	41.183	-12.589	1.022
2900	9.219	77.161	69.044	23.534	40.988	-13.597	1.073
3000	9.230	77.476	69.325	24.464	40.792	-14.597	1.173
3100	9.241	77.779	69.593	25.377	40.596	-15.591	1.240
3200	9.252	78.073	69.853	26.302	40.400	-16.576	1.303
3300	9.263	78.356	70.107	27.228	40.203	-17.556	1.361
3400	9.274	78.631	70.354	28.154	40.007	-18.532	1.416
3500	9.284	78.903	70.594	29.083	39.809	-19.502	1.468
3600	9.294	79.165	70.828	30.012	39.609	-20.466	1.518
3700	9.310	79.420	71.057	30.942	39.408	-21.448	1.573
3800	9.329	79.668	71.280	31.874	39.206	-22.426	1.623
3900	9.348	79.911	71.497	32.804	39.004	-23.402	1.673
4000	9.368	80.147	71.712	33.741	38.801	-24.375	1.723
4100	9.381	80.378	71.921	34.677	38.597	-25.346	1.773
4200	9.395	80.604	72.125	35.613	38.392	-26.314	1.823
4300	9.409	80.826	72.324	36.549	38.187	-27.280	1.873
4400	9.423	81.041	72.519	37.484	37.982	-28.244	1.923
4500	9.439	81.252	72.712	38.422	37.777	-29.206	1.973
4600	9.455	81.459	72.900	39.375	37.571	-30.166	2.023
4700	9.471	81.663	73.084	40.319	37.365	-31.123	2.073
4800	9.486	81.864	73.262	41.263	37.159	-32.078	2.123
4900	9.502	82.059	73.436	42.207	36.953	-33.032	2.173
5000	9.520	82.437	73.788	43.162	36.746	-33.985	2.223
5100	9.539	82.622	73.956	44.113	36.539	-34.937	2.273
5200	9.558	82.803	74.121	45.066	36.332	-35.888	2.323
5300	9.578	82.981	74.283	46.016	36.125	-36.837	2.373
5400	9.598	83.159	74.443	46.973	35.918	-37.784	2.423
5500	9.619	83.332	74.600	47.936	35.711	-38.729	2.473
5600	9.641	83.502	74.755	48.897	35.504	-39.672	2.523
5700	9.661	83.668	74.907	49.860	35.297	-40.613	2.573
5800	9.681	83.836	75.057	50.823	35.090	-41.552	2.623
5900	9.701	83.999	75.205	51.786	34.883	-42.490	2.673
6000	9.716	84.161	75.353	52.750	34.676	-43.427	2.723

Dec. 31, 1960; Sept. 30, 1967

Electronic Levels and Quantum Weights

State	e_j , cm ⁻¹	g_j
X $2\pi_{1/2}$	0	2
$2\pi_{3/2}$	207.2	2
A $2\pi^*$	22993.5	2
B $2\pi^*$	34192	2
B' $2\pi_{1/2}$	35618	4
C 2π	41245	4
D 2π	44940	4

$$\omega_e = 533.75 \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = 0.25416 \text{ cm}^{-1} \quad r_e = 2.058 \text{ \AA}$$

Heat of Formation

The adopted value is based on $D_0^\circ = 90 \pm 15$ kcal/mol which is calculated from $D_0^\circ/D'(\text{LHX}) = 1.01$ and $D'(\text{LHX}) = 89$ kcal/mol. The latter value comes from linear Birge-Sponer extrapolation of ground state vibrational constants obtained by Verma (1). From the B'-X system. The ratio $D_0^\circ/D'(\text{LHX}) = 1.01$ is calculated from an empirical relationship proposed by Hildenbrand (2): $D_0^\circ/D'(\text{LHX}) = 0.365(r_e/x_e) + 0.448$ and $x_e = 14.40/(\text{IP-EA})$, where IP is the ionization potential of the more electronegative element and EA is the electron affinity of the more electronegative element. A similar calculation using $\omega_e/x_e = 2.1 \text{ cm}^{-1}$ obtained from the B-X system (2) would give $D_0^\circ = 98$ kcal/mol. These values for D_0° may be compared with average (per bond) heats of atomization of 101 kcal/mol for SiCl_2 and 94 kcal/mol for SiCl_4 .

Gaydon (3) selected $D_0^\circ = 7612$ kcal/mol on the assumption that $D_0^\circ/D'(\text{LHX}) = 0.8$, but Ovcharenko (4) suggested that this was too low by comparison with $D_0^\circ = 117$ kcal/mol obtained from the B' state. The latter value is calculated from $D'(\text{LHX}) = 33$ kcal/mol and presumes that $\text{Si}(\text{D})$ is the excited atomic product. The B and C states could also correlate to give values fairly consistent with $D_0^\circ = 117$. This interpretation seems unlikely, however, because it would involve a crossing of the potential curves for the B and B' states. Since the potential curves may be distorted due to the close proximity of the B and B' states, it seems preferable to obtain D_0° from constants for the ground state.

Heat Capacity and Entropy

Electronic levels of the B and C states are taken from the B-X and C-X systems reported by Ovcharenko et al. (5, 6). The A level is that assigned by Sanii (10) from analysis of the A-X system. The D level is that derived by Herzberg (7) from data of Jevons (8), but it is assigned as π as suggested by Verma (1). The B' level is from Verma and is confirmed by the earlier analysis of Ovcharenko (4). All vibrational and rotational constants for the ground state are those obtained by Verma (1) from the B'-X system. Values only slightly different were obtained from the B-X system by Ovcharenko (5, 6). The adopted constants are adjusted to the natural isotopic abundances of Si and Cl.

References

1. R. D. Verma, Can. J. Phys. **42**, 2345 (1964).
2. I. E. Ovcharenko and Yu. Ya. Kuzakov, Opt. Spectry, USSR (English Transl.) **13**, 362 (1962).
3. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.
4. I. E. Ovcharenko, Yu. Ya. Kuzakov and V. M. Tatevskii, Opt. Spectry, USSR (English Transl.), Supplement 2, Molecular Spectroscopy, pp. 6-7 (1966), original Russian published in 1963.
5. I. E. Ovcharenko and Yu. Ya. Kuzakov, Opt. Spectry, USSR (English Transl.) **20**, 14 (1966); **13**, 362 (1962).
6. I. E. Ovcharenko and Yu. Ya. Kuzakov, Opt. Spectry, USSR (English Transl.) **8**, 993 (1960).
7. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
8. W. Jevons, Proc. Phys. Soc. (London) **44**, 563 (1936).
9. D. L. Hildenbrand, CFTA Publication No. 146, Vol. 1, 83 (1967).
10. N. Sanii and R. D. Verma, Can. J. Phys. **43**, 960 (1965).

CISI

Titanium Monochloride (TiCl)
(Ideal Gas) GFW = 83.353

TITANIUM MONOCHLORIDE (TiCl)
(IDEAL GAS)

Ground State Configuration [⁴2]
S²_{298.15} = 59.54 ± 2.0 gibbs/mol

GFW = 83.353
ΔH_{f,0}⁰ = [36.8 ± 10.0] kcal/mol
ΔH_{f,298.15}⁰ = [36.9 ± 10.0] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	$\frac{g_i}{g_0}$
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

$$\omega_e = 379.7 \text{ cm}^{-1} \quad \omega_e x_e = 3.41 \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = [0.146] \text{ cm}^{-1} \quad \alpha_e = [0.0013] \text{ cm}^{-1} \quad r_e = [2.3] \text{ \AA}$$

Heat of Formation

The heat of formation, ΔH_{f,298}⁰ of TiCl (g) is calculated from the dissociation energy, D₀⁰, which is estimated as 105 kcal/mol. This estimate is obtained from the relation D(TiCl) < D₀⁰(TiCl) < D(TiCl₂), where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF₂(g) by Zmbov and Margrave (1).

Extrapolations of the vibrational levels reported by Shenyavskaya (2), Rao (3) and Mace and Packer (4) yield values of the dissociation energy which are very low when considered with respect to bond energy relations.

Heat Capacity and Entropy

The vibrational frequency, ω_e, and anharmonic vibrational term, ω_ex_e, were reported by Shenyavskaya et al. (2). The interatomic distance is estimated from Guggenheimer's relation (5). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti³⁺(g). α_e is estimated from the Morse potential function.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. E. A. Shenyavskaya, Yu. Ya. Kuzakov, and V. M. Tatevskii, Opt. Spectrosc. (USSR) **12**, 197 (1962).
3. V. R. Rao, Indian J. Phys. **23**, 535 (1949).
4. K. R. Mace and A. H. Packer, Phys. Rev. **52**, 1150 (1937).
5. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
6. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

T, °K	C _p ⁰	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H^\circ_{298})/T}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG ⁰	Log K _p
0	0.000	INFINITE	2.314	36.835	INFINITE
100	7.230	50.812	36.943	34.427	75.240
200	8.167	56.128	60.331	31.809	34.759
298	8.915	59.538	59.538	29.277	21.460
300	8.927	59.583	59.583	29.229	21.284
400	9.451	62.283	59.886	26.691	14.583
500	9.883	64.406	60.588	24.178	10.568
600	10.138	66.232	61.380	21.685	7.499
700	10.285	67.806	62.169	19.210	5.998
800	10.376	69.166	62.876	16.756	4.876
900	10.416	70.410	63.738	14.307	3.974
1000	10.442	71.569	64.461	11.880	2.596
1100	10.458	72.505	65.148	9.473	1.682
1200	10.470	73.416	65.799	7.121	1.097
1300	10.481	74.251	66.416	4.828	0.737
1400	10.489	75.031	66.999	2.582	0.461
1500	10.509	75.756	67.565	0.378	0.239
1600	10.526	76.434	68.098	34.143	0.273
1700	10.545	77.073	68.608	34.143	0.273
1800	10.564	77.678	69.097	34.143	0.273
1900	10.581	78.254	69.567	34.143	0.273
2000	10.606	78.792	70.010	34.143	0.273
2100	10.628	79.310	70.440	34.143	0.273
2200	10.649	79.805	70.855	34.143	0.273
2300	10.669	80.279	71.250	34.143	0.273
2400	10.688	80.733	71.623	34.143	0.273
2500	10.708	81.170	72.012	34.143	0.273
2600	10.725	81.590	72.373	34.143	0.273
2700	10.742	81.995	72.722	34.143	0.273
2800	10.758	82.386	73.059	34.143	0.273
2900	10.772	82.764	73.386	34.143	0.273
3000	10.786	83.129	73.707	34.143	0.273
3100	10.798	83.483	74.016	34.143	0.273
3200	10.810	83.826	74.318	34.143	0.273
3300	10.821	84.152	74.611	34.143	0.273
3400	10.832	84.461	74.891	34.143	0.273
3500	10.840	84.766	75.175	34.143	0.273
3600	10.849	85.102	75.446	34.143	0.273
3700	10.857	85.399	75.711	34.143	0.273
3800	10.864	85.689	75.970	34.143	0.273
3900	10.870	85.970	76.223	34.143	0.273
4000	10.878	86.246	76.470	34.143	0.273
4100	10.884	86.515	76.712	34.143	0.273
4200	10.891	86.777	76.948	34.143	0.273
4300	10.897	87.034	77.180	34.143	0.273
4400	10.903	87.284	77.407	34.143	0.273
4500	10.909	87.529	77.629	34.143	0.273
4600	10.915	87.769	77.847	34.143	0.273
4700	10.921	88.004	78.060	34.143	0.273
4800	10.926	88.234	78.267	34.143	0.273
4900	10.931	88.459	78.474	34.143	0.273
5000	10.939	88.680	78.677	34.143	0.273
5100	10.945	88.897	78.876	34.143	0.273
5200	10.952	89.109	79.070	34.143	0.273
5300	10.958	89.316	79.259	34.143	0.273
5400	10.966	89.523	79.450	34.143	0.273
5500	10.973	89.724	79.635	34.143	0.273
5600	10.980	89.922	79.817	34.143	0.273
5700	10.987	90.117	79.996	34.143	0.273
5800	10.994	90.310	80.172	34.143	0.273
5900	10.999	90.496	80.345	34.143	0.273
6000	11.011	90.681	80.516	34.143	0.273

T, °K	Cp°	gibbs/mol		H°-H° ₂₉₈	kcal/mol		Log Kp
		S°	-(G°-H° ₂₉₈)/T		ΔH°	ΔG°	
0	0.000	0.000	INFINITE	2.240	132.346	132.346	INFINITE
100	7.082	56.196	69.617	1.542	132.540	129.407	283.257
200	7.942	59.335	63.316	0.796	132.443	126.704	138.455
298	8.327	62.567	62.567	0.000	132.300	123.917	90.834
300	8.334	62.619	62.567	0.015	132.297	123.865	90.235
400	8.582	65.058	62.698	0.863	132.140	121.077	66.154
500	8.718	66.985	63.529	1.728	131.978	118.330	51.722
600	8.802	68.583	64.242	2.604	131.809	115.616	42.113
700	8.903	70.000	64.872	3.496	131.636	112.932	34.152
800	9.003	71.330	65.562	4.376	131.464	110.272	30.129
900	9.045	72.581	66.327	5.264	131.290	107.638	26.138
1000	9.085	73.726	67.061	6.165	131.045	105.025	22.953
1100	9.027	73.984	67.561	7.065	130.833	102.433	20.351
1200	8.971	74.259	68.029	7.963	130.643	99.862	18.177
1300	8.916	74.546	68.468	8.858	130.473	97.320	16.359
1400	8.861	74.837	68.881	9.754	130.321	94.771	14.794
1500	8.811	75.130	69.269	10.713	129.909	92.254	13.441
1600	8.767	75.426	70.134	11.636	129.659	89.752	12.260
1700	8.730	75.723	71.006	12.529	129.437	87.284	11.249
1800	8.693	76.020	71.847	13.397	129.137	84.794	10.295
1900	8.659	76.317	72.655	14.243	128.865	82.337	9.471
2000	8.639	76.492	73.434	15.064	128.584	79.897	8.731
2100	8.624	76.653	74.181	15.871	128.295	77.470	8.062
2200	8.610	76.808	74.903	16.665	127.998	75.064	7.450
2300	8.597	76.958	75.605	17.448	127.694	72.654	6.904
2400	8.585	77.103	76.288	18.220	127.382	70.270	6.399
2500	8.579	77.243	76.952	18.983	127.061	67.896	5.935
2600	8.574	77.378	77.600	19.738	126.733	65.536	5.509
2700	8.569	77.508	78.234	20.484	126.400	63.196	5.115
2800	8.565	77.633	78.857	21.224	126.063	60.858	4.750
2900	8.562	77.753	79.468	21.952	125.723	58.533	4.411
3000	8.560	77.868	80.068	22.668	125.379	56.227	4.096
3100	8.557	77.978	80.658	23.372	125.032	53.934	3.802
3200	8.555	78.083	81.238	24.068	124.682	51.659	3.528
3300	8.553	78.183	81.808	24.756	124.329	49.399	3.272
3400	8.551	78.278	82.369	25.436	123.973	47.164	3.032
3500	8.549	78.369	82.921	26.111	123.614	44.943	2.806
3600	8.547	78.456	83.464	26.782	123.252	42.747	2.595
3700	8.545	78.539	84.000	27.448	122.887	40.577	2.400
3800	8.543	78.618	84.528	28.110	122.519	38.437	2.226
3900	8.541	78.693	85.048	28.768	122.148	36.327	2.061
4000	8.539	78.764	85.561	29.422	121.774	34.246	1.905
4100	8.537	78.831	86.068	30.072	121.397	32.195	1.757
4200	8.535	78.894	86.569	30.718	121.018	30.176	1.616
4300	8.533	78.953	87.112	31.360	120.636	28.188	1.482
4400	8.531	79.008	87.649	31.998	120.252	26.231	1.354
4500	8.529	79.060	88.181	32.632	119.866	24.305	1.233
4600	8.527	79.109	88.708	33.262	119.478	22.409	1.116
4700	8.525	79.155	89.231	33.887	119.088	20.543	1.003
4800	8.523	79.198	89.750	34.508	118.696	18.707	0.895
4900	8.521	79.239	90.265	35.124	118.302	16.900	0.792
5000	8.519	79.278	90.776	35.736	117.906	15.122	0.695
5100	8.517	79.314	91.283	36.343	117.508	13.374	0.607
5200	8.515	79.347	91.786	36.946	117.108	11.656	0.524
5300	8.513	79.378	92.285	37.545	116.706	9.968	0.446
5400	8.511	79.406	92.780	38.140	116.302	8.310	0.373
5500	8.509	79.432	93.271	38.732	115.896	6.683	0.306
5600	8.507	79.457	93.758	39.320	115.488	5.095	0.244
5700	8.505	79.480	94.242	39.904	115.078	3.547	0.187
5800	8.503	79.502	94.723	40.484	114.666	2.039	0.135
5900	8.501	79.522	95.200	41.060	114.252	0.571	0.087
6000	8.500	79.540	95.673	41.633	113.836	-0.964	0.042
6100	8.498	79.557	96.142	42.203	113.418	-2.491	0.000
6200	8.496	79.572	96.608	42.769	112.998	-4.015	-0.192
6300	8.494	79.586	97.071	43.332	112.576	-5.536	-0.385
6400	8.492	79.599	97.531	43.891	112.152	-7.052	-0.577
6500	8.490	79.611	97.987	44.446	111.726	-8.563	-0.769
6600	8.488	79.622	98.440	44.997	111.298	-10.069	-0.961
6700	8.486	79.632	98.889	45.545	110.868	-11.570	-1.154
6800	8.484	79.641	99.335	46.089	110.436	-13.066	-1.347
6900	8.482	79.649	99.778	46.630	110.002	-14.558	-1.540
7000	8.480	79.656	100.218	47.168	109.566	-16.045	-1.733
7100	8.478	79.662	100.654	47.703	109.128	-17.528	-1.926
7200	8.476	79.668	101.087	48.234	108.688	-19.007	-2.119
7300	8.474	79.673	101.517	48.762	108.245	-20.481	-2.312
7400	8.472	79.678	101.943	49.287	107.799	-21.950	-2.505
7500	8.470	79.682	102.366	49.809	107.351	-23.414	-2.697
7600	8.468	79.686	102.785	50.328	106.900	-24.873	-2.889
7700	8.466	79.689	103.201	50.844	106.446	-26.327	-3.081
7800	8.464	79.692	103.614	51.357	105.989	-27.776	-3.273
7900	8.462	79.695	104.024	51.867	105.530	-29.220	-3.465
8000	8.460	79.697	104.431	52.374	105.068	-30.659	-3.657
8100	8.458	79.699	104.836	52.878	104.604	-32.093	-3.849
8200	8.456	79.701	105.239	53.379	104.137	-33.522	-4.041
8300	8.454	79.703	105.639	53.877	103.668	-34.946	-4.233
8400	8.452	79.705	106.035	54.372	103.196	-36.365	-4.425
8500	8.450	79.707	106.428	54.864	102.722	-37.779	-4.617
8600	8.448	79.709	106.818	55.353	102.246	-39.188	-4.809
8700	8.446	79.711	107.205	55.839	101.768	-40.592	-5.001
8800	8.444	79.713	107.589	56.322	101.288	-41.991	-5.193
8900	8.442	79.715	107.970	56.802	100.806	-43.385	-5.385
9000	8.440	79.717	108.348	57.279	100.322	-44.774	-5.577
9100	8.438	79.719	108.722	57.753	99.836	-46.158	-5.769
9200	8.436	79.721	109.093	58.224	99.348	-47.537	-5.961
9300	8.434	79.723	109.461	58.692	98.858	-48.911	-6.153
9400	8.432	79.725	109.826	59.157	98.366	-50.280	-6.345
9500	8.430	79.727	110.189	59.619	97.872	-51.644	-6.537
9600	8.428	79.729	110.549	60.078	97.376	-53.003	-6.729
9700	8.426	79.731	110.906	60.534	96.878	-54.357	-6.921
9800	8.424	79.733	111.260	60.987	96.378	-55.706	-7.113
9900	8.422	79.735	111.611	61.438	95.876	-57.050	-7.305
10000	8.420	79.737	111.959	61.886	95.372	-58.389	-7.497

June 30, 1967

TUNGSTEN MONOCHLORIDE (WCl)

(IDEAL GAS)

GFW = 219.303

Ground State Configuration [2]

 $\Delta H_f^\circ = 132.3 \pm 10$ kcal/mol $S_{298.15}^\circ = 62.6$ gibbs/mol $\Delta H_f^\circ = 132.3 \pm 10$ kcal/mol

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	g_i
0	[4]
[5000]	[2]
[15000]	[20]

 $\omega_e X_e = [455.4] \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e = [1.46] \text{ cm}^{-1}$ $r_e = [2.26] \text{ \AA}$ $\alpha_e = [0.00042] \text{ cm}^{-1}$

Heat of Formation

The heat of formation, ΔH_f° (WCl, g) = 132.3 kcal/mol, is calculated from the bond dissociation energy, D_{298}° (W-Cl) = 100 ± 10 kcal/mol. This estimated D_{298}° is obtained from the average bond dissociation energy for WCl_x (g) + W(g) + xCl(g) where x = 2, 4, 5, 6, using all JANAF values.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WCl₂(g). This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency ω_e (K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1944)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4D_0 + 0.5 \omega_e = 0.0032$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function. The moment of inertia is $25.20 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for Wf(g). See Wf(g) table (March 31, 1967) for details.

CIW

Zirconium Monochloride (ZrCl)

(Ideal Gas)

GFV = 126.673

ZIRCONIUM MONOCHLORIDE (ZrCl)

(IDEAL GAS)

GFV = 126.673

 $\Delta H_f^\circ = 49.3 \pm 5$ kcal/mol $\Delta H_{298.15}^\circ = 49.1 \pm 5$ kcal/molGround State Configuration $[4f]$ $S_{298.15}^\circ = [60.8 \pm 2]$ gibbs/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

 $\omega_e x_e = [437]$ cm⁻¹ $\omega_e x_e = [1.1]$ cm⁻¹ $\sigma = 1$ $B_e = [0.1248]$ cm⁻¹ $a_e = [0.00042]$ cm⁻¹ $r_e = [2.3]$ Å

Heat of Formation

Potter (1) investigated mass spectrometrically the gaseous equilibria among ZrCl, ZrCl₂, ZrCl₃ and ZrCl₄. Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equilibrium constants for the reaction ZrCl₃(g) + ZrCl(g) = 2 ZrCl₂(g) in the temperature range 1978-2274°K, second and third law analyses give the heats of reaction at 298°K as -10.36 and -12.83 kcal/mol, respectively. The third law drift is 1.4 ± 2.5 eu. Based on the third law ΔH_{298}° and ΔH_{298}° (ZrCl₂, g) = -44.5 kcal/mol (2), and ΔH_{298}° (ZrCl₃, g) = -125.3 kcal/mol (3), we obtain ΔH_{298}° (ZrCl, g) = 49.1 kcal/mol which is adopted in the tabulation.

Farber et al. (4) also studied mass spectrometrically the reaction Zr(c) + Cl(g) + ZrCl(g). They reported a second law heat of reaction, $\Delta H_{298}^\circ = 8.7 \pm 1.4$ kcal/mol. Using the equilibrium constants $K = I(\text{ZrCl})/I(\text{Cl})$ which we calculated from their reported ion intensities of run 3 in the temperature range 1667-1896°K, we obtain $\Delta H_{298}^\circ = 20.3$ kcal/mol by the third law method. The third law drift is 6.1 ± 2.4 eu. The heat of formation is derived as ΔH_{298}° (ZrCl, g) = 49.2 kcal/mol.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in ZrCl₄(g). The bond distance is then used with Guggenheimer's relation (5) for polar molecules to calculate the fundamental vibrational frequency ω_e . The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/(v_e^2 + 0.5 \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of a_e is calculated from the Morse potential function. The moment of inertia is 22.425×10^{-39} g cm².

The ground state configuration is taken from the ground state multiplet of Zr⁺ reported by Moore (6). The electronic levels and the quantum weights are estimated to be the same as those of Zr(fg).

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF ZrCl₂(g) table dated Dec. 31, 1969.
3. JANAF ZrCl₃(g) table dated Dec. 31, 1969.
4. H. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
5. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
6. C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952.

T, °K	C _p ^o	S ^o	gibbs/mol	-(G ^o -H ^o) ₂₉₈ /T	H ^o -H ^o ₂₉₈	kcal/mol	ΔH ^o	ΔG ^o	Log Kp
0	0.000	INFINITE	INFINITE	2.249	49.269	49.269	INFINITE	INFINITE	INFINITE
100	7.107	52.333	67.866	1.551	49.407	49.407	102.207	46.766	10.572
200	7.695	57.503	74.811	1.161	49.426	49.426	102.207	46.766	10.572
298	8.166	60.754	78.954	1.000	49.426	49.426	102.207	46.766	10.572
300	8.372	60.806	60.754	0.015	49.097	41.661	30.350	41.661	30.350
400	8.612	63.251	61.086	0.666	48.909	39.211	21.424	39.211	21.424
500	8.761	65.189	61.720	1.735	48.701	36.810	16.069	36.810	16.069
600	8.888	66.798	62.636	2.617	48.471	34.453	12.569	34.453	12.569
700	9.021	68.178	63.160	3.513	48.221	32.135	10.033	32.135	10.033
800	9.162	69.392	63.684	4.422	47.954	29.856	8.156	29.856	8.156
900	9.309	70.479	64.240	5.345	47.671	27.610	6.705	27.610	6.705
1000	9.453	71.468	64.814	6.284	47.373	25.397	5.550	25.397	5.550
1100	9.591	72.375	65.797	7.236	47.069	23.214	4.612	23.214	4.612
1200	9.720	73.215	66.381	8.201	46.757	21.112	3.845	21.112	3.845
1300	9.836	73.998	66.937	9.179	46.437	19.055	3.203	19.055	3.203
1400	9.940	74.731	67.468	10.166	46.112	17.011	2.656	17.011	2.656
1500	10.031	75.420	67.975	11.167	45.784	15.079	2.182	15.079	2.182
1600	10.110	76.070	68.461	12.176	45.459	13.256	1.770	13.256	1.770
1700	10.178	76.685	68.927	13.189	45.121	11.500	1.408	11.500	1.408
1800	10.235	77.268	69.374	14.209	44.783	9.850	1.087	9.850	1.087
1900	10.283	77.823	69.804	15.235	44.445	8.302	0.801	8.302	0.801
2000	10.323	78.351	70.218	16.266	44.107	6.856	0.545	6.856	0.545
2100	10.355	78.856	70.618	17.300	43.770	5.511	0.314	5.511	0.314
2200	10.382	79.338	71.003	18.337	43.421	4.266	0.123	4.266	0.123
2300	10.403	79.800	71.376	19.376	43.066	3.120	0.045	3.120	0.045
2400	10.420	80.243	71.736	20.417	42.706	2.074	0.019	2.074	0.019
2500	10.433	80.669	72.085	21.460	42.341	1.127	0.009	1.127	0.009
2600	10.443	81.078	72.423	22.504	41.974	0.276	0.001	0.276	0.001
2700	10.451	81.473	72.751	23.548	41.606	0.000	0.000	0.000	0.000
2800	10.458	81.853	73.069	24.594	41.236	0.000	0.000	0.000	0.000
2900	10.462	82.220	73.379	25.640	40.866	0.000	0.000	0.000	0.000
3000	10.466	82.575	73.679	26.686	40.496	0.000	0.000	0.000	0.000
3100	10.469	82.918	73.972	27.733	40.126	0.000	0.000	0.000	0.000
3200	10.471	83.250	74.257	28.780	39.756	0.000	0.000	0.000	0.000
3300	10.473	83.573	74.534	29.827	39.386	0.000	0.000	0.000	0.000
3400	10.474	83.885	74.804	30.874	39.016	0.000	0.000	0.000	0.000
3500	10.476	84.189	75.068	31.922	38.646	0.000	0.000	0.000	0.000
3600	10.478	84.484	75.326	32.970	38.276	0.000	0.000	0.000	0.000
3700	10.479	84.771	75.577	34.018	37.906	0.000	0.000	0.000	0.000
3800	10.481	85.051	75.823	35.066	37.536	0.000	0.000	0.000	0.000
3900	10.483	85.323	76.063	36.114	37.166	0.000	0.000	0.000	0.000
4000	10.486	85.588	76.298	37.162	36.796	0.000	0.000	0.000	0.000
4100	10.488	85.847	76.527	38.211	36.426	0.000	0.000	0.000	0.000
4200	10.491	86.100	76.752	39.260	36.056	0.000	0.000	0.000	0.000
4300	10.494	86.347	76.973	40.309	35.686	0.000	0.000	0.000	0.000
4400	10.498	86.588	77.188	41.359	35.316	0.000	0.000	0.000	0.000
4500	10.502	86.824	77.400	42.409	34.946	0.000	0.000	0.000	0.000
4600	10.506	87.055	77.607	43.459	34.576	0.000	0.000	0.000	0.000
4700	10.510	87.281	77.811	44.510	34.206	0.000	0.000	0.000	0.000
4800	10.515	87.502	78.011	45.561	33.836	0.000	0.000	0.000	0.000
4900	10.519	87.719	78.209	46.613	33.466	0.000	0.000	0.000	0.000
5000	10.524	87.932	78.399	47.665	33.096	0.000	0.000	0.000	0.000
5100	10.530	88.140	78.588	48.718	32.726	0.000	0.000	0.000	0.000
5200	10.535	88.345	78.773	49.771	32.356	0.000	0.000	0.000	0.000
5300	10.541	88.545	78.956	50.825	31.986	0.000	0.000	0.000	0.000
5400	10.546	88.743	79.135	51.879	31.616	0.000	0.000	0.000	0.000
5500	10.552	88.936	79.312	52.934	31.246	0.000	0.000	0.000	0.000
5600	10.558	89.126	79.485	53.990	30.876	0.000	0.000	0.000	0.000
5700	10.564	89.313	79.656	55.046	30.506	0.000	0.000	0.000	0.000
5800	10.570	89.497	79.824	56.102	30.136	0.000	0.000	0.000	0.000
5900	10.576	89.678	79.990	57.160	29.766	0.000	0.000	0.000	0.000
6000	10.582	89.856	80.153	58.218	29.396	0.000	0.000	0.000	0.000

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	7.000	∞	INFINITE	2,104	∞	∞	∞
100	7.001	45,150	60,130	1,498	∞	∞	∞
200	7.576	50,156	54,016	.772	∞	∞	∞
298	8.111	53,289	53,289	∞	∞	∞	∞
300	8.119	53,339	53,289	.015	∞	∞	∞
400	8.631	55,729	53,121	.845	∞	∞	∞
500	8.624	57,628	54,231	1,698	∞	∞	∞
600	8.741	59,212	54,933	2,567	∞	∞	∞
700	8.821	60,565	55,643	3,445	∞	∞	∞
800	8.877	61,769	56,354	4,331	∞	∞	∞
900	8.922	62,851	57,064	5,217	∞	∞	∞
1000	8.956	63,737	57,623	6,115	∞	∞	∞
1100	8.985	64,592	58,218	7,012	∞	∞	∞
1200	9.010	65,375	58,782	7,912	∞	∞	∞
1300	9.032	66,107	59,316	8,814	∞	∞	∞
1400	9.051	66,797	59,816	9,718	∞	∞	∞
1500	9.069	67,452	60,310	10,624	∞	∞	∞
1600	9.086	67,978	60,771	11,532	∞	∞	∞
1700	9.102	68,530	61,211	12,441	∞	∞	∞
1800	9.117	69,050	61,633	13,352	∞	∞	∞
1900	9.131	69,556	62,038	14,264	∞	∞	∞
2000	9.144	70,013	62,423	15,179	∞	∞	∞
3100	9.166	70,459	62,795	16,094	∞	∞	∞
3200	9.184	70,866	63,154	17,012	∞	∞	∞
3300	9.199	71,243	63,500	17,932	∞	∞	∞
3400	9.223	71,587	63,832	18,852	∞	∞	∞
3500	9.245	72,064	64,154	19,776	∞	∞	∞
2600	9.268	72,427	64,465	20,701	∞	∞	∞
2700	9.293	72,777	64,766	21,629	∞	∞	∞
2800	9.316	73,116	65,057	22,561	∞	∞	∞
2900	9.346	73,443	65,342	23,493	∞	∞	∞
3000	9.374	73,760	65,617	24,429	∞	∞	∞
3100	9.403	74,068	65,885	25,368	∞	∞	∞
3200	9.432	74,367	66,145	26,310	∞	∞	∞
3300	9.459	74,657	66,399	27,256	∞	∞	∞
3400	9.490	74,943	66,646	28,202	∞	∞	∞
3500	9.518	75,216	66,887	29,153	∞	∞	∞
3600	9.546	75,485	67,122	30,106	∞	∞	∞
3700	9.573	75,747	67,352	31,062	∞	∞	∞
3800	9.600	76,003	67,576	32,020	∞	∞	∞
3900	9.622	76,252	67,795	32,981	∞	∞	∞
4000	9.645	76,496	68,010	33,945	∞	∞	∞
4100	9.666	76,734	68,220	34,910	∞	∞	∞
4200	9.685	76,967	68,425	35,878	∞	∞	∞
4300	9.703	77,195	68,624	36,848	∞	∞	∞
4400	9.718	77,419	68,818	37,818	∞	∞	∞
4500	9.732	77,637	69,017	38,761	∞	∞	∞
4600	9.743	77,851	69,207	39,764	∞	∞	∞
4700	9.754	78,061	69,393	40,739	∞	∞	∞
4800	9.765	78,267	69,576	41,715	∞	∞	∞
4900	9.768	78,468	69,755	42,692	∞	∞	∞
5000	9.774	78,665	69,931	43,669	∞	∞	∞
5100	9.778	78,859	70,105	44,646	∞	∞	∞
5200	9.783	79,049	70,275	45,624	∞	∞	∞
5300	9.787	79,235	70,442	46,602	∞	∞	∞
5400	9.790	79,418	70,607	47,582	∞	∞	∞
5500	9.792	79,598	70,768	48,561	∞	∞	∞
5600	9.794	79,774	70,928	49,540	∞	∞	∞
5700	9.795	79,947	71,084	50,520	∞	∞	∞
5800	9.797	80,117	71,238	51,500	∞	∞	∞
5900	9.797	80,285	71,391	52,479	∞	∞	∞
6000	9.798	80,450	71,540	53,459	∞	∞	∞

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

CHLORINE, DIATOMIC (Cl₂) (IDEAL GAS - REFERENCE STATE)

MOL. WT. = 70.906

Ground State Configuration 1Σ⁺
S°_{298.15} = 53.29 ± 0.01 cal. deg.⁻¹ mole⁻¹
ΔH°_f 0 = 0
ΔH°_f 298 = 0

Electronic Levels and Multiplicities

State	E, cm. ⁻¹	E ₁
1Σ ⁺	0	1
3Π ⁺	18,147 ± 500	1
3Π ₁	17,841 ± 500	2
3Π ₂	17,560 ± 500	2

ω_e = 561.1 cm.⁻¹
ω_e x_e = 4.0 cm.⁻¹
B_e = 0.2408 cm.⁻¹
r_e = 1.986 Å
σ_e = 0.0017 cm.⁻¹
σ = 2

Heat of Formation.

The heat of formation (ΔH°_f) for Cl₂(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here were calculated by R. L. Fottler, J. Chem. Phys. 31, 1100 (1959) using a direct summation over the energy levels not including those of non-bonding states. The functions are for the naturally occurring isotopic composition.

The absorption spectrum of chlorine has been observed by A. Elliott, Proc. Roy. Soc. A 127, 638 (1930); C. P. Goodeve and B. A. Stephens, Trans. Faraday Soc. 32, 151.7 (1936); H. Stammreich, R. Fornieris and Y. Tavares, Spectrochim. Acta, 17, 775 (1961); Y. V. Rao and P. Venkateswarlu, J. Mol. Spectr. 9, 173 (1962); and A. E. Douglas, C. K. Møller and B. P. Stoicheff, Can. J. Phys. 41, 1174 (1963). There is disagreement over the vibrational assignments. The listed ground state spectroscopic constants for the naturally occurring isotopic composition are based upon the abundances given by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The molecular structure of gaseous chlorine was determined by the sector-microphotometer method of electron diffraction by S. Shibata, J. Phys. Chem. 57, 2256 (1963). The value of r_e(Cl-Cl) was found to be 1.986 Å. The other r_e values, 1.983 - 1.989 Å, were reported by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., 1950; W. G. Richards and R. F. Barrow, Proc. Chem. Soc., 297 (1962), and L. S. Bartell and K. Kuchitsu, presented at the International Conference on Magnetism and Crystallography, 1961, quoted by S. Shibata, loc. cit.

Cesium Chloride, Dimeric (Cs₂Cl₂)

GFW = 336.716

(Ideal Gas)

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	-∞	∞	∞	∞	∞	∞	∞
100	17.135	71.237	106.595	-4.990	-156.808	-156.808	INFINITE
200	19.063	83.699	93.368	-3.737	-157.277	-157.277	333.686
298	19.507	91.614	81.614	-3.000	-157.446	-157.446	171.750
300	19.511	91.734	81.614	-3.036	-157.400	-157.400	115.078
400	19.667	97.372	82.382	1.996	-156.101	-156.361	85.431
500	19.740	101.769	83.636	3.667	-155.481	-155.632	66.027
600	19.780	105.372	85.467	5.943	-150.858	-150.858	56.305
700	19.864	108.423	87.106	7.922	-140.237	-151.957	46.007
800	19.860	111.069	88.689	9.504	-160.621	-153.035	41.407
900	19.831	113.404	100.157	11.886	-161.007	-152.062	36.926
1000	19.839	115.484	101.624	13.870	-193.559	-149.407	32.653
1100	19.846	117.385	102.972	15.958	-193.648	-148.095	28.608
1200	19.849	119.112	104.216	17.938	-193.374	-140.593	25.605
1300	19.852	120.700	105.452	19.823	-193.285	-136.194	22.697
1400	19.855	122.172	106.584	21.609	-193.199	-131.812	20.577
1500	19.857	123.542	107.679	23.794	-193.114	-127.428	18.566
1600	19.858	124.833	108.711	25.780	-193.038	-123.053	16.808
1700	19.860	126.057	109.694	27.766	-192.957	-118.640	15.297
1800	19.861	127.167	110.633	29.752	-192.886	-114.314	13.660
1900	19.862	128.163	111.532	31.738	-192.820	-109.948	12.647
2000	19.863	129.155	112.393	33.725	-192.764	-105.589	11.538
2100	19.864	130.144	113.219	35.711	-192.719	-101.332	10.335
2200	19.865	131.118	114.013	37.697	-192.689	-97.076	9.092
2300	19.865	132.031	114.777	39.684	-192.671	-92.821	8.751
2400	19.866	132.877	115.514	41.671	-192.673	-88.167	8.059
2500	19.866	133.688	116.225	43.657	-192.699	-83.813	7.337
2600	19.867	134.467	116.912	45.644	-192.747	-79.856	6.670
2700	19.867	135.217	117.576	47.630	-192.825	-75.997	6.079
2800	19.867	135.939	118.219	49.617	-192.935	-70.735	5.521
2900	19.868	136.637	118.842	51.604	-193.076	-66.368	5.002
3000	19.868	137.310	119.446	53.591	-193.264	-61.996	4.516
3100	19.868	137.962	120.033	55.578	-193.498	-57.617	4.062
3200	19.868	138.592	120.603	57.564	-193.776	-53.231	3.625
3300	19.869	139.204	121.158	59.551	-194.110	-48.833	3.234
3400	19.869	139.797	121.697	61.538	-194.502	-44.423	2.855
3500	19.869	140.373	122.223	63.525	-194.962	-40.005	2.498
3600	19.869	140.933	122.735	65.512	-195.494	-35.570	2.159
3700	19.869	141.477	123.234	67.500	-196.103	-31.116	1.838
3800	19.869	142.007	123.721	69.486	-196.796	-26.650	1.533
3900	19.869	142.523	124.197	71.473	-197.582	-22.161	1.242
4000	19.870	143.026	124.661	73.460	-198.467	-17.653	0.965
4100	19.870	143.517	125.115	75.447	-199.455	-13.122	0.699
4200	19.870	143.995	125.556	77.434	-200.555	-8.562	0.454
4300	19.870	144.463	125.993	79.421	-201.772	-3.982	0.202
4400	19.870	144.920	126.418	81.408	-203.108	0.638	-0.032
4500	19.870	145.366	126.834	83.395	-204.570	5.261	-0.256
4600	19.870	145.803	127.242	85.382	-206.158	9.943	-0.473
4700	19.870	146.230	127.641	87.369	-207.876	14.682	-0.683
4800	19.870	146.649	128.033	89.356	-209.723	19.434	-0.895
4900	19.870	147.056	128.417	91.343	-211.699	24.231	-1.081
5000	19.870	147.460	128.794	93.330	-213.799	29.066	-1.270
5100	19.870	147.853	129.157	95.317	-216.019	33.927	-1.455
5200	19.870	148.236	129.527	97.304	-218.356	38.870	-1.635
5300	19.870	148.618	129.894	99.291	-220.800	43.838	-1.808
5400	19.871	148.989	130.234	101.278	-223.344	48.854	-1.977
5500	19.871	149.354	130.578	103.265	-225.976	53.922	-2.143
5600	19.871	149.712	130.917	105.252	-228.688	59.033	-2.304
5700	19.871	150.063	131.250	107.239	-231.469	64.193	-2.461
5800	19.871	150.409	131.577	109.226	-234.305	69.410	-2.615
5900	19.871	150.749	131.899	111.213	-237.186	74.667	-2.766
6000	19.871	151.083	132.216	113.200	-240.101	79.980	-2.913

June 30, 1968

CESIUM CHLORIDE, DIMERIC (Cs₂Cl₂)

(IDEAL GAS)

GFW = 336.716

Point Group [D_{2h}]

ΔHf° = -156.8 ± 2.5 kcal/mol

S°_{298.15} = [91.6 ± 2.1 gibbs/mol]

ΔHf°_{298.15} = -157.7 ± 2.5 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[140] (1)	[76] (1)
[87] (1)	[151] (1)
[141] (1)	[156] (1)

Bond Distance: Cs-Cl = [3.18] Å

Bond Angle: Cl-Cs-Cl = [93.2°]

Product of the Moments of Inertia: I_AI_BI_C = [3.8076 × 10⁻¹¹¹] g³ cm⁶

σ = [4]

Heat of Formation

Datz (1) studied the molecular association equilibrium in cesium chloride vapors by measuring the temperature dependence of the molecular weight of gaseous CsCl. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. The pressure sensing element was a fused silica manometer containing Au(t). Based on the reported results, we derive the equilibrium constants for the reaction Cs₂Cl₂(g) = 2CsCl(g) in the temperature range 1224 - 1418°K. The enthalpy change of this reaction is evaluated by the second and third law method as 39.3 ± 1.1 and 42.9 ± 0.6 kcal/mol, respectively. The drift in the third law value is equivalent to an entropy error of 2.7 ± 0.8 eu. Using the third law ΔHf° and ΔHf°₂₉₈ (CsCl, g) = -57.4 kcal/mol, we obtain ΔHf°₂₉₈ = -157.7 ± 2.5 kcal/mol for Cs₂Cl₂(g), which is adopted.

Schrier (2) determined the vapor pressures of molten cesium chloride at temperatures between 1165 and 1387°K by the boiling point or manometric method. The vapor analysis was performed using the transpiration method. An inert gas, N₂, was passed over the CsCl sample at a given temperature. The salt vapor entrained by the carrier gas was collected, weighed and analyzed. The data obtained were combined with the boiling point measurements to yield the average molecular weight of the vapor. Association into dimer was postulated. The mole fraction in the vapor and the partial pressure of CsCl(g) and Cs₂Cl₂(g) were calculated. The equilibrium constants, 1203 - 1350°K, for dissociation of the Cs₂Cl₂ dimer were derived. Using the reported equilibrium constants, we evaluate the enthalpy change (ΔHf°₂₉₈) of the reaction Cs₂Cl₂(g) = 2CsCl(g) to be 34.1 ± 2.9 and 43.2 ± 0.9 kcal/mol by the second and third law methods. Based on the third law ΔHf°₂₉₈ value and ΔHf°₂₉₈ (CsCl, g) = -57.4 kcal/mol, we obtain ΔHf°₂₉₈ = -158.0 kcal/mol for Cs₂Cl₂(g), which is in agreement with the adopted value.

Miller and Kusch (3) made an analysis of the velocity distribution of the CsCl molecules which escape through an ideal aperture from an isothermal enclosure. They found that there was no definite evidence that any species other than diatomic molecules were present in the beams in measurable amounts, in other words, the dimerization must be small, e.g. <1.5 per cent. However, according to our calculation the concentration of dimer is 15 - 34 per cent in the temperature range 600 - 900°K, and 33 - 20 per cent at the temperatures 1000 - 1600°K.

Heat Capacity and Entropy

The molecular structure is assumed to be planar, having D_{2h} symmetry. Based on the bond distances of Cs-Cs and Cl-Cl estimated by Berkowitz (4), the Cs-Cl bond distance and Cl-Cs-Cl bond angle are calculated. The vibrational frequencies were calculated by Berkowitz (5), on the basis of the potential function for an ionic model. The three principal moments of inertia are: I_A = 2.105 × 10⁻³⁷, I_B = 6.272 × 10⁻³⁷, and I_C = 2.732 × 10⁻³⁷ g cm².

References

1. S. Datz, Oak Ridge National Laboratory, ORNL-2933, Oak Ridge, Tennessee, May 1960.
2. E. E. Schrier, Ph. D. Thesis, Rensselaer Polytechnic Institute, 1961.
3. R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).
4. J. Berkowitz, J. Chem. Phys. 29, 1386 (1958).
5. J. Berkowitz, J. Chem. Phys. 32, 1519 (1960).

Cl₂Os₂

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	11.160	9.804	3.581	-49.392	-49.392	INFINITE
200	15.656	13.456	3.012	-49.083	-45.905	100.326
298	17.280	15.653	2.626	-49.497	-42.183	46.095
300	17.190	25.039	25.833	∞	36.655	28.335
400	17.940	30.994	26.517	-49.194	-38.500	28.112
500	18.470	35.057	27.832	1.791	-48.862	19.180
600	18.830	38.458	29.327	3.612	-48.510	13.858
700	19.110	41.382	30.845	5.478	-48.146	10.337
800	19.332	43.946	32.326	7.376	-47.771	7.840
900	19.516	46.236	33.747	9.298	-47.397	5.983
1000	19.687	48.301	35.101	11.240	-47.007	4.450
1100	19.838	50.185	36.398	13.201	-46.618	3.413
1200	19.983	51.917	37.611	15.177	-46.225	2.691
1300	20.122	53.522	38.774	17.168	-45.830	2.129
1400	20.256	55.018	39.881	19.173	-45.431	1.680
1500	20.384	56.420	40.938	21.192	-45.024	1.330
				23.224	-44.618	.931

COPPER DICHLORIDE (CuCl₂)

(CRYSTAL)

MOL. WT. = 134.446

$\Delta H_{f,0}^{\circ} = -49.39 \pm 1.5 \text{ kcal. mole}^{-1}$

$\Delta H_{f,298.15}^{\circ} = -49.2 \pm 1.5 \text{ kcal. mole}^{-1}$

$S_{298.15}^{\circ} = 25.833 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_d = [766]^{\circ}\text{K.}$

Heat of Formation.

S. A. Shchukarev and M. A. Oranskaya, Zhur. Obshchei Khim. 24, 1928 (1954) have reported equilibrium constants for the dissociation $\text{CuCl}_2(\text{c}) \rightarrow \text{CuCl}(\text{c}) + 0.5 \text{ Cl}_2(\text{g})$, which are in general agreement with earlier reports by P. Ephraïm, Ber. 50, 1089 (1917) and D. I. Tarasenko, A. I. Origorovich and A. V. Boroslovskaya, Collected Works of the Central State Institute for Non-Ferrous Metallurgy, Part 1, 2, 89 (1929). These data were subjected to third law analysis which revealed a significant trend of $13 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole.}$, indicating that equilibrium conditions were not reached. However an average value of $\Delta H_{f,298}^{\circ} = 16.5 \pm 1.9 \text{ kcal. mole}^{-1}$ yields a heat of formation of $\text{CuCl}_2(\text{c}) = -49.5 \pm 2.5 \text{ kcal. mole}^{-1}$ which is in good agreement with the adopted value taken from Natl. Bureau Std. Circular 500, Washington, 1952.

Heat Capacity and Entropy.

The low temperature heat capacity has been measured from 11-300°K. by J. W. Stout and R. C. Chisholm, J. Chem. Phys. 36, 979 (1962). The integration of this data from $S_{10}^{\circ} = 0.111 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ gave $S_{298}^{\circ} = 25.833 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The heat capacity above 298° was obtained by smooth extrapolation of the above data, since the heat capacities of A. N. Krestovnikov and G. A. Karetnikov, Journ. Gen. Chem. (USSR) 5, 955 (1956) were not compatible with the low temperature data.

Decomposition Data.

The temperature of decomposition was estimated from the table for $\text{CuCl}_2(\text{c})$, $\text{CuCl}(\text{l})$ and $\text{Cl}_2(\text{g})$ so that the pressure of Cl_2 is 1 atm.

Phosphoryl Fluoride Dichloride (POCl₂F)
(Ideal Gas) Mol. Wt. = 136.889

PHOSPHORYL FLUORIDE DICHLORIDE (POCl₂F) (IDEAL GAS) MOL. WT. = 136.889

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	10.444	60.497	91.125	-3.4927	-177.779	-177.779	-177.779	INFINITE
200	15.843	69.590	78.193	-3.063	-178.410	-178.410	-178.410	383.932
298	18.938	76.348	70.548	-2.800	-179.002	-179.002	-179.002	186.799
300	19.003	76.666	70.549	-2.800	-179.002	-179.002	-179.002	126.448
400	20.951	82.420	71.320	-2.040	-179.101	-179.101	-179.101	123.639
500	22.223	87.242	71.836	-1.4203	-179.131	-179.131	-179.131	91.030
600	23.083	91.374	72.589	-0.871	-179.156	-179.156	-179.156	71.458
700	23.698	94.981	73.498	-0.471	-179.175	-179.175	-179.175	58.409
800	24.117	98.173	74.510	-0.262	-179.189	-179.189	-179.189	48.252
900	24.435	101.033	75.687	-0.152	-179.200	-179.200	-179.200	39.590
1000	24.674	103.620	77.023	-0.087	-179.208	-179.208	-179.208	32.662
1100	24.859	105.981	78.405	-0.054	-179.214	-179.214	-179.214	26.712
1200	25.000	108.056	79.737	-0.036	-179.218	-179.218	-179.218	21.646
1300	25.119	110.000	81.110	-0.024	-179.220	-179.220	-179.220	17.266
1400	25.212	112.022	82.593	-0.016	-179.221	-179.221	-179.221	13.506
1500	25.289	113.764	84.166	-0.010	-179.222	-179.222	-179.222	10.015
1600	25.352	115.298	85.837	-0.006	-179.223	-179.223	-179.223	6.761
1700	25.401	116.730	87.597	-0.003	-179.224	-179.224	-179.224	3.745
1800	25.436	118.060	89.446	-0.002	-179.225	-179.225	-179.225	2.478
1900	25.468	119.300	91.384	-0.001	-179.226	-179.226	-179.226	1.585
2000	25.521	121.075	93.417	-0.001	-179.227	-179.227	-179.227	1.071
2100	25.569	122.321	95.552	-0.001	-179.228	-179.228	-179.228	0.687
2200	25.617	123.577	97.789	-0.001	-179.229	-179.229	-179.229	0.410
2300	25.660	124.847	100.130	-0.001	-179.230	-179.230	-179.230	0.243
2400	25.698	126.130	102.580	-0.001	-179.231	-179.231	-179.231	0.153
2500	25.732	127.426	105.140	-0.001	-179.232	-179.232	-179.232	0.095
2600	25.762	128.736	107.810	-0.001	-179.233	-179.233	-179.233	0.055
2700	25.788	130.060	110.590	-0.001	-179.234	-179.234	-179.234	0.031
2800	25.812	131.400	113.480	-0.001	-179.235	-179.235	-179.235	0.016
2900	25.833	132.750	116.400	-0.001	-179.236	-179.236	-179.236	0.008
3000	25.852	134.110	119.450	-0.001	-179.237	-179.237	-179.237	0.004
3100	25.869	135.480	122.630	-0.001	-179.238	-179.238	-179.238	0.002
3200	25.883	136.860	125.840	-0.001	-179.239	-179.239	-179.239	0.001
3300	25.895	138.250	129.080	-0.001	-179.240	-179.240	-179.240	0.000
3400	25.906	139.650	132.350	-0.001	-179.241	-179.241	-179.241	0.000
3500	25.916	141.060	135.660	-0.001	-179.242	-179.242	-179.242	0.000
3600	25.925	142.480	139.010	-0.001	-179.243	-179.243	-179.243	0.000
3700	25.933	143.910	142.400	-0.001	-179.244	-179.244	-179.244	0.000
3800	25.940	145.350	145.830	-0.001	-179.245	-179.245	-179.245	0.000
3900	25.946	146.800	149.300	-0.001	-179.246	-179.246	-179.246	0.000
4000	25.951	148.260	152.810	-0.001	-179.247	-179.247	-179.247	0.000
4100	25.955	149.730	156.360	-0.001	-179.248	-179.248	-179.248	0.000
4200	25.959	151.210	160.000	-0.001	-179.249	-179.249	-179.249	0.000
4300	25.962	152.700	163.680	-0.001	-179.250	-179.250	-179.250	0.000
4400	25.965	154.200	167.410	-0.001	-179.251	-179.251	-179.251	0.000
4500	25.968	155.710	171.180	-0.001	-179.252	-179.252	-179.252	0.000
4600	25.971	157.230	175.000	-0.001	-179.253	-179.253	-179.253	0.000
4700	25.974	158.760	178.870	-0.001	-179.254	-179.254	-179.254	0.000
4800	25.977	160.300	182.790	-0.001	-179.255	-179.255	-179.255	0.000
4900	25.979	161.850	186.760	-0.001	-179.256	-179.256	-179.256	0.000
5000	25.981	163.410	190.780	-0.001	-179.257	-179.257	-179.257	0.000
5100	25.983	164.980	194.850	-0.001	-179.258	-179.258	-179.258	0.000
5200	25.985	166.560	198.970	-0.001	-179.259	-179.259	-179.259	0.000
5300	25.987	168.150	203.140	-0.001	-179.260	-179.260	-179.260	0.000
5400	25.989	169.750	207.360	-0.001	-179.261	-179.261	-179.261	0.000
5500	25.991	171.360	211.630	-0.001	-179.262	-179.262	-179.262	0.000
5600	25.993	172.980	215.950	-0.001	-179.263	-179.263	-179.263	0.000
5700	25.995	174.610	220.320	-0.001	-179.264	-179.264	-179.264	0.000
5800	25.997	176.250	224.740	-0.001	-179.265	-179.265	-179.265	0.000
5900	25.999	177.900	229.210	-0.001	-179.266	-179.266	-179.266	0.000
6000	26.000	179.560	233.730	-0.001	-179.267	-179.267	-179.267	0.000

March 31, 1963

Point Group C_{2v}

S_{298.15} = 76.548 cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
207 (1)	372 (1)	620 (1)
254 (1)	894 (1)	894 (1)
330 (1)	547 (1)	1331 (1)

Bond Distances: P-Cl = 1.99 ± 0.04 Å P-P = 1.50 ± 0.03 Å P-O = 1.54 ± 0.03 Å

Bond Angle: Cl-P-Cl = 103° σ = 1

Product of the Moments of Inertia: I_AI_BI_C = 4.70732540 X 10⁻¹¹³ g.³ cm.⁶

Heat of Formation.

The ΔH_f^o 298.15 of POCl₂F was estimated to be -179 kcal. mole⁻¹ from the ΔH_f^o 298.15 of POCl₃ by assuming bond energies of 120 kcal. for D(P-F) and 80 kcal. for D(P-Cl). The D(P-F) and D(P-Cl) values were taken from E. Meale and L. T. D. Williams, J. Chem. Soc., 2485 (1955) Part I and E. Neale, L. T. D. Williams, and V. T. Moores, J. Chem. Soc. 422 (1956) Part II.

Essentially the same ΔH_f^o 298.15 may be obtained by assuming a ΔH_f^o = 0 for the following reaction:



Heat Capacity and Entropy.

The molecular constants were determined by L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. 60, 1836 (1938) and by Q. Williams, J. Sheridan, and M. Gordy, J. Chem. Phys., 20, 164 (1952). Brockway and Beach used electron diffraction. Q. Williams et al. measured microwave spectra. Brockway and Beach assumed that the P-P-F and P-P-Cl angles were equal in POCl₂F and POCl₂F. An analysis of their data by Q. Williams et al. indicates that the angles in POCl₂F, POCl₂F, and POCl₂F should be 103° rather than the reported 106° ± 3°. The principal moments of inertia calculated from these parameters were I_A = 2.69184 X 10⁻³⁸, I_B = 3.79516 X 10⁻³⁸, and I_C = 4.60780 X 10⁻³⁸.

The Raman spectra and vibrational frequencies for POCl₂F were reported by M. L. Delvaux and P. Francois, Compt. Rend. 222, 550 (1946). These frequency assignments are summarized in J. Chim. Phys. 46, 87 (1949) by M. L. Delvaux and P. Francois.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	0.000	INFINITE	3.889	- 82.320	- 82.320	INFINITE
100	12.164	43.476	3.277	- 82.512	- 78.017	172.465
200	16.806	29.628	1.748	- 82.116	- 75.452	82.446
298	18.323	28.190	0.000	- 81.700	- 72.270	52.979
300	18.340	28.303	- 0.34	- 81.492	- 72.211	52.604
400	19.041	33.681	1.905	- 80.172	- 69.115	37.041
500	19.512	37.083	3.834	- 80.876	- 66.120	26.500
600	19.863	41.572	5.803	- 80.506	- 63.204	23.021
700	20.166	45.657	7.804	- 80.172	- 60.348	19.840
800	20.437	49.288	9.826	- 79.876	- 57.422	16.968
900	20.675	52.577	11.891	- 79.609	- 54.733	14.398
1000	20.876	55.676	13.969	- 79.368	- 52.085	11.961
1100	21.036	58.576	16.065	- 79.144	- 49.203	9.775
1200	21.165	61.275	18.175	- 78.937	- 46.424	7.855
1300	21.270	63.774	20.299	- 78.746	- 43.848	6.188
1400	21.340	66.088	22.427	- 78.569	- 41.421	4.753
1500	21.393	68.187	24.563	- 78.406	- 39.215	3.508
1600	21.435	70.045	26.705	- 78.281	- 37.131	2.485
1700	21.467	71.675	28.960	- 78.180	- 35.262	1.662
1800	21.489	73.104	31.327	- 78.100	- 33.598	0.988
1900	21.500	74.355	33.707	- 78.034	- 32.124	0.521
2000	21.500	75.458	36.207	- 78.000	- 30.821	0.248

$$\Delta H_f^0 = -82.32 \pm 0.12 \text{ kcal. mole}^{-1}$$
$$\Delta H_f^{298.15} = -81.70 \pm 0.12 \text{ kcal. mole}^{-1}$$
$$\Delta H_m^0 = 10.28 \pm 0.05 \text{ kcal. mole}^{-1}$$
$$\Delta H_m^{298.15} = 46.2 \pm 0.7 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 28.190 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$T_m = 950^\circ \text{K.}$$

Heat of Formation.

The enthalpy change, $\Delta H_f^{298.15} = -4.06 \pm 0.05 \text{ kcal. mole}^{-1}$, for the reaction $\text{Fe}(\text{cl}) + 2(\text{HCl} \cdot 12.731 \text{ H}_2\text{O}) (\text{l}) = \text{FeCl}_2(\text{c}) + \text{H}_2(\text{g}) + 25.462 \text{ H}_2\text{O} (\text{l})$ was reported by M. F. Kohler and J. P. Coughlin, J. Phys. Chem. 63, 605 (1959). The value of $\Delta H_f^{298.15}(\text{FeCl}_2, \text{c})$ was then derived. The enthalpy change, $\Delta H_f^{298.15} = -19.5 \pm 0.2 \text{ kcal. mole}^{-1}$, for the reaction $\text{FeCl}_2(\text{c}) = \text{Fe}^{++}(\text{aq.}) + 2 \text{ Cl}^{-}(\text{aq.})$ was determined by J. C. M. Li and N. W. Gregory, J. Am. Chem. Soc. 74, 4670 (1952), yielding $\Delta H_f^{298.15} = -81.4 \pm 0.2 \text{ kcal. mole}^{-1}$ which is in agreement with the adopted value reported by M. F. Kohler and J. P. Coughlin. The equilibrium constants for the reaction $\text{FeCl}_2(\text{c}) + \text{H}_2(\text{g}) = \text{Fe}(\text{c}) + 2\text{HCl}(\text{g})$ were determined by W. Kangro and E. Petersen, Z. Anorg. Chem. 261, 157 (1950). By use of the second and third law methods the enthalpy change ($\Delta H_f^{298.15}$) of this reaction was evaluated as 37.81 ± 0.68 and $38.24 \text{ kcal. mole}^{-1}$, respectively. Based on the third law value for $\Delta H_f^{298.15}$, the value of $\Delta H_f^{298.15}(\text{FeCl}_2, \text{c})$ was derived to be $-82.37 \text{ kcal. mole}^{-1}$ which is in reasonable agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature ($53.2-295.0^\circ \text{K.}$) heat capacities were determined by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. 65, 1264 (1943). The high temperature ($670.5-941.0^\circ \text{K.}$) heat capacities were measured by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). The two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 941.0°K. were obtained by graphical extrapolation. The C_p values, $60-500^\circ \text{C.}$, were also reported by P. L. Oetting and N. W. Gregory, J. Phys. Chem. 65, 138 (1961) which are in good agreement with those determined by G. E. Moore, loc. cit. $S_{298.15}^0$ was derived from the smoothed C_p values, using $S_{53.2}^0 = 4.950 \text{ e.u.}$ The $S_{298.15}^0$ value was determined by E. F. Westrum, Jr. quoted by L. E. Wilson and N. W. Gregory in J. Phys. Chem. 62, 437 (1958). The entropy at 298° is assumed to include the uncoupling energy of Fe^{++} which is calculated to be 3.2 e.u. which corresponds to R in 5.

Melting Data.

T_m and ΔH_m^0 were taken from G. E. Moore, loc. cit.

Heat of Sublimation.

The difference between $\Delta H_f^{298.15}$ for $\text{FeCl}_2(\text{g})$ and $\text{FeCl}_2(\text{c})$ is $\Delta H_m^{298.15}$. The former was obtained by the second and third law analyses on the equilibrium pressure data as described in $\text{FeCl}_2(\text{g})$ table.

Iron Dichloride (FeCl₂)

Mol. Wt. = 126.753

(Liquid)

Cl₂Fe

MOL. WT. = 126.753

(LIQUID)

IRON DICHLORIDE (FeCl₂)

T, °K.	C _p	S°	(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	33.432	33.432	-	.000	- 74.411	- 66.544	48.776
200	33.583	33.432		.045	- 74.392	- 66.495	48.439
300	34.057	34.350		2.484	- 74.306	- 64.014	24.974
400	36.019	36.199		4.929	- 72.482	- 61.772	26.596
500	38.224	38.224		7.371	- 71.649	- 59.709	21.746
600	40.255	40.255		9.813	- 70.874	- 57.782	18.059
700	42.216	42.216		12.255	- 70.186	- 55.961	15.287
800	44.117	44.117		14.697	- 69.582	- 54.343	12.582
900	45.965	45.965		17.139	- 69.058	- 52.922	11.460
1000	47.510	47.510		19.581	- 68.609	- 50.867	10.106
1100	48.984	48.984		22.023	- 68.236	- 49.236	8.967
1200	50.312	50.312		24.465	- 67.931	- 47.866	8.010
1300	51.517	51.517		26.907	- 67.694	- 46.744	7.199
1400	52.592	52.592		29.349	- 67.521	- 45.824	6.501
1500	53.539	53.539			- 67.406	- 45.100	
1600	54.362	54.362			- 67.346	- 44.566	
1700	55.065	55.065			- 67.340	- 44.183	
1800	55.643	55.643			- 67.388	- 43.940	
1900	56.093	56.093			- 67.484	- 43.853	
2000	56.417	56.417			- 67.628	- 43.826	
2100	56.619	56.619			- 67.818	- 43.851	
2200	56.788	56.788			- 68.052	- 43.911	
2300	56.922	56.922			- 68.333	- 44.001	
2400	57.029	57.029			- 68.657	- 44.128	
2500	57.104	57.104			- 69.024	- 44.291	
2600	57.146	57.146			- 69.433	- 44.491	
2700	57.154	57.154			- 69.884	- 44.728	
2800	57.127	57.127			- 70.377	- 45.001	
2900	57.061	57.061			- 70.904	- 45.311	
3000	56.954	56.954			- 71.467	- 45.653	

$\Delta H_f^{298.15} = -74.411 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta H_m^{298.15} = 10.28 \pm 0.05 \text{ kcal. mole}^{-1}$
 $\Delta H_v^{298.15} = 29.83 \text{ kcal. mole}^{-1}$

Heat of Formation.

The value of $\Delta H_f^{298.15}(\text{FeCl}_2, l)$ was obtained from $\Delta H_f^{298.15}(\text{FeCl}_2, c)$ by adding $\Delta H_m^{298.15}$ and the difference between $H_m^{298.15} - H_{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity (850-1100°K.) for FeCl₂(l) was reported as 24.42 cal. deg.⁻¹ mole⁻¹ by O. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). A constant C_p was assumed for all the other temperatures. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and $\Delta H_m^{298.15}$ were taken from G. M. Moore, loc. cit.

Vaporization Data.

The boiling point (T_b) is determined as the temperature at which the free energy change ($\Delta F_v^{298.15}$) for the reaction FeCl₂(l) = FeCl₂(g) approaches zero. The corresponding enthalpy change ($\Delta H_v^{298.15}$) at T_b is the heat of vaporization ($\Delta H_v^{298.15}$).

Iron Dichloride (FeCl₂)

(Ideal Gas) Mol. Wt. = 126.753

T, °K.	C _p ^o	ent. mole ¹ /deg. ⁻¹ S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	3.394	-35.625	-	INFINITE
100	15.080	63.128	70.016	-35.556	-37.250	40.747
200	16.830	68.710	80.000	-35.500	-38.151	27.964
300	18.854	68.802	88.711	-35.499	-38.168	27.804
400	19.667	73.526	91.560	-35.422	-38.069	21.746
500	19.897	76.734	94.451	-35.369	-38.068	17.476
600	19.892	79.633	97.473	-35.377	-40.011	14.901
700	19.826	82.078	73.053	-35.458	-41.829	13.059
800	19.759	84.187	74.313	-35.633	-42.730	11.673
900	19.706	85.640	75.518	-35.926	-43.599	10.507
1000	19.675	87.053	76.654	-36.408	-44.430	9.710
1100	19.654	88.186	77.726	-37.113	-45.193	8.979
1200	19.642	89.548	78.749	-37.612	-45.912	8.361
1300	19.635	91.769	79.696	-37.773	-46.596	7.833
1400	19.631	94.536	80.603	-37.895	-47.268	7.379
1500	19.627	97.638	81.463	-38.169	-47.927	6.983
1600	19.624	99.044	82.280	-38.363	-48.573	6.634
1700	19.619	99.992	83.059	-38.885	-49.197	6.324
1800	19.614	99.884	83.603	-39.225	-49.793	6.045
1900	19.608	99.729	84.051	-39.481	-50.361	5.793
2000	19.598	99.529	85.193	-43.664	-50.342	5.523
2100	19.588	99.289	86.868	-44.080	-50.873	5.204
2200	19.576	100.014	86.675	-44.504	-51.187	5.085
2300	19.564	100.706	87.079	-44.933	-51.482	4.802
2400	19.551	101.361	87.471	-45.361	-51.761	4.547
2500	19.538	102.003	88.222	-45.816	-52.034	4.302
2600	19.524	102.612	88.764	-46.268	-52.253	4.247
2700	19.509	103.198	89.288	-46.728	-52.478	4.112
2800	19.495	103.762	89.795	-47.197	-52.680	4.004
2900	19.481	104.303	90.285	-47.674	-52.864	3.884
3000	19.465	104.830	90.762	-48.158	-53.039	3.804
3100	19.451	105.337	91.224	-48.651	-53.193	3.750
3200	19.436	105.827	91.672	-49.158	-53.336	3.544
3300	19.422	106.302	92.109	-49.687	-53.466	3.269
3400	19.408	106.763	92.533	-50.236	-53.581	3.011
3500	19.394	107.208	92.948	-50.807	-53.681	2.767
3600	19.380	107.642	93.348	-51.457	-53.755	2.537
3700	19.367	108.063	93.740	-52.194	-53.803	2.319
3800	19.354	108.473	94.122	-53.000	-53.829	2.112
3900	19.341	108.871	94.496	-53.876	-53.846	1.916
4000	19.330	109.259	94.860	-54.820	-53.857	1.729
4100	19.318	109.638	95.216	-55.834	-53.854	1.551
4200	19.307	110.007	95.563	-56.918	-53.842	1.382
4300	19.295	110.367	95.904	-58.072	-53.820	1.220
4400	19.283	110.718	96.236	-59.296	-53.789	1.065
4500	19.274	111.062	96.562	-60.590	-53.751	0.910
4600	19.264	111.397	96.881	-61.956	-53.708	0.776
4700	19.255	111.726	97.193	-63.392	-53.653	0.660
4800	19.245	112.047	97.499	-64.897	-53.588	0.510
4900	19.235	112.361	97.799	-66.472	-53.515	0.384
5000	19.227	112.669	98.094	-68.116	-53.435	0.284
5100	19.219	112.970	98.382	-69.829	-53.349	0.148
5200	19.211	113.266	98.666	-71.611	-53.258	0.036
5300	19.203	113.555	98.944	-73.464	-53.162	-0.072
5400	19.195	113.838	99.217	-75.389	-53.061	-0.186
5500	19.188	114.116	99.490	-77.387	-52.956	-0.276
5600	19.181	114.392	99.769	-79.459	-52.848	-0.373
5700	19.174	114.660	100.009	-81.604	-52.737	-0.467
5800	19.167	114.924	100.264	-83.824	-52.624	-0.559
5900	19.159	115.184	100.514	-86.120	-52.509	-0.648
6000	19.154	115.438	100.761	-88.493	-52.392	-0.732

June 30, 1965

IRON DICHLORIDE (FeCl₂)

(IDEAL GAS)

MOL. WT. = 126.753

Point Group [D_{∞h}]ΔH_f^o 0 = -35.83 ± 2.0 kcal. mole⁻¹S_{298.15} = [69.71] cal. deg.⁻¹ mole⁻¹ΔH_f^o 298.15 = -35.50 ± 2.0 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E ₁ , cm. ⁻¹	E ₂
0	[5]
[800]	[10]
[3000]	[5]
[5000]	[5]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹
327 (1)
[135] (2)
492 (1)

Bond Distances: Fe-Cl = [2.09] Å

Bond Angles: Cl-Fe-Cl = [180]°

Rotational Constant: B₀ = [0.05442] cm.⁻¹

Heat of Formation.

The equilibrium pressures for the reactions (1) FeCl₂(l) = FeCl₂(g), (2) FeCl₂(c) = FeCl₂(g), and (3) Fe(c) + 2HCl(g) = FeCl₂(g) + H₂(g) were determined by several investigators. Using the reported data, the corresponding enthalpy changes (ΔH_f^o 298.15) for these reactions were evaluated by both the second and third law methods. Hence the respective ΔH_f^o 298.15 values for FeCl₂(g) were derived, based on the third law values for ΔH_f^o 298.15. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	ΔH _f ^o 298.15, kcal. mole ⁻¹
Beuman ¹	(1)	980.2-1167.2	37.07 ± 0.61	36.42	-35.45 ± 0.30
Schoonmaker and Porter ²	(2)	621.0-701.0	45.61 ± 0.10	46.14	-35.56 ± 0.20
H. Schäfer, et al. ³	(1)	981.0-1107.0	38.95 ± 0.10	37.77	-36.10 ± 0.30
Schäfer and Krehl ⁴	(1)	980.7-1106.7	40.56 ± 1.45	37.78	-36.11 ± 0.30
C. O. Meier ⁵	(1)	972.1-1266.0	36.68 ± 0.16	37.95	-35.92 ± 0.30
Schäfer and Krehl ⁴	(3)	1205.2-1573.2	4.10 ± 0.13	8.01	-36.13 ± 0.50

¹ C. Beuman, "Activities in the KCl-FeCl₂ and LiCl-FeCl₂ Systems", ORNL-2323, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1957.

² R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **29**, 118 (1958).

³ H. Schäfer, L. Bayer, O. Breil, K. Etzel and K. Krehl, Z. anorg. allgem. Chem. **278**, 300 (1955).

⁴ H. Schäfer and K. Krehl, Z. anorg. allgem. Chem. **269**, 35 (1952).

The value of ΔH_f^o 298.15 for FeCl₂(g) adopted is -35.5 ± 2.0 kcal. mole⁻¹.

Heat Capacity and Entropy.

The molecular structure, bond distance and angle, and two vibrational frequencies (ν₁ and ν₂) were obtained from L. Brewer, O. R. Sonayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963). The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe²⁺(g) reported by C. E. Moore, "Atomic Energy Levels", Circular of the National Bureau of Standards 467, Vol. II, 1952, using the reasoning suggested by J. T. Hougen, O. E. Leroi and F. C. James, J. Chem. Phys. **34**, 1970 (1961). The total 2S for the quantum weight was obtained from the ground multiplet of Fe²⁺ and was split arbitrarily. The bending frequency (ν₃) was derived such that the calculated free energy functions are consistent with the experimental equilibrium data. In other words, the free energy functions were adjusted by choosing a proper value for ν₃ in order to make the second and third law values of ΔH_f^o for the reactions in reasonable agreement. The moment of inertia (I) is 5.125 x 10⁻³⁶ g. cm.².

Cl₂F₈

Dichlorosilane (SiH₂Cl₂)

(Ideal Gas) Mol. Wt. = 101.02

INTERIM TABLE

T, °K.	C _p ^a	S° ^b	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^c	ΔF _f ^c	Log K _p
100	9.080	56.063	106.111	3.494	73.920	73.920	10.111
200	11.836	68.488	89.758	2.359	73.920	73.920	10.111
298	14.931	77.179	80.488	1.632	73.920	73.920	10.111
300	15.879	78.191	80.488	1.632	73.920	73.920	10.111
400	17.076	83.181	70.335	3.422	75.010	68.871	10.170
500	18.659	87.518	60.689	5.349	75.010	68.871	10.170
600	19.437	90.669	51.774	7.361	75.010	68.871	10.170
700	20.274	92.820	43.820	9.481	75.010	68.871	10.170
800	21.068	94.111	36.820	11.709	75.010	68.871	10.170
900	21.818	95.518	30.727	14.048	75.010	68.871	10.170
1000	22.525	96.931	25.525	16.481	75.010	68.871	10.170
1100	23.193	98.350	21.121	18.999	75.010	68.871	10.170
1200	23.820	99.771	17.521	21.599	75.010	68.871	10.170
1300	24.410	101.193	14.721	24.279	75.010	68.871	10.170
1400	24.961	102.615	12.621	26.929	75.010	68.871	10.170
1500	25.483	104.037	11.121	29.549	75.010	68.871	10.170
1600	25.975	105.459	10.121	32.129	75.010	68.871	10.170
1700	26.437	106.881	9.521	34.649	75.010	68.871	10.170
1800	26.869	108.303	9.121	37.109	75.010	68.871	10.170
1900	27.271	109.725	8.821	39.509	75.010	68.871	10.170
2000	27.643	111.147	8.521	41.849	75.010	68.871	10.170
2100	27.985	112.569	8.221	44.129	75.010	68.871	10.170
2200	28.297	113.991	7.921	46.349	75.010	68.871	10.170
2300	28.579	115.413	7.621	48.509	75.010	68.871	10.170
2400	28.831	116.835	7.321	50.609	75.010	68.871	10.170
2500	29.053	118.257	7.021	52.649	75.010	68.871	10.170
2600	29.245	119.679	6.721	54.629	75.010	68.871	10.170
2700	29.407	121.101	6.421	56.549	75.010	68.871	10.170
2800	29.549	122.523	6.121	58.409	75.010	68.871	10.170
2900	29.671	123.945	5.821	60.209	75.010	68.871	10.170
3000	29.773	125.367	5.521	61.949	75.010	68.871	10.170
3100	29.855	126.789	5.221	63.629	75.010	68.871	10.170
3200	29.917	128.211	4.921	65.249	75.010	68.871	10.170
3300	29.959	129.633	4.621	66.809	75.010	68.871	10.170
3400	29.991	131.055	4.321	68.309	75.010	68.871	10.170
3500	30.003	132.477	4.021	69.749	75.010	68.871	10.170
3600	30.005	133.899	3.721	71.129	75.010	68.871	10.170
3700	30.007	135.321	3.421	72.449	75.010	68.871	10.170
3800	30.009	136.743	3.121	73.709	75.010	68.871	10.170
3900	30.011	138.165	2.821	74.909	75.010	68.871	10.170
4000	30.013	139.587	2.521	76.049	75.010	68.871	10.170
4100	30.015	141.009	2.221	77.129	75.010	68.871	10.170
4200	30.017	142.431	1.921	78.149	75.010	68.871	10.170
4300	30.019	143.853	1.621	79.109	75.010	68.871	10.170
4400	30.021	145.275	1.321	80.009	75.010	68.871	10.170
4500	30.023	146.697	1.021	80.849	75.010	68.871	10.170
4600	30.025	148.119	0.721	81.629	75.010	68.871	10.170
4700	30.027	149.541	0.421	82.349	75.010	68.871	10.170
4800	30.029	150.963	0.121	83.009	75.010	68.871	10.170
4900	30.031	152.385	0.021	83.609	75.010	68.871	10.170
5000	30.033	153.807	0.000	84.149	75.010	68.871	10.170
5100	30.035	155.229		84.629	75.010	68.871	10.170
5200	30.037	156.651		85.049	75.010	68.871	10.170
5300	30.039	158.073		85.409	75.010	68.871	10.170
5400	30.041	159.495		85.709	75.010	68.871	10.170
5500	30.043	160.917		85.949	75.010	68.871	10.170
5600	30.045	162.339		86.129	75.010	68.871	10.170
5700	30.047	163.761		86.249	75.010	68.871	10.170
5800	30.049	165.183		86.309	75.010	68.871	10.170
5900	30.051	166.605		86.349	75.010	68.871	10.170
6000	30.053	168.027		86.369	75.010	68.871	10.170

December 31, 1960.

Cl₂H₂Si

Dichlorosilane (SiH₂Cl₂) (Ideal Gas)

Mol. Wt. = 101.02

ΔH_f^o 298.15 = [-80 ± 15] kcal. mole⁻¹

S^o 298.15 = 68.531 cal. deg.⁻¹ mole⁻¹

Point group C_{2v}

Vibrational Frequencies and Degeneracies

cm.⁻¹

2200 (1) 188 (1) 610 (1)

953 (1) 710 (1) 877 (1)

531 (1) 2200 (1) 592 (1)

SI-H distance = 1.48 Å all angles = [109° 28']

SI-Cl distance = 2.05 Å = 2

Product of Moments of Inertia: I_AI_BI_C = 7.9175 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation. ΔH_f^o 298.15 taken from Henderson and Scheffee,

"Survey of Thermochemical Data," Atlantic Research Corp.,

Alexandria, Va., January, 1960.

Heat Capacity and Entropy. Molecular constants taken from Janz

and Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961).

Cl₂H₂Si

Mercury Dichloride (HgCl₂)
(Crystal) Mol. Wt. = 271.524

INTERIM TABLE

T, °K.	C _p	S° -(R°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹ H°-H° ₂₉₈	cal. mole ⁻¹ ΔH° _f	ΔF° _f	Log K _p
0						
100						
298	17.664	34.535	.000	55.000	43.991	32.245
300	17.680	34.644	.033	54.994	43.972	31.976
400	18.500	35.776	1.133	54.861	43.766	31.106
500	19.500	36.902	3.707	54.316	43.118	30.069
600	19.520	47.503	38.123	53.913	33.236	12.106
700	20.066	50.555	39.686	67.486	28.255	8.621
800	20.480	53.263	41.217	66.940	22.694	6.200
900	20.946	55.702	42.693	66.135	17.211	4.800
1000	21.393	57.932	44.107	65.426	11.618	3.583
1100	21.818	59.991	45.458	64.662	6.493	1.290
1200	22.220	61.907	46.750	63.857	1.241	.226
1300	22.601	63.701	47.986	63.014	3.963	-.683
1400	22.960	65.389	49.169	62.139	6.762	-1.645
1500	23.320	66.983	50.304	61.229	14.116	-2.037

March 31, 1962

MERCURY DICHLORIDE (HgCl₂) (Crystal)

Mol. Wt. = 271.524

 $\Delta H_f^{298.15} = -55.000 \pm 1.0$ kcal. mole⁻¹ $S_{298.15}^{298.15} = [34.535] \pm 1.5$ cal. deg.⁻¹ mole⁻¹ $T_m = 550^\circ K$ $\Delta H_m = 4.64 \pm 0.05$ kcal. mole⁻¹

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," (1952).

Heat Capacity and Entropy. C_p was determined from the heat content data of L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960) and R. Ewald, Ann. d. Physik u. Chem. (4) 44, 1213 (1914).

Above 550° the curve was smoothly extrapolated. The entropy was estimated by adjusting the value to give the best fit of the melting, sublimation, and vaporization data.

Melting. T_m was taken from National Bureau of Standards Circular 500 (loc. cit.) ΔH_m was given by L. E. Topol and L. D. Ransom (loc. cit.).

Mercury Dichloride (HgCl₂)

(Liquid) Mol. Wt. = 271.524

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100								
200								
298	17.664	40.771	40.771	40.771	.000	- 51.404	- 42.239	30.961
300	17.680	40.830	40.771	.033	- 51.398	- 42.182	- 42.182	30.728
400	24.400	46.550	41.447	2.041	- 50.881	- 39.162	- 39.162	21.368
500	24.400	51.995	43.032	4.481	- 49.946	- 36.348	- 36.348	15.885
600	24.400	56.464	44.908	6.921	- 49.024	- 33.711	- 33.711	12.279
700	24.400	60.205	46.832	9.361	- 48.137	- 31.260	- 31.260	9.260
800	24.400	63.411	48.791	11.801	- 47.284	- 28.961	- 28.961	6.804
900	24.400	66.337	50.781	14.241	- 46.461	- 26.807	- 26.807	4.575
1000	24.400	68.908	52.726	16.681	- 45.677	- 24.851	- 24.851	3.571
1100	24.400	71.233	54.650	19.121	- 44.931	- 23.028	- 23.028	2.841
1200	24.400	73.359	56.537	21.561	- 44.221	- 21.328	- 21.328	2.241
1300	24.400	75.237	58.441	24.001	- 43.541	- 19.741	- 19.741	1.741
1400	24.400	77.118	59.547	26.441	- 42.881	- 18.261	- 18.261	1.261
1500	24.400	78.401						

MERCURY DICHLORIDE (HgCl₂) (liquid)

Mol. Wt. = 271.524
 ΔH_f^o 298.15 = -51.404 ± 1.0 kcal. mole⁻¹
 $S_{298.15}^o$ = [40.771] ± 1.5 cal. deg.⁻¹ mole⁻¹
 T_m = 550°K
 ΔH_m = 4.64 ± 0.05 kcal. mole⁻¹
 T_b = 577°K
 ΔH_v = 14.079 ± 0.25 kcal. mole⁻¹

Heat of Formation. Calculated from $\Delta H_f^o(c)$.

Heat Capacity and Entropy. The heat capacity was estimated to conform with the bromide and iodide, the value given by L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960) was counted. A glass type transition was assumed at 367°K below which the heat capacity was equal to that of the crystal. The entropy was obtained from $S^o(c)$, the entropy of fusion and the estimated heat capacity.

Fusion and Vaporization. T_m and T_b were taken from National Bureau of Standards (U.S.) Circular 500 (1952). ΔH_m was given by L. E. Topol and L. D. Ransom, J. Phys. Chem. 64, 1339 (1960) and ΔH_v was obtained from the data of E. B. R. Frideux, J. Chem. Soc. (London) 97, 2033 (1910) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Mercury Dichloride (HgCl₂)
(Ideal Gas) Mol. Wt. = 271.524 INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ log _e ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	-0000	INFINITE	-	3.874	-	34.014	-	INFINITE
100	11.099	56.705	82.117	2.591	-	34.188	-	34.450
200	13.015	65.049	71.680	1.326	-	34.311	-	37.873
298	13.889	70.833	70.833	1.000	-	34.365	-	25.404
300	13.900	70.833	70.833	0.984	-	34.357	-	25.246
400	14.299	74.579	70.948	1.438	-	34.531	-	18.671
500	14.504	77.794	72.036	2.479	-	35.109	-	15.038
600	14.621	80.450	73.223	4.336	-	35.170	-	12.479
700	14.742	82.676	74.581	7.092	-	35.254	-	10.157
800	14.782	84.476	75.841	9.782	-	35.354	-	8.045
900	14.776	86.014	76.691	8.750	-	35.468	-	6.245
1000	14.800	87.072	77.743	10.229	-	35.590	-	5.555
1100	14.818	88.343	78.738	11.710	-	35.723	-	4.992
1200	14.831	89.663	79.649	13.192	-	35.869	-	4.544
1300	14.841	90.961	80.571	14.611	-	36.028	-	4.196
1400	14.851	92.261	81.417	16.011	-	36.198	-	3.940
1500	14.858	93.566	82.222	17.464	-	36.378	-	3.676
1600	14.863	94.845	82.987	18.932	-	36.568	-	3.406
1700	14.872	96.096	83.715	20.406	-	36.768	-	3.132
1800	14.879	97.300	84.415	21.886	-	36.978	-	2.854
1900	14.878	98.463	85.083	23.353	-	37.198	-	2.572
2000	14.878	99.563	85.723	24.801	-	37.428	-	2.286
2100	14.880	100.607	86.337	26.259	-	37.668	-	1.996
2200	14.884	101.593	86.927	27.722	-	37.918	-	1.702
2300	14.884	102.526	87.497	29.192	-	38.178	-	1.406
2400	14.886	103.407	88.046	30.668	-	38.448	-	1.106
2500	14.888	104.234	88.575	32.152	-	38.728	-	0.806
2600	14.890	105.007	89.087	33.641	-	39.018	-	0.506
2700	14.890	105.730	89.582	35.136	-	39.318	-	0.206
2800	14.891	106.403	90.061	36.639	-	39.628	-	-0.094
2900	14.892	107.026	90.526	38.158	-	39.948	-	-0.394
3000	14.893	107.599	90.977	39.688	-	40.278	-	-0.694
3100	14.893	108.122	91.416	41.227	-	40.618	-	-0.994
3200	14.895	108.595	91.845	42.776	-	40.968	-	-1.294
3300	14.895	109.019	92.263	44.336	-	41.328	-	-1.594
3400	14.895	109.393	92.656	45.905	-	41.698	-	-1.894
3500	14.896	109.718	93.028	47.484	-	42.078	-	-2.194
3600	14.896	109.993	93.380	49.073	-	42.468	-	-2.494
3700	14.897	110.217	93.712	50.672	-	42.868	-	-2.794
3800	14.897	110.390	94.025	52.281	-	43.278	-	-3.094
3900	14.897	110.514	94.318	53.899	-	43.698	-	-3.394
4000	14.898	110.588	94.592	55.527	-	44.128	-	-3.694
4100	14.898	110.612	94.845	57.166	-	44.568	-	-3.994
4200	14.899	110.686	95.079	58.815	-	45.018	-	-4.294
4300	14.899	110.710	95.292	60.474	-	45.478	-	-4.594
4400	14.900	110.784	95.495	62.143	-	45.948	-	-4.894
4500	14.900	110.808	95.688	63.822	-	46.428	-	-5.194
4600	14.900	110.832	95.871	65.511	-	46.918	-	-5.494
4700	14.900	110.856	96.044	67.210	-	47.418	-	-5.794
4800	14.900	110.880	96.207	68.919	-	47.928	-	-6.094
4900	14.900	110.904	96.360	70.638	-	48.448	-	-6.394
5000	14.900	110.928	96.503	72.367	-	48.978	-	-6.694
5100	14.900	110.952	96.636	74.106	-	49.518	-	-6.994
5200	14.901	110.976	96.759	75.855	-	50.068	-	-7.294
5300	14.901	110.999	96.872	77.614	-	50.628	-	-7.594
5400	14.901	111.023	96.975	79.383	-	51.198	-	-7.894
5500	14.901	111.047	97.068	81.162	-	51.778	-	-8.194
5600	14.901	111.071	97.151	82.951	-	52.368	-	-8.494
5700	14.901	111.095	97.224	84.750	-	52.968	-	-8.794
5800	14.901	111.119	97.287	86.569	-	53.578	-	-9.094
5900	14.901	111.143	97.340	88.408	-	54.198	-	-9.394
6000	14.902	111.167	97.383	90.267	-	54.828	-	-9.694

March 31, 1962

MERCURY DICHLORIDE (HgCl₂) (Ideal Gas)

Mol. Wt. = 271.524
ΔH_f[°] 298.15 = -34.965 ± 1.5 kcal. mole⁻¹
S_{298.15}[°] = 70.433 cal. deg.⁻¹ mole⁻¹
Point Group D_{2h}

Vibrational Levels and Multiplicities

ω, cm. ⁻¹
380 (1)
70 (2)
415 (1)

Hg-Cl distance = 2.31 Å

Moment of Inertia = 62.022 X 10⁻³⁹ g. cm.²

σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952 was combined with the 3rd law heat of sublimation at 298°K from the data of K. Naka and Z. Shibata, J. Fac. Sci. Hokkaido Imp. Univ. Ser. III, 2, 183 (1958); R. Ruf and W. D. Treadwell, Helv. Chim. Acta 37, 1941 (1954) and P. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The bond length is a weighted average of the values given by H. Braune and S. Knoke Naturwiss. 21, 349 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. P. Jones and L. E. Sutton Trans. Farad. Soc. 33, 852, 1937; L. R. Maxwell and V. M. Morley Phys. Rev. 57, 21 (1940) and P. A. Akishin, V. P. Spiridonov and A. N. Knochchenkov, Zhur. Fiz. Khim. 33, 20 (1959).



Mercury Monochloride, Dimeric (Hg_2Cl_2)

(Crystal) Mol. Wt. = 472.134 **INTERIM TABLE**

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	-0.000	INFINITE	5.611	62.269	62.269	INFINITE
100	19.820	22.586	2.323	62.954	58.560	15.950
200	25.820	28.202	.000	63.319	50.315	36.680
298	24.371	46.017	.045	63.312	50.234	36.584
300	24.390	46.168	2.533	62.559	41.705	36.584
400	25.340	53.318	5.107	62.559	41.705	36.584
500	26.130	59.060	7.755	62.559	41.705	36.584
600	26.800	63.884	10.464	62.559	41.705	36.584
700	27.380	68.060	13.230	62.559	41.705	36.584
800	27.920	71.752	16.046	62.559	41.705	36.584
900	28.400	75.089	18.909	62.559	41.705	36.584
1000	28.840	78.084	21.813	62.559	41.705	36.584
1100	29.240	80.852	24.755	62.559	41.705	36.584
1200	29.600	83.412	27.732	62.559	41.705	36.584
1300	29.916	85.794	30.737	62.559	41.705	36.584
1400	30.189	88.021	33.768	62.559	41.705	36.584
1500	30.420	90.112		62.559	41.705	36.584

MERCURY MONOCHLORIDE, DIMERIC (Hg_2Cl_2) (CRYSTAL)

MOL. WT. = 472.134

ΔH_f^0 298.15 = -63.319 ± 0.05 kcal mole⁻¹

$S_{298.15}^0$ = 46.017 cal deg⁻¹ mole⁻¹

$T_{\text{sub.}} = 655^\circ\text{K}$ (decomp.)

Heat of Formation

Based on the average free energy of formation, -50.315 kcal mole⁻¹, as measured by R. H. Gerke, J. Am. Chem. Soc. 44, 1684 (1922) and G. J. Hills and D. J. G. Ives, J. Chem. Soc. (London) 318, (1951), and the entropy of formation.

Heat Capacity

The data of F. Pollitzer, Zeits. f. Electrochemie 19, 513 (1913), from 22-199°K was treated by K. K. Kelley, U. S. Bureau of Mines Bulletin 592 (1960). The heat capacities listed by Kelley were raised by 0.06 to match the entropy data of Gerke (loc. cit.). Data above room temperature were obtained by smooth extrapolation.

Entropy

A mean value of the entropy of formation of -46.614 e.u. was adopted from the cell measurements of R. H. Gerke (loc. cit.).

Sublimation

The vapor pressure over mercurous chloride reaches 1 atmosphere at 655°K according to A. Smith and A. W. C. Menzies, J. Am. Chem. Soc. 32, 1541 (1910). At this point the vapor is dissociated into Hg(g) and HgCl₂(g).

Potassium Chloride, Dimeric (K₂Cl₂)
(Ideal Gas) Mol. Wt. = 149.110

POTASSIUM CHLORIDE, DIMERIC (K₂Cl₂) (IDEAL GAS) MOL. WT. = 149.110

T, °K.	C _p	S°	(F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _P
0	∞	∞	∞	∞	∞	∞	∞
100	16.145	64.482	100.078	3.650	-146.852	-146.852	INFINITE
200	18.714	76.700	84.309	3.650	-146.852	-146.852	322.243
298	19.327	84.309	76.700	3.650	-146.852	-146.852	161.286
300	19.333	84.309	76.700	3.650	-146.852	-146.852	108.231
400	19.673	94.405	64.482	3.650	-146.852	-146.852	107.564
500	19.773	97.998	60.000	3.650	-146.852	-146.852	60.451
600	19.770	101.043	54.516	3.650	-146.852	-146.852	53.311
700	19.743	103.684	49.771	3.650	-146.852	-146.852	45.504
800	19.703	105.989	45.516	3.650	-146.852	-146.852	39.637
900	19.653	107.998	41.836	3.650	-146.852	-146.852	34.862
1000	19.622	109.103	38.430	3.650	-146.852	-146.852	31.395
1100	19.630	109.994	35.663	3.650	-146.852	-146.852	27.980
1200	19.637	110.720	33.677	3.650	-146.852	-146.852	24.845
1300	19.642	111.318	32.126	3.650	-146.852	-146.852	22.193
1400	19.645	111.811	30.750	3.650	-146.852	-146.852	19.953
1500	19.649	112.214	29.500	3.650	-146.852	-146.852	17.953
1600	19.652	112.535	28.345	3.650	-146.852	-146.852	16.232
1700	19.654	112.780	27.270	3.650	-146.852	-146.852	14.714
1800	19.656	112.967	26.270	3.650	-146.852	-146.852	13.365
1900	19.658	113.103	25.340	3.650	-146.852	-146.852	12.163
2000	19.659	113.196	24.460	3.650	-146.852	-146.852	11.073
2100	19.660	113.249	23.620	3.650	-146.852	-146.852	10.092
2200	19.661	113.273	22.810	3.650	-146.852	-146.852	9.200
2300	19.662	113.284	22.020	3.650	-146.852	-146.852	8.395
2400	19.663	113.287	21.250	3.650	-146.852	-146.852	7.635
2500	19.664	113.282	20.500	3.650	-146.852	-146.852	6.913
2600	19.664	113.273	19.770	3.650	-146.852	-146.852	6.319
2700	19.664	113.260	19.060	3.650	-146.852	-146.852	5.733
2800	19.664	113.243	18.370	3.650	-146.852	-146.852	5.163
2900	19.664	113.223	17.710	3.650	-146.852	-146.852	4.613
3000	19.664	113.200	17.070	3.650	-146.852	-146.852	4.083
3100	19.664	113.175	16.450	3.650	-146.852	-146.852	3.563
3200	19.664	113.148	15.850	3.650	-146.852	-146.852	3.053
3300	19.664	113.119	15.270	3.650	-146.852	-146.852	2.553
3400	19.664	113.089	14.710	3.650	-146.852	-146.852	2.063
3500	19.664	113.058	14.160	3.650	-146.852	-146.852	1.583
3600	19.664	113.026	13.620	3.650	-146.852	-146.852	1.113
3700	19.664	112.993	13.090	3.650	-146.852	-146.852	0.653
3800	19.664	112.959	12.570	3.650	-146.852	-146.852	0.203
3900	19.664	112.924	12.060	3.650	-146.852	-146.852	-0.247
4000	19.664	112.889	11.560	3.650	-146.852	-146.852	-0.707
4100	19.664	112.853	11.070	3.650	-146.852	-146.852	-1.167
4200	19.664	112.817	10.590	3.650	-146.852	-146.852	-1.627
4300	19.664	112.781	10.120	3.650	-146.852	-146.852	-2.087
4400	19.664	112.745	9.660	3.650	-146.852	-146.852	-2.547
4500	19.664	112.709	9.210	3.650	-146.852	-146.852	-3.007
4600	19.664	112.673	8.770	3.650	-146.852	-146.852	-3.467
4700	19.664	112.637	8.340	3.650	-146.852	-146.852	-3.927
4800	19.664	112.601	7.910	3.650	-146.852	-146.852	-4.387
4900	19.664	112.565	7.490	3.650	-146.852	-146.852	-4.847
5000	19.664	112.529	7.070	3.650	-146.852	-146.852	-5.307
5100	19.664	112.493	6.660	3.650	-146.852	-146.852	-5.767
5200	19.664	112.457	6.250	3.650	-146.852	-146.852	-6.227
5300	19.664	112.421	5.850	3.650	-146.852	-146.852	-6.687
5400	19.664	112.385	5.450	3.650	-146.852	-146.852	-7.147
5500	19.664	112.349	5.060	3.650	-146.852	-146.852	-7.607
5600	19.664	112.313	4.670	3.650	-146.852	-146.852	-8.067
5700	19.664	112.277	4.290	3.650	-146.852	-146.852	-8.527
5800	19.664	112.241	3.910	3.650	-146.852	-146.852	-8.987
5900	19.664	112.205	3.540	3.650	-146.852	-146.852	-9.447
6000	19.664	112.169	3.170	3.650	-146.852	-146.852	-9.907
6100	19.664	112.133	2.810	3.650	-146.852	-146.852	-10.367
6200	19.664	112.097	2.460	3.650	-146.852	-146.852	-10.827
6300	19.664	112.061	2.110	3.650	-146.852	-146.852	-11.287
6400	19.664	112.025	1.770	3.650	-146.852	-146.852	-11.747
6500	19.664	111.989	1.430	3.650	-146.852	-146.852	-12.207
6600	19.664	111.953	1.100	3.650	-146.852	-146.852	-12.667
6700	19.664	111.917	0.770	3.650	-146.852	-146.852	-13.127
6800	19.664	111.881	0.450	3.650	-146.852	-146.852	-13.587
6900	19.664	111.845	0.130	3.650	-146.852	-146.852	-14.047
7000	19.664	111.809	0.000	3.650	-146.852	-146.852	-14.507

Dec. 31, 1961 Mar. 31, 1966

Point Group D_{2h}
S_{298.15} = [84.3] cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = 1

ΔH_f⁰ = -146.85 kcal. mole⁻¹
ΔH_f^{298.15} = -147.62 ± 1.0 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
(219)(1)	(104)(1)
(108)(1)	(184)(1)
(180)(1)	(100)(1)

Bond Distances: Cl-K = [2.352] Å
Bond Angle: Cl-K-Cl = [100.8°]
Product of the Moments of Inertia: I_AI_BI_C = [2.875 X 10⁻¹¹²] g.³ cm.⁶

σ = 4

Heat of Formation

The heat of formation is calculated from that of KCl(g) using ΔH_f²⁹⁸ = 45.0 kcal./mole for K₂O₂(g) → 2KCl(g) as selected from data analyses summarized below. The three experimental techniques include PVT measurements (source 1), combination of total vapor pressure and transpiration data (sources 2,3,4), and mass spectrometric studies of the variation of ion intensities with temperature (source 5). The results are reasonably consistent, considering the uncertainties inherent in the problem.

The resulting tables were tested by comparison with other data. Calculated total vapor pressures are in satisfactory agreement with the observed values over the range 820-1500°K.; however, near the boiling point they are lower by 6-18 percent [see KCl(g)]. Knudsen effusion data and transpiration data over KCl(c) have been reviewed by A. C. P. Pugh and R. F. Barron, Trans. Faraday Soc. 58, 671 (1958). These data suggest negligible dimer formation when combined with the total vapor pressures of V. Dietz, J. Chem. Phys. 4, 575 (1936). Calculated dimer formation (22 mole percent at 900°K.) agrees with the latter combination but calculated total pressures agree with those of Pugh & Barron. Velocity distribution studies of R. C. Miller and P. Kusch, J. Chem. Phys. 27, 961 (1957); 25, 860 (1956) suggest about 10 mole percent of dimer at 800°K. Thus, while minor inconsistencies do exist, it is not apparent that they exceed the combined experimental errors.

Source	Method	No. of Points	Temp. °K.	ΔH _f ²⁹⁸ kcal./mole	Drift eu
1. Dietz (1936)	PVT data	15	1310-1404	46.70±2.1	-0.51±.6
2. Schrier (1967)	Trans. + Vap. Press.	10	1263-1372	46.7±1.5	-0.75±.7
3. Barron et al. (1959)	Trans. + Vap. Press.	15	1263-1372	44.3±1.5	0.75±.4
4. Barron et al. (1959)	Trans. + Vap. Press.	7	1250-1475	42.5±2.9	2.22±.3
5. Milne et al. (1960)	Mass Spectrometry	—	774-1016	41.9±3	—

1. S. Dietz, ORNL-2933, Oak Ridge, Tenn., May 1960.
2. E. E. Schrier, Ph.D. thesis, Rensselaer Polytechnic Inst., Troy, N.Y., Jun 1961.
3. R. F. Barron and H. M. Klein, J. Phys. Chem. 63, 1785 (1959); 60, 1413 (1956).
4. J. L. Barron and H. M. Klein, J. Phys. Chem. 63, 1785 (1959); 60, 1413 (1956).
5. T. A. Milne and H. M. Klein, AFOSR TN 60-512, Menlo Park, Calif., Jun 1960.

Heat Capacity and Entropy

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960); 22, 1386 (1958). The sixth fundamental was arbitrarily lowered from 206 to 100 cm.⁻¹ since the resulting entropy increase (1.4 eu at 1300°K.) improved the overall agreement with the equilibrium data. Based on electron diffraction studies of the monomer-dimer vapor, P. A. Akashin and N. G. Rambidi, Zhur. Neorg. Khim. 4, 718 (1959) have derived the bond distance and angle to be 2.81 Å and 98°. Interpretation of the diffraction data, however, is complicated by the presence of only about 30 mole percent of dimer at the temperature of measurement. Adoption of this dimer structure would reduce the entropy by 0.23 eu, I_B = 60.13 X 10⁻³⁹, and I_C = 105.45 X 10⁻³⁹ g. cm.² Berkowitz structure are I_A = 45.31 X 10⁻³⁹, I_B = 60.13 X 10⁻³⁹, and I_C = 105.45 X 10⁻³⁹ g. cm.²

Lithium Chloride, Dimeric (LiCl)₂

(Ideal Gas) Mol. Wt. = 84.794 INTERIM TABLE

T, K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	3.704	-182.353	-182.353	INFINITE
100	9.920	53.937	2.666	-182.557	-182.557	312.466
200	14.975	62.525	1.597	-182.789	-182.789	156.656
298	17.255	68.993	0.993	-183.056	-183.056	105.250
300	17.283	69.009	0.992	-183.061	-183.061	104.604
400	18.263	74.231	0.666	-183.941	-183.941	78.597
500	19.044	78.391	0.423	-184.175	-184.175	62.750
600	19.456	81.845	0.256	-184.569	-184.569	52.191
700	19.779	84.812	0.142	-185.023	-185.023	44.608
800	19.956	87.402	0.075	-185.523	-185.523	38.908
900	20.034	89.744	0.038	-186.069	-186.069	33.991
1000	20.034	91.781	0.023	-186.651	-186.651	30.191
1100	19.650	93.632	0.015	-187.262	-187.262	27.979
1200	19.685	95.333	0.009	-187.891	-187.891	25.540
1300	19.713	96.920	0.005	-188.531	-188.531	23.472
1400	19.735	98.402	0.003	-189.181	-189.181	21.722
1500	19.752	99.784	0.002	-189.841	-189.841	20.112
1600	19.767	101.019	0.001	-190.511	-190.511	18.799
1700	19.779	102.218	0.000	-191.191	-191.191	17.262
1800	19.787	103.379	0.000	-191.881	-191.881	15.907
1900	19.791	104.509	0.000	-192.581	-192.581	14.707
2000	19.805	105.634	0.000	-193.291	-193.291	13.639
2100	19.811	106.401	0.000	-194.011	-194.011	11.900
2200	19.816	107.322	0.000	-194.741	-194.741	10.865
2300	19.821	108.203	0.000	-195.481	-195.481	9.950
2400	19.825	109.044	0.000	-196.231	-196.231	9.144
2500	19.829	109.857	0.000	-196.991	-196.991	8.429
2600	19.832	110.634	0.000	-197.761	-197.761	7.554
2700	19.835	111.383	0.000	-198.541	-198.541	6.644
2800	19.838	112.104	0.000	-199.331	-199.331	6.212
2900	19.841	112.804	0.000	-200.131	-200.131	5.844
3000	19.842	113.479	0.000	-200.941	-200.941	5.505
3100	19.844	114.124	0.000	-201.761	-201.761	5.195
3200	19.846	114.754	0.000	-202.591	-202.591	4.902
3300	19.848	115.367	0.000	-203.431	-203.431	4.631
3400	19.850	115.959	0.000	-204.281	-204.281	4.381
3500	19.850	116.532	0.000	-205.141	-205.141	4.151
3600	19.852	117.082	0.000	-206.011	-206.011	3.941
3700	19.853	117.636	0.000	-206.891	-206.891	3.751
3800	19.854	118.163	0.000	-207.781	-207.781	3.581
3900	19.855	118.681	0.000	-208.681	-208.681	3.431
4000	19.856	119.183	0.000	-209.591	-209.591	3.291
4100	19.856	119.674	0.000	-210.511	-210.511	3.161
4200	19.857	120.152	0.000	-211.441	-211.441	3.041
4300	19.858	120.617	0.000	-212.381	-212.381	2.931
4400	19.859	121.072	0.000	-213.331	-213.331	2.831
4500	19.859	121.522	0.000	-214.291	-214.291	2.741
4600	19.860	121.959	0.000	-215.261	-215.261	2.661
4700	19.860	122.386	0.000	-216.241	-216.241	2.591
4800	19.861	122.804	0.000	-217.231	-217.231	2.531
4900	19.861	123.213	0.000	-218.231	-218.231	2.471
5000	19.862	123.615	0.000	-219.241	-219.241	2.411
5100	19.862	124.008	0.000	-220.261	-220.261	2.351
5200	19.863	124.394	0.000	-221.291	-221.291	2.291
5300	19.863	124.773	0.000	-222.331	-222.331	2.231
5400	19.863	125.143	0.000	-223.381	-223.381	2.171
5500	19.864	125.508	0.000	-224.441	-224.441	2.111
5600	19.864	125.866	0.000	-225.511	-225.511	2.051
5700	19.864	126.217	0.000	-226.591	-226.591	1.991
5800	19.865	126.563	0.000	-227.681	-227.681	1.931
5900	19.865	126.903	0.000	-228.781	-228.781	1.871
6000	19.865	127.236	0.000	-229.891	-229.891	1.811

June 30, 1962

Cl₂Li₂

Lithium Chloride, Dimeric (LiCl)₂ (Ideal Gas)

Mol. Wt. = 84.794
 ΔH_f^0 298.15 = -143.056 ± 3.0 kcal. mole⁻¹
 $S_{298.15}^0$ = 86.993 cal. deg.⁻¹ mole⁻¹
 Point group = D_{2h}

Vibrational Levels and Multiplicities
 ω , cm.⁻¹ ω_e , cm.⁻¹
 {350} {1}
 {298} {1}
 {395} {1}
 {460} {1}

Bond Lengths and Angles
 Li-Cl distance = 2.23 Å
 Li-Li distance = 2.82 Å
 Cl-Li-Cl angle = 108 ± 4° $\sigma = 4$
 Moment of Inertia $I_{A-B-C} = 6418 \times 10^{-11}$ g.² cm.²

Heat of Formation. A heat of sublimation at 298° of 52.1 kcal. mole⁻¹ was chosen to fit the vapor pressure data and relative concentrations of monomer, dimer and trimer as described in the table for LiCl(g). This value is in reasonable agreement with the value of 53.5 kcal. mole⁻¹ from a 3rd law analysis of the vapor pressure data of An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) and the relative concentrations of monomer, dimer, and trimer from the work of R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956). Also a value of 54.1 kcal. mole⁻¹ was found by T. A. Milne and H. M. Klein, J. Chem. Phys. 33, 1628 (1960), from mass spectrometer studies.

Heat Capacity and Entropy. W. Klemperer and W. G. Norris, J. Chem. Phys. 34, 1071 (1961), observed two bands in the infra-red spectrum and made tentative assignments. The remaining four frequencies were calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), from a reasonable model. The bond lengths and angles were determined from the electron diffraction experiments of S. H. Bauer, T. Ino and R. P. Porter, J. Chem. Phys. 33, 665 (1960).

Cl₂Li₂

Magnesium Dichloride (MgCl₂)

(Crystal) Mol. wt. = 95.218

Cl₂Mg

MAGNESIUM DICHLORIDE (MgCl₂)

(CRYSTAL)

MOL. WT. = 95.218

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	+0.00	INFINITE	- 3.288	- 153.248	- 153.248	INFINITE
100	9.630	6.204	- 2.888	- 153.703	- 149.577	326.884
200	15.195	14.977	- 2.026	- 153.688	- 145.545	159.037
298	17.060	21.422	+0.00	- 153.350	- 141.519	103.731
300	17.088	21.527	-0.932	- 153.344	- 141.466	103.038
400	18.095	24.562	1.706	- 153.024	- 137.528	75.138
500	18.677	30.701	3.636	- 152.679	- 133.692	58.434
600	19.090	34.144	5.525	- 152.328	- 129.928	47.324
700	19.420	37.111	7.451	- 151.973	- 126.222	39.406
800	19.680	39.667	9.404	- 151.615	- 122.566	33.485
900	20.040	42.067	11.397	- 151.259	- 118.956	28.489
1000	20.350	44.134	13.417	- 150.902	- 115.290	25.176
1100	20.654	46.148	15.467	- 152.731	- 111.430	22.138
1200	20.951	47.998	17.547	- 152.378	- 107.692	19.612
1300	21.242	49.626	19.656	- 152.033	- 104.020	17.177
1400	21.526	51.231	21.795	- 151.695	- 100.375	15.582
1500	21.805	52.726	23.962	- 151.269	- 93.975	13.691
1600	22.076	54.142	26.156	- 150.480	- 88.182	12.045
1700	22.342	55.498	28.377	- 149.665	- 82.435	10.507
1800	22.604	56.807	30.631	- 148.829	- 76.747	9.177
1900	22.864	58.001	32.897	- 147.963	- 71.092	8.177
2000	23.100	59.180	35.195	- 147.075	- 65.491	7.156

Dec. 31, 1960; Dec. 31, 1965

S°_{298.15} = 21.422 cal. deg.⁻¹ mole⁻¹
 T_m = 987°K.
 ΔH_f^o 0 = -153.25 ± 0.11 kcal. mole⁻¹
 ΔH_f^o 298.15 = -153.35 ± 0.11 kcal. mole⁻¹
 ΔH_m = 10.30 ± 0.05 kcal. mole⁻¹
 ΔH_g^o 298.15 = 57.5 ± 1.5 kcal. mole⁻¹

Heat of Formation.

The adopted ΔH_f^o 298.15 = -153.35 ± 0.11 kcal. mole⁻¹ is from heat of solution measurements reported by C. H. Shomate and E. H. Huffman, J. Am. Chem. Soc. 65, 1625 (1943). Shomate and Huffmans heat of solution of Mg in 1 M HCl (ΔH = -111.322 ± 0.041 kcal. mole⁻¹), has been substantiated for calibration purposes by S. R. Gunn and B. B. Cunningham, J. Am. Chem. Soc., 79, 1563 (1957) (ΔH = -111.3 kcal. mole⁻¹) and by E. F. Westrum Jr. and L. Eyring, J. Am. Chem. Soc., 74, 2045 (1952) (ΔH = -111.27 kcal. mole⁻¹). Auxiliary heat of dilution and heat of formation data for HCl were taken from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NBS-RS-2, Nat'l. Bur. Stds., April 1965 and from D. D. Vagman et al., N.B.S. Technical Note 270-1, Oct. 1965.

Heat Capacity and Entropy.

High temperature heat content data by G. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943) were joined by Shomate correlation with low temperature heat capacity data reported by K. K. Kelley and G. E. Moore, J. Am. Chem. Soc. 65, 1264 (1943). C_p(c) above T_m is a linear extrapolation from 700°K. S°_{298.15} is derived from the low temperature data and is based on S°_{53.6} = 2.006 cal. deg.⁻¹ mole⁻¹.

Melting Data.

ΔH_m = 10.30 ± 0.05 kcal. mole⁻¹ is taken from heat content measurements of Moore loc. cit. T_m = 987°K. is from National Bureau of Standards Circular 500, 1952.

Sublimation Data.

The value of ΔH_g^o 298.15 was derived by 2nd and 3rd law analyses of vapor pressure data. See the MgCl₂(g) table for details.

Cl₂Mg

Magnesium Dichloride (MgCl₂)

(Liquid) Mol. wt. = 95.218

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	°K.	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0				100	30.949	30.949	0.000	-143.779	98.798
100	17.060			200	31.055	30.949	0.000	-143.779	98.798
200	17.088	31.055	30.949	300	31.633	31.633	1.766	-143.773	98.148
300	18.095	36.123	31.633	400	18.467	40.228	32.955	-143.768	97.991
400	18.467	40.228	32.955	500	19.090	43.694	34.459	-143.777	97.972
600	19.090	43.694	34.459	800	22.000	49.745	37.534	-141.695	95.919
800	22.000	49.745	37.534	900	22.000	52.336	39.038	-141.146	95.956
1000	22.000	52.336	39.038	1100	22.000	56.751	41.870	-142.258	95.921
1200	22.000	60.492	42.150	1300	22.000	60.492	42.150	-142.258	95.921
1400	22.000	62.056	43.650	1500	22.000	63.574	46.795	-170.491	95.921
1600	22.000	64.994	47.899	1700	22.000	67.581	50.936	-167.318	95.921
1800	22.000	67.581	50.936	1900	22.000	68.775	50.936	-167.318	95.921
2000	22.000	69.903	51.819	2100	22.000	70.977	52.706	-165.742	95.921
2200	22.000	72.978	54.393	2300	22.000	73.914	55.177	-163.391	95.921
2400	22.000	74.812	55.965	2500	22.000	75.675	56.687	-161.836	95.921
2600	22.000	75.675	56.687	2700	22.000	76.103	57.103	-160.293	95.921
2800	22.000	76.103	57.103	2900	22.000	76.103	57.103	-158.764	95.921
3000	22.000	76.103	57.103						

Cl₂Mg

MOL. WT. = 95.218

(LIQUID)

MAGNESIUM DICHLORIDE (MgCl₂)

S_{298.15} = 30.949 cal. deg.⁻¹ mole⁻¹
 T_m = 987°K.
 T_b = [1710]°K.
 ΔH_f⁰ 298.15 = -143.779 kcal. mole⁻¹
 ΔH_m⁰ = 10.50 ± 0.05 kcal. mole⁻¹
 ΔH_v⁰ = [37.34] kcal. mole⁻¹

Heat of Formation.

ΔH_f⁰ 298.15(1) was calculated from ΔH_f⁰ 298.15(c) by adding ΔH_m⁰ and the difference between H_m⁰ - H₂₉₈⁰ for crystal and liquid.

Heat Capacity and Entropy.

A constant C_p(1) = 22.0 cal. deg.⁻¹ mole⁻¹ over the temperature range 1006-1428°K. is from the high temperature heat content data of O. E. Moore, J. Am. Chem. Soc. 65, 1700 (1943). This constant value was assumed to hold from an assumed glass transition of 660°K. to 3000°K. C_p(1) below 860°K. is taken to be that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See MgCl₂(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction MgCl₂(l) = MgCl₂(g) approaches zero. The difference between ΔH_f⁰ for MgCl₂(l) and MgCl₂(g) at T_b is ΔH_v⁰.

Cl₂Mg

Point Group D_{2h} $\Delta H_f^\circ = -93.82 \pm 0.5 \text{ kcal/mol}$ $S_{298.15}^\circ = 66.184 \pm 0.5 \text{ gibbs/mol}$ $\Delta H_f^\circ = -93.80 \pm 0.5 \text{ kcal/mol}$

Ground State Quantum Weight = 1

Magnesium Dichloride (MgCl₂)

(Ideal Gas) QFV = 95.218

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^c	Log K _p
0	11.000	52.626	0.000	0.000	0.000	19.171
100	11.006	52.626	0.000	0.000	0.000	19.171
200	11.012	52.626	0.000	0.000	0.000	19.171
300	11.018	52.626	0.000	0.000	0.000	19.171
400	11.024	52.626	0.000	0.000	0.000	19.171
500	11.030	52.626	0.000	0.000	0.000	19.171
600	11.036	52.626	0.000	0.000	0.000	19.171
700	11.042	52.626	0.000	0.000	0.000	19.171
800	11.048	52.626	0.000	0.000	0.000	19.171
900	11.054	52.626	0.000	0.000	0.000	19.171
1000	11.060	52.626	0.000	0.000	0.000	19.171
1100	11.066	52.626	0.000	0.000	0.000	19.171
1200	11.072	52.626	0.000	0.000	0.000	19.171
1300	11.078	52.626	0.000	0.000	0.000	19.171
1400	11.084	52.626	0.000	0.000	0.000	19.171
1500	11.090	52.626	0.000	0.000	0.000	19.171
1600	11.096	52.626	0.000	0.000	0.000	19.171
1700	11.102	52.626	0.000	0.000	0.000	19.171
1800	11.108	52.626	0.000	0.000	0.000	19.171
1900	11.114	52.626	0.000	0.000	0.000	19.171
2000	11.120	52.626	0.000	0.000	0.000	19.171
2100	11.126	52.626	0.000	0.000	0.000	19.171
2200	11.132	52.626	0.000	0.000	0.000	19.171
2300	11.138	52.626	0.000	0.000	0.000	19.171
2400	11.144	52.626	0.000	0.000	0.000	19.171
2500	11.150	52.626	0.000	0.000	0.000	19.171
2600	11.156	52.626	0.000	0.000	0.000	19.171
2700	11.162	52.626	0.000	0.000	0.000	19.171
2800	11.168	52.626	0.000	0.000	0.000	19.171
2900	11.174	52.626	0.000	0.000	0.000	19.171
3000	11.180	52.626	0.000	0.000	0.000	19.171
3100	11.186	52.626	0.000	0.000	0.000	19.171
3200	11.192	52.626	0.000	0.000	0.000	19.171
3300	11.198	52.626	0.000	0.000	0.000	19.171
3400	11.204	52.626	0.000	0.000	0.000	19.171
3500	11.210	52.626	0.000	0.000	0.000	19.171
3600	11.216	52.626	0.000	0.000	0.000	19.171
3700	11.222	52.626	0.000	0.000	0.000	19.171
3800	11.228	52.626	0.000	0.000	0.000	19.171
3900	11.234	52.626	0.000	0.000	0.000	19.171
4000	11.240	52.626	0.000	0.000	0.000	19.171
4100	11.246	52.626	0.000	0.000	0.000	19.171
4200	11.252	52.626	0.000	0.000	0.000	19.171
4300	11.258	52.626	0.000	0.000	0.000	19.171
4400	11.264	52.626	0.000	0.000	0.000	19.171
4500	11.270	52.626	0.000	0.000	0.000	19.171
4600	11.276	52.626	0.000	0.000	0.000	19.171
4700	11.282	52.626	0.000	0.000	0.000	19.171
4800	11.288	52.626	0.000	0.000	0.000	19.171
4900	11.294	52.626	0.000	0.000	0.000	19.171
5000	11.300	52.626	0.000	0.000	0.000	19.171
5100	11.306	52.626	0.000	0.000	0.000	19.171
5200	11.312	52.626	0.000	0.000	0.000	19.171
5300	11.318	52.626	0.000	0.000	0.000	19.171
5400	11.324	52.626	0.000	0.000	0.000	19.171
5500	11.330	52.626	0.000	0.000	0.000	19.171
5600	11.336	52.626	0.000	0.000	0.000	19.171
5700	11.342	52.626	0.000	0.000	0.000	19.171
5800	11.348	52.626	0.000	0.000	0.000	19.171
5900	11.354	52.626	0.000	0.000	0.000	19.171
6000	11.360	52.626	0.000	0.000	0.000	19.171

Dec. 31, 1960; Dec. 31, 1965; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	
590 (1)	
88 (2)	
[273] (1)	

Bond Distance: Mg-Cl = 2.18 Å

Bond Angle: Cl-Mg-Cl = 180°

Rotational Constant: B₀ = 0.05003 cm⁻¹

σ = 2

Heat of Formation

Analysis of vapor pressure data on MgCl₂ is clouded by conflicting evidence for the amount of dimer in the vapor. Berkowitz and Marquart (1) by mass spectrometer studies found about 21 dimer at 920°K and derived $\Delta H_p^\circ = -39.2 \text{ kcal/mol}$ and $\Delta S_p^\circ = -29.9 \text{ gibbs/mol}$. Schrier and Clark (2) from gas transpiration data calculated about 30% dimer in the saturated vapor at 1300°K, with $\Delta H_p^\circ = -32.0 \text{ kcal/mol}$ and $\Delta S_p^\circ = -18.8 \text{ gibbs/mol}$. Thermodynamic functions for the gaseous monomer adopted here are clearly not compatible with large amounts of dimer and it is assumed for the present that the mass spectrometer results are correct.

Several vapor pressure studies have been published and third law analyses are given below. Berkowitz and Marquart (1) gave a single point while the remaining publications gave only equations but not individual points. Total pressures calculated from the equations were corrected for dimer.

Source	Method	Temperature Range (°K)	$\Delta H_{f298}^\circ (\text{kcal/mol})$
Berkowitz and Marquart (1)	Mass spectrometer	920	58.10
Schrier and Clark (2)	Boiling Point	1208-1413	59.55-59.68
Hildenbrand et al. (3)	Torsion-effusion	802-985	59.55-59.19
Hildenbrand et al. (4)	Torsion-effusion	800-970	59.53-59.38
Fischer et al. (5)	"Hall" method (total vapor pressures)	1136-1435	59.30-59.56

The selected value for ΔH_{f298}° is 59.55 kcal/mol which is combined with ΔH_{f298}° of the crystal to give $\Delta H_{f298}^\circ(\text{g}) = -93.80 \text{ kcal/mol}$.

Heat Capacity and Entropy

White, Mann, and co-workers (6) by matrix infrared spectroscopy determined the molecule to be linear with the asymmetric stretching frequency at 590 cm⁻¹ and the doubly degenerate bending frequency at 88 cm⁻¹. The symmetric stretching frequency was estimated as 273 cm⁻¹. The asymmetric stretching was observed by Buchler and Klemperer (7) at 597 cm⁻¹ and by Randall et al. (8) at 598 cm⁻¹, both by infrared spectroscopy of the vapor at high temperature. Electric deflection experiments by Klemperer and co-workers as summarized by Hayes (9) and the electron diffraction data of Aikshin and Spiridonov (10) agree with the linear structure within their error limits of about 20°. The Mg-Cl bond length was determined as 2.18 Å by Aikshin and Spiridonov (10).

References

1. J. Berkowitz and J. R. Marquart, *J. Chem. Phys.* **37**, 1853 (1962).
2. E. E. Schrier and H. M. Clark, *J. Phys. Chem.* **67**, 1259 (1963).
3. D. L. Hildenbrand, W. F. Hall, J. Yu, and W. D. Porter, *J. Chem. Phys.* **40**, 2882 (1964).
4. D. L. Hildenbrand et al., *Aeronautics Report U-2183*, June, 1965.
5. W. Fischer, T. Petzal, and S. Lauter, *Z. anorg. allgem. Chem.* **333**, 226 (1964).
6. Unpublished work cited by D. L. Hildenbrand, *J. Chem. Phys.*, in press.
7. A. Buchler and W. Klemperer, *J. Chem. Phys.* **29**, 121 (1958).
8. S. P. Randall, F. T. Greene, and J. L. Margrave, *J. Phys. Chem.* **63**, 758 (1959).
9. E. F. Hayes, *J. Phys. Chem.* **70**, 3740 (1966).
10. P. A. Aikshin and V. P. Spiridonov, *Kristallografiya* **2**, 475 (1957).

Sodium Chloride, Dimeric ((NaCl)₂)
(Ideal Gas) Mol. Wt. = 116.896



T, °K.	C _p	S° - (F° - H ₂₉₈ ⁰)/T	H° - H ₂₉₈ ⁰	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	INFINITE	- 4.409	- 134.433	- 134.433	INFINITE
100	13.734	50.181	3.421	- 134.786	- 135.057	295.175
200	18.483	77.757	1.944	- 135.067	- 135.262	146.145
298	18.831	77.757	.000	- 135.300	- 135.262	98.145
300	18.843	77.873	.075	- 135.304	- 135.260	98.432
400	19.278	83.362	1.944	- 136.913	- 135.100	73.811
500	19.487	87.689	3.881	- 137.104	- 134.598	58.830
600	19.603	91.253	5.838	- 137.665	- 134.022	48.815
700	19.674	94.281	7.802	- 137.991	- 133.362	41.645
800	19.720	96.911	9.772	- 138.297	- 132.713	36.254
900	19.752	99.235	11.746	- 138.583	- 132.051	32.051
1000	19.775	101.318	13.722	- 138.891	- 131.248	28.683
1100	19.792	103.203	15.701	- 139.201	- 130.471	25.921
1200	19.804	104.926	17.680	- 139.512	- 129.748	23.447
1300	19.814	106.512	19.661	- 139.817	- 129.081	21.111
1400	19.822	107.960	21.643	- 140.119	- 128.461	18.910
1500	19.829	109.348	23.626	- 140.424	- 127.886	16.837
1600	19.834	110.628	25.609	- 140.734	- 127.356	14.985
1700	19.839	111.831	27.593	- 141.049	- 126.869	13.349
1800	19.842	112.965	29.577	- 141.369	- 126.424	11.910
1900	19.845	114.038	31.561	- 141.694	- 126.020	10.661
2000	19.848	115.056	33.546	- 142.024	- 125.656	9.591
2100	19.850	116.024	35.531	- 142.359	- 125.331	8.603
2200	19.852	116.947	37.516	- 142.699	- 125.046	7.777
2300	19.854	117.830	39.501	- 143.044	- 124.800	7.077
2400	19.856	118.675	41.486	- 143.394	- 124.594	6.486
2500	19.857	119.486	43.472	- 143.749	- 124.429	5.991
2600	19.859	120.264	45.458	- 144.109	- 124.304	5.589
2700	19.859	121.014	47.444	- 144.474	- 124.219	5.264
2800	19.860	121.736	49.430	- 144.844	- 124.164	4.999
2900	19.861	122.434	51.416	- 145.219	- 124.139	4.774
3000	19.862	123.106	53.402	- 145.599	- 124.134	4.589
3100	19.862	123.758	55.388	- 145.984	- 124.149	4.434
3200	19.863	124.388	57.374	- 146.374	- 124.174	4.304
3300	19.864	124.999	59.361	- 146.769	- 124.209	4.189
3400	19.864	125.592	61.347	- 147.169	- 124.254	4.089
3500	19.865	126.168	63.333	- 147.574	- 124.309	4.004
3600	19.865	126.728	65.320	- 147.984	- 124.374	3.934
3700	19.865	127.272	67.306	- 148.400	- 124.449	3.879
3800	19.866	127.800	69.293	- 148.824	- 124.534	3.834
3900	19.866	128.318	71.280	- 149.254	- 124.629	3.799
4000	19.866	128.821	73.266	- 149.689	- 124.734	3.774
4100	19.867	129.312	75.253	- 150.129	- 124.849	3.754
4200	19.867	129.790	77.240	- 150.574	- 124.974	3.739
4300	19.867	130.258	79.226	- 151.024	- 125.109	3.724
4400	19.868	130.714	81.213	- 151.479	- 125.254	3.709
4500	19.868	131.161	83.200	- 151.939	- 125.409	3.694
4600	19.868	131.598	85.187	- 152.404	- 125.574	3.679
4700	19.868	132.025	87.174	- 152.874	- 125.749	3.664
4800	19.868	132.443	89.160	- 153.349	- 125.924	3.649
4900	19.868	132.853	91.147	- 153.829	- 126.109	3.634
5000	19.869	133.254	93.134	- 154.314	- 126.294	3.619
5100	19.869	133.648	95.121	- 154.804	- 126.489	3.604
5200	19.869	134.034	97.108	- 155.299	- 126.684	3.589
5300	19.869	134.412	99.095	- 155.799	- 126.879	3.574
5400	19.869	134.783	101.081	- 156.304	- 127.074	3.559
5500	19.869	135.148	103.068	- 156.814	- 127.269	3.544
5600	19.869	135.506	105.055	- 157.329	- 127.464	3.529
5700	19.870	135.858	107.042	- 157.849	- 127.659	3.514
5800	19.870	136.203	109.029	- 158.374	- 127.854	3.499
5900	19.870	136.543	111.016	- 158.904	- 128.049	3.484
6000	19.870	136.877	113.003	- 159.439	- 128.244	3.469

Dec. 31, 1964

SODIUM CHLORIDE, DIMERIC (NaCl)₂
(IDEAL GAS)



Point Group D_{2h}
ΔH_f⁰ = -134.4 ± 2 kcal. mole⁻¹
ΔH_f⁰ 298.15 = -135.3 ± 2 kcal. mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies
ω, cm. ⁻¹
(265) (1)
(155) (1)
(159) (1)
(222) (1)
(260) (1)

Bond Distance: Cl-Cl = [2.624] Å
Bond Angle: Cl-Cl-Cl = [108.4°]
Product of the Moments of Inertia: I_AI_BI_C = [6.849 X 10⁻¹¹³] g.³ cm.⁶

σ = 4

Heat of Formation.

An analysis is given below of the more extensive measurements relating to the dimer dissociation, (NaCl)₂(g) → 2NaCl(g). The mass spectrometric studies suggest that higher polymeric species may be neglected. Velocity distribution analyses are consistent with this procedure. When reduced to 298.15°K, the observed heats of dissociation of the dimer show a range of more than 7 kcal., reflecting the considerable uncertainty involved in such measurements. A value of ΔH_f⁰ 298 = 48.6 kcal. was selected for the dissociation; combining this with ΔH_f⁰ 298 = 54.9 kcal. mole⁻¹ for sublimation to the monomer leads to ΔH_f⁰ 298 = 61.2 kcal. mole⁻¹ for sublimation to the dimer.

Source	Method	ΔH _f ⁰ , T (kcal. mole ⁻¹)	T (°K.)	ΔH _f ⁰ , 298 (kcal. mole ⁻¹)
1	Molecular weight from vapor pressures	51.0	1350	52.8
2	Molecular weight from P-V-T measurements	50.6	1337	52.4
3	Double oven effusion with mass spectrometer	47.4	1002	54.1
4	Knudsen effusion with mass spectrometer	47.3	870	48.6
5	Knudsen effusion with mass spectrometer	44.5	930	48.3
6	Velocity distribution analysis	49.8	940	45.6
7	Velocity distribution analysis	46.6	980	50.9
1)	J. L. Barton, H. Bloom, J. Phys. Chem. 63 , 1785 (1959).			47.8
2)	S. Datz, W. T. Smith, E. H. Taylor, J. Chem. Phys. 34 , 558 (1961).			
3)	P. A. Akishin, L. N. Gorokhov, L. N. Sidorov, Zhur. Fiz. Khim. 33 , 2822 (1959); Vestn. Mosk. Univ. Ser. Mat. Mekh. Astron. Fiz. Khim. 1959 , No. 6, 194 (1959).			
4)	L. N. Gorokhov, Yu. S. Knodnev, P. A. Akishin, Zhur. Neorg. Khim. 3 , 2597 (1958).			
5)	T. A. Milne, H. M. Klein, J. Chem. Phys. 33 , 1628 (1960).			
6)	M. Eisenstadt, V. S. Rao, G. M. Rothberg, J. Chem. Phys. 30 , 604 (1959).			
7)	R. C. Miller, P. Kusch, J. Chem. Phys. 27 , 981 (1957); 25 , 860 (1956).			

Heat Capacity and Entropy.

The structure and vibrational frequencies are those calculated from an ionic model by J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960); **29**, 1386 (1958). Electron diffraction studies by Akishin and Rabinovich, Z. physik. Chem. (Leipzig) **213**, 111 (1960) gave a similar bond angle (108°) and a slightly shorter bond distance (2.50 Å); however, interpretation of the diffraction pattern was complicated by uncertainty in the monomer-dimer ratio for the vapor. Principal moments of inertia for the Berkowitz structure are I_A = 18.01 X 10⁻³⁹, I_B = 53.31 X 10⁻³⁹ and I_C = 71.32 X 10⁻³⁹ g. cm.².

Titanium Oxide Dichloride (TiOCl₂)

(Ideal Gas) Mol. Wt. = 134.814

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞.000	INFINITE	- 3.993	- 130.002	- 130.002	INFINITE	INFINITE
100	12.291	60.411	- 3.061	- 130.241	- 129.491	282.989	282.989
200	15.642	70.130	- 2.619	- 130.338	- 128.698	140.628	140.628
298	17.197	76.697	∞.000	- 130.390	- 127.878	93.733	93.733
300	17.219	76.803	∞.032	- 130.391	- 127.863	93.143	93.143
400	18.102	81.889	77.384	1.802	- 130.426	- 127.015	69.395
500	18.630	85.990	78.709	3.661	- 130.435	- 126.158	55.141
600	19.061	89.418	80.216	5.521	- 130.494	- 125.295	45.636
700	19.178	92.358	81.745	7.429	- 130.567	- 124.429	39.849
800	19.329	94.930	83.236	9.355	- 130.616	- 123.567	33.750
900	19.436	97.213	84.665	11.293	- 130.700	- 122.657	29.784
1000	19.515	99.265	86.024	13.241	- 130.799	- 121.759	26.609
1100	19.574	101.128	87.146	15.196	- 130.915	- 120.851	24.010
1200	19.620	102.833	88.537	17.116	- 131.095	- 119.893	21.834
1300	19.656	104.405	89.698	19.110	- 131.160	- 118.878	19.984
1400	19.685	105.863	90.801	21.087	- 132.280	- 117.853	18.397
1500	19.709	107.222	91.851	23.056	- 132.471	- 116.815	17.019
1600	19.728	108.494	92.852	25.028	- 132.656	- 115.764	15.812
1700	19.745	109.691	93.807	27.002	- 132.854	- 114.742	14.745
1800	19.758	110.820	94.722	28.977	- 133.065	- 113.629	13.796
1900	19.770	111.888	95.594	30.954	- 133.289	- 112.541	12.945
2000	19.780	112.903	96.437	32.931	- 137.201	- 111.351	12.167
2100	19.788	113.868	97.245	34.909	- 137.301	- 110.093	11.453
2200	19.796	114.789	98.021	36.889	- 137.385	- 108.787	10.802
2300	19.802	115.669	98.770	38.868	- 137.783	- 107.430	10.208
2400	19.808	116.512	99.491	40.849	- 137.984	- 106.107	9.662
2500	19.813	117.320	100.188	42.830	- 138.191	- 104.775	9.159
2600	19.817	118.098	100.862	44.812	- 138.400	- 103.435	8.694
2700	19.821	118.846	101.515	46.793	- 138.616	- 102.086	8.263
2800	19.825	119.567	102.147	48.776	- 138.836	- 100.728	7.862
2900	19.828	120.262	102.759	50.758	- 139.060	- 99.363	7.488
3000	19.831	120.935	103.354	52.741	- 139.290	- 97.992	7.138
3100	19.834	121.585	103.932	54.725	- 139.524	- 96.608	6.811
3200	19.836	122.215	104.493	56.708	- 139.763	- 95.226	6.502
3300	19.838	122.825	105.040	58.692	- 140.008	- 93.876	6.214
3400	19.840	123.417	105.571	60.676	- 140.256	- 92.424	5.941
3500	19.842	123.992	106.090	62.660	- 140.510	- 91.016	5.683
3600	19.844	124.551	106.595	64.644	- 243.270	- 88.452	5.451
3700	19.845	125.091	107.087	66.629	- 243.519	- 86.952	5.235
3800	19.847	125.624	107.568	68.613	- 243.812	- 85.473	5.031
3900	19.848	126.140	108.038	70.598	- 244.131	- 84.019	4.841
4000	19.849	126.642	108.497	72.583	- 244.466	- 82.589	4.671
4100	19.850	127.133	108.945	74.568	- 244.816	- 81.174	4.545
4200	19.851	127.611	109.376	76.558	- 245.184	- 79.780	4.438
4300	19.852	128.078	109.813	78.558	- 245.564	- 78.400	4.338
4400	19.853	128.534	110.234	80.553	- 245.959	- 77.034	4.254
4500	19.854	128.981	110.645	82.559	- 246.368	- 75.685	4.182
4600	19.855	129.417	111.049	84.594	- 246.788	- 74.355	4.121
4700	19.856	129.844	111.444	86.680	- 247.222	- 73.045	4.067
4800	19.856	130.262	111.832	88.845	- 247.667	- 71.752	4.021
4900	19.857	130.671	112.212	90.451	- 248.123	- 70.483	3.982
5000	19.858	131.073	112.585	92.436	- 248.588	- 69.244	3.948
5100	19.858	131.466	112.952	94.472	- 249.063	- 68.028	3.917
5200	19.859	131.851	113.311	96.498	- 249.546	- 66.834	3.888
5300	19.859	132.230	113.665	98.594	- 250.038	- 65.664	3.860
5400	19.860	132.601	114.012	100.760	- 250.537	- 64.517	3.833
5500	19.860	132.965	114.353	102.966	- 251.043	- 63.392	3.807
5600	19.861	133.323	114.680	105.212	- 251.556	- 62.288	3.781
5700	19.861	133.675	115.019	107.496	- 252.076	- 61.206	3.756
5800	19.861	134.020	115.344	109.824	- 252.598	- 60.146	3.731
5900	19.862	134.360	115.663	112.197	- 253.127	- 59.107	3.706
6000	19.862	134.693	115.977	114.620	- 253.660	- 58.088	3.681

Sept. 30, 1963

Ti₂O₃

MOL. WT. = 134.814

TITANIUM OXIDE DICHLORIDE (TiOCl₂) (IDEAL GAS) $\Delta H_f^\circ = [-130.0] \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ = [-130.4] \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = [76.697] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$ $\omega, \text{ cm.}^{-1}$

Bond Distances: O-Ti = [1.62] Å

Bond Angles: O-Ti-Cl = [120°]

Product of Moments of Inertia: $I_A I_B I_C = [4.628 \times 10^{-115}] \text{ g.}^3 \text{ cm.}^6$ Heat of Formation: $\Delta H_f^\circ = [-130 \text{ kcal. mole}^{-1}]$ by J. S. Gordon, AstroSystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH_f° 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moments were: $I_A = 42.72 \times 10^{-39} \text{ g. cm.}^2$, $I_B = 17.88 \times 10^{-39} \text{ g. cm.}^2$, and $I_C = 60.80 \times 10^{-39} \text{ g. cm.}^2$.Cl₂O₇

Tungsten Dioxychloride (WO_2Cl_2)
(Crystal) GFW = 286.7548

T, °K	C_p°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100						
200						
298	24.954	48.000	48.000	.000	-167.985	173.136
300	25.000	48.155	48.000	-.046	-167.871	122.298
400	27.500	55.489	49.011	2.671	-161.733	88.367
500	30.000	62.096	51.002	5.547	-155.742	66.075
600	32.500	67.781	53.331	8.669	-149.909	54.604
700	34.500	72.845	55.211	11.557	-144.050	44.604
800	36.000	77.485	56.717	14.257	-138.738	37.904
900	37.250	81.986	60.422	19.228	-133.391	32.392
1000	38.000	85.953	62.959	22.994	-128.197	28.0

TUNGSTEN DIOXYCHLORIDE (WO_2Cl_2)

(CRYSTAL)

GFW = 286.7548

$\Delta H_f^\circ = \text{Unknown}$

$S_{298.15}^\circ = [48.0] \text{ gibbs/mol}$

Td = 642°K



Heat of Formation.

S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov¹ measured calorimetrically the heats of reaction (1) and (2) at 298°K as -67.3 ± 0.2 and $-13.6 \pm 0.11 \text{ kcal/mol}$, respectively. The reactions are given as follows:

- (1) $\text{WO}_2\text{Cl}_2(\text{c}) + 4 \text{ NaOH}(16.3\text{H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(80,000 \text{ H}_2\text{O}) + 2 \text{ NaCl}(40,000 \text{ H}_2\text{O}) + 2 \text{ H}_2\text{O}(1)$
- (2) $\text{H}_2\text{WO}_4(\text{c}) + 2 \text{ NaOH}(16.3 \text{ H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(20,000 \text{ H}_2\text{O}) + 2 \text{ H}_2\text{O}(1)$.

Based on these data and the heats of dilution for $\text{NaOH}(\text{aq})^2$, $\text{NaCl}(\text{aq})^2$ and $\text{Na}_2\text{WO}_4(\text{aq})^3$, we obtain $\Delta H_f^\circ = 53.77 \pm 1.0 \text{ kcal/mol}$ for $\text{WO}_2\text{Cl}_2(\text{c}) + 2 \text{ OH}^-(\infty \text{ H}_2\text{O}) \rightarrow \text{H}_2\text{WO}_4(\text{c}) + 2 \text{ Cl}^-(\infty \text{ H}_2\text{O})$. This leads to $\Delta H_f^\circ(\text{WO}_2\text{Cl}_2, \text{c}) = -186.5 \text{ kcal/mol}$ using $\Delta H_f^\circ(\text{H}_2\text{WO}_4, \text{c}) = -270.5 \pm 0.4 \text{ kcal/mol}$ ⁵.

Heat Capacity and Entropy.

$CP_{300} = 25.0 \text{ gibbs/mol}$ is estimated using Kopp's rule. Heat capacities at higher temperature are estimated from those of $\text{WO}_2(\text{c})$, $\text{WO}_3(\text{c})$, $\text{WOCl}_6(\text{c})$. The entropy, $S_{298}^\circ = 48.0 \text{ eu}$, is calculated from $\Delta S_{298.6}^\circ = 32.27 \pm 1.3 \text{ eu}$ for $\text{WO}_2\text{Cl}_2(\text{c}) \rightarrow \text{WO}_2\text{Cl}_2(\text{g})$. The value of $\Delta S_{298.6}^\circ$ is obtained from the second law analysis of the vapor pressure data given by S. A. Shchukarev and A. V. Suvorov⁴.

Temperature of Decomposition.

Shchukarev and Suvorov⁴ found that $\text{WO}_2\text{Cl}_2(\text{c})$ does not melt but decomposes. The saturated vapor over $\text{WO}_2\text{Cl}_2(\text{c})$ consists mainly of $\text{WOCl}_4(\text{g})$ which will disproportionate to form $\text{WO}_2\text{Cl}_2(\text{g})$ and $\text{WO}_2(\text{g})$. The estimated Td is derived by interpolation to one atmosphere in the total pressures of $\text{WOCl}_4(\text{g})$, $\text{WO}_2\text{Cl}_2(\text{g})$ reported by Shchukarev and Suvorov⁴.

References.

1. S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. **3**, 2642 (1958).
2. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NBS-RS-NBS2, Natl. Bur. Std., Washington, D.C., Apr. 1965.
3. We have assumed $\Delta H_f^\circ \text{dil} = 0$ for $\text{Na}_2\text{WO}_4(20,000 \text{ H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(80,000 \text{ H}_2\text{O})$.
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **18**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev et al, Zh. Neorg. Khim. **3**, 2630 (1958); **5**, 1650 (1960), have been revised and they are not used here.
5. JANAF $\text{H}_2\text{WO}_4(\text{c})$ table dated Mar. 31, 1967.



T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	+0.000	INFINITE	-	-159.703	-159.703	INFINITE
100	14.105	63.365	-3.661	-159.703	-159.703	344.964
200	16.346	76.692	-1.962	-160.432	-159.795	309.454
298	20.341	84.563	0.000	-160.500	-152.486	112.069
300	20.374	84.692	0.039	-160.500	-152.486	111.344
400	22.334	90.512	2.204	-160.465	-150.290	92.114
500	23.287	94.006	4.489	-160.365	-147.756	64.584
600	23.222	100.312	8.951	-160.238	-145.266	42.006
700	22.665	107.308	13.716	-159.665	-140.792	26.326
800	21.886	114.226	18.432	-158.832	-137.438	13.472
900	20.886	121.026	23.197	-157.710	-135.402	5.592
1000	20.054	127.556	27.791	-156.498	-132.678	2.420
1100	19.181	133.822	32.384	-155.200	-130.260	1.020
1200	18.260	139.876	36.968	-153.828	-128.058	0.378
1300	17.298	145.764	41.548	-152.388	-126.078	0.104
1400	16.298	151.520	46.121	-150.884	-124.324	0.031
1500	15.262	157.176	50.688	-149.328	-122.792	0.000
1600	14.198	162.764	55.252	-147.716	-121.384	-0.020
1700	13.108	168.308	59.808	-146.048	-120.096	-0.040
1800	11.998	173.824	64.356	-144.324	-118.824	-0.060
1900	10.868	179.324	68.896	-142.548	-117.568	-0.080
2000	9.718	184.808	73.428	-140.720	-116.320	-0.100
2100	8.548	190.272	77.952	-138.848	-115.088	-0.120
2200	7.358	195.720	82.468	-136.928	-113.868	-0.140
2300	6.148	201.152	86.976	-134.960	-112.656	-0.160
2400	4.918	206.568	91.476	-132.948	-111.456	-0.180
2500	3.668	211.968	95.968	-130.896	-110.268	-0.200
2600	2.408	217.352	100.452	-128.808	-109.092	-0.220
2700	1.138	222.720	104.928	-126.676	-107.928	-0.240
2800	-0.132	228.072	109.396	-124.500	-106.776	-0.260
2900	-1.402	233.408	113.856	-122.280	-105.632	-0.280
3000	-2.672	238.728	118.308	-120.020	-104.496	-0.300
3100	-3.942	244.032	122.752	-117.720	-103.368	-0.320
3200	-5.212	249.320	127.188	-115.376	-102.248	-0.340
3300	-6.482	254.592	131.616	-112.988	-101.136	-0.360
3400	-7.752	259.848	136.036	-110.556	-100.032	-0.380
3500	-9.022	265.088	140.448	-108.080	-98.944	-0.400
3600	-10.292	270.312	144.852	-105.560	-97.864	-0.420
3700	-11.562	275.520	149.248	-103.000	-96.792	-0.440
3800	-12.832	280.712	153.628	-100.400	-95.728	-0.460
3900	-14.102	285.888	157.992	-97.760	-94.672	-0.480
4000	-15.372	291.048	162.340	-95.056	-93.624	-0.500
4100	-16.642	296.192	166.672	-92.308	-92.584	-0.520
4200	-17.912	301.320	170.988	-89.520	-91.552	-0.540
4300	-19.182	306.432	175.288	-86.696	-90.528	-0.560
4400	-20.452	311.528	179.576	-83.832	-89.512	-0.580
4500	-21.722	316.608	183.852	-80.928	-88.504	-0.600
4600	-22.992	321.672	188.112	-77.984	-87.504	-0.620
4700	-24.262	326.720	192.352	-75.000	-86.512	-0.640
4800	-25.532	331.752	196.576	-72.000	-85.528	-0.660
4900	-26.802	336.768	200.788	-68.960	-84.552	-0.680
5000	-28.072	341.768	204.988	-65.880	-83.584	-0.700
5100	-29.342	346.752	209.176	-62.760	-82.624	-0.720
5200	-30.612	351.720	213.352	-59.600	-81.672	-0.740
5300	-31.882	356.672	217.512	-56.400	-80.728	-0.760
5400	-33.152	361.608	221.656	-53.160	-79.792	-0.780
5500	-34.422	366.528	225.784	-49.880	-78.864	-0.800
5600	-35.692	371.432	229.896	-46.560	-77.944	-0.820
5700	-36.962	376.320	233.992	-43.200	-77.032	-0.840
5800	-38.232	381.192	238.076	-39.808	-76.128	-0.860
5900	-39.502	386.048	242.148	-36.376	-75.232	-0.880
6000	-40.772	390.888	246.208	-32.900	-74.344	-0.900

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN DIOXYDCHLORIDE (WO₂Cl₂)

(IDEAL GAS)

OPW = 286.7548

Point Group [C_{2v}]ΔH_f^o = -159.7 ± 6 kcal/molΔH_f^o = -160.5 ± 6 kcal/molS_{298.15} = [84.6] g/bbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W ₂ , cm ⁻¹	W ₂ , cm ⁻¹	W ₂ , cm ⁻¹
984 (1)	(400) (1)	(150) (1)
972 (1)	(300) (1)	(100) (1)
(400) (1)	(300) (1)	(100) (1)

Bond Distance W-Cl = [2.26] Å

Bond Angle Cl-W-Cl = [113°]

Product of the Moments of Inertia: I_AI_BI_C = [1.185 × 10⁻¹¹²] g³ cm⁶

W-O = [1.81] Å

O-W-O = [109.4°]

σ = [2]

Heat of Formation.

The adopted heat of formation, ΔH_f^o (WO₂Cl₂, g) = -160.5 kcal/mol, is obtained from ΔH_f^o = 26.0 kcal/mol for WO₂Cl₂(c) → WO₂Cl₂(g). The latter is calculated by the third law method from the partial pressures of WO₂Cl₂(g) given by S. A. Shchukarev and A. V. Suvorov⁶. Second law analysis gives ΔH_f^o = 24.1 ± 0.8 kcal/mol (ΔH_f^o = 26.0 kcal/mol). These reported partial vapor pressures of WO₂Cl₂(g) were derived by the optical tensimetric method from total pressures over WO₂Cl₂(c) considering the species WOCl₄(g), WO₂Cl₂(g) and WCl₆(g). Since the decomposition of WO₂Cl₂(c) was very complicated, we tentatively assign 6 kcal/mol uncertainty to the adopted heat of formation.

Shchukarev and Suvorov⁶ have also derived a log K_p equation for the disproportionation process,

2 WOCl₄(g) → WO₂Cl₂(g) + WCl₆(g). Third law analysis gives ΔH_f^o = 10.3 kcal/mol for the above process. This leads to ΔH_f^o = -145.7 ± 16 kcal/mol. The second law ΔH_f^o is 11.0 kcal/mol (ΔH_f^o = 10.1 kcal/mol). The drift in the third law analysis is 0.3 eu.

Heat Capacity and Entropy.

The molecular configuration is assumed to be a distorted tetrahedron of C_{2v} symmetry, similar to that of MoO₂Cl₂(g)¹, and CrO₂Cl₂(g)². The bond distances W-O and W-Cl are estimated to be the same as those in WO₃(g) and WCl₆(g), respectively. The bond angles are assumed to be the same as those in MoO₂Cl₂(g)¹. The three principal moments of inertia are I_A = 6.419 × 10⁻³⁸, I_B = 5.342 × 10⁻³⁸ and I_C = 3.397 × 10⁻³⁸ g cm².

The vibrational frequencies, 984 cm⁻¹ and 972 cm⁻¹, were observed in the infrared spectra by C. G. Barraclough and J. Stala³. They tentatively assigned these two as the symmetric and asymmetric W-O stretching frequencies. The rest of the frequencies are estimated by comparison with those observed in the infrared and Raman spectra for CrO₂Cl₂(g)^{4,5}. They are not listed in point group order.

References.

1. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.
2. K. J. Palmer, J. Am. Chem. Soc. 60, 2360 (1938).
3. C. G. Barraclough and J. Stala, Aust. J. Chem. 19, 741 (1966).
4. H. Stammreich, K. Kawai and Y. Tazawa, Spectrochim. Acta 1959, 438 (1959).
5. P. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta 1959, 709 (1959).
6. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Phys. i Khim., No. 1, 87 (1961).

Earlier data reported by Shchukarev et al., Zh. Neorg. Khim. 3, 2630 (1958), 5, 1650 (1960), have been revised and they are not used here.

Lead Dichloride (PbCl₂)

(Crystal) Mol. Wt. = 278.12

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
		cal. mole ⁻¹ deg. ⁻¹		kcal. mole ⁻¹			
0	.000	.000	INFINITE	4.049	-86.412	-86.412	INFINITE
100	13.810	18.887	47.347	3.236	-86.723	-82.623	161.000
200	16.690	25.697	34.072	1.676	-86.486	-79.000	86.323
298	17.463	28.360	32.360	.000	-86.291	-79.366	55.237
300	17.500	32.498	39.500	.032	-86.196	-75.319	54.867
400	18.490	37.777	33.198	1.631	-85.679	-71.740	39.195
500	19.491	42.010	34.349	3.730	-85.506	-68.248	29.930
600	20.480	45.691	34.103	5.729	-85.066	-64.635	23.615
700	21.480	48.883	32.702	7.827	-85.216	-61.313	19.142
800	22.480	51.614	30.266	10.023	-85.127	-57.866	15.606
900	23.160	54.894	40.829	12.299	-84.455	-54.488	13.233
1000	23.960	56.976	47.321	14.655	-83.699	-51.210	11.191
1100	24.760	59.297	43.760	17.091	-82.659	-48.001	9.536
1200	25.560	61.486	45.146	19.607	-81.934	-44.871	8.172
1300	26.360	63.563	46.484	22.203	-80.926	-41.823	7.031
1400	27.160	65.536	47.775	24.879	-79.839	-38.857	6.065
1500	27.960	67.447	49.024	27.635	-78.673	-35.968	5.240
1600	28.760	69.277	50.233	30.471	-77.432	-33.162	4.529
1700	29.560	71.045	51.405	33.387	-76.114	-30.432	3.912
1800	30.360	72.757	52.544	36.383	-74.723	-27.768	3.374
1900	31.160	74.420	53.652	39.459	-73.257	-25.219	2.901
2000	31.960	76.038	54.731	42.615	-71.719	-22.730	2.484
2100	32.760	77.617	55.783	45.851	-70.112	-20.304	2.123
2200	33.560	79.159	56.811	49.167	-68.436	-17.948	1.825
2300	34.360	80.669	57.815	52.563	-66.692	-15.663	1.580
2400	35.160	82.148	58.799	56.039	-64.888	-13.448	1.386
2500	35.960	83.600	59.762	59.595	-63.025	-11.295	1.243

Lead Dichloride (PbCl₂) (Crystal)

Mol. Wt. = 278.12
 $\Delta H_f^{298.15} = -86.20 \pm 0.07$ kcal. mole⁻¹
 $S^{298.15} = 32.5 \pm 0.5$ cal. deg.⁻¹ mole⁻¹
 $\Delta F^{298.15} = 45.59 \pm 0.70$ kcal. mole⁻¹
 $T_m = 768^\circ K$
 $\Delta H_m = 5.70$ kcal. mole⁻¹

Heat of Formation. Recalculated from the data reported by E. J. Salstrom, J. Am. Chem. Soc. 55, 2426 (1933) and A. Wichter, J. Am. Chem. Soc. 54, 2271 (1932).

Heat Capacity, Entropy and Melting Data. C_p (15.3° to 305.5°K.) reported by W. Nernst, Ann. Physik, 35, 395 (1911) and adjusted so that $S^{298.15}$ is equal to the value reported by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1951). C_p above 298.15°K. obtained from K. K. Kelley, U. S. Bur. Mines Bull. 584 (1950) and joined smoothly to the low temperature heat capacity curve by graphical extrapolation. T_m and ΔH_m obtained from M. Blanc and G. Petit, Compt. rend. 249, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of R. D. Eastman and L. H. Duschak, U. S. Bur. Mines Tech. Paper 225 (1919), C. G. Maier, U. S. Bur. Mines Tech. Paper 360, 28 (1925), H. V. Martenberg and O. Boese, Z. Elektrochem. 28, 384 (1922), and M. Jahn-Held and K. Jellinek, Z. Elektrochem. 43, 491 (1937), which are in good agreement. Vapor pressure was also measured by F. Volmer, Physik. Z. 30, 590 (1929), J. L. Barton and H. Bloom, J. Phys. Chem. 60, 1413 (1956), B. Greiner and K. Jellinek, Z. Physik. Chem. A165, 97 (1933), and K. Mino, M. Sato and M. Yoshiyama, J. Faculty Sci. Hokkaido Imp. Univ. Ser. III, 2, 17 (1940).

INTERIM TABLE

March 31, 1962

T, °K.	C _p ^a	S ^a	-(F°-H _{298°)/T}	ΔH _f ^b	ΔF _f ^b	Log K _p
	cal. mole ⁻¹ deg. ⁻¹			kcal. mole ⁻¹		
0						
100						
200						
298	17.4465	36.336	34.336	.000	- 81.488	- 72.413
300						53.078
300	17.5000	36.444	34.336	.032	- 81.483	- 72.357
400	18.6000	38.163	34.336	1.032	- 81.466	- 72.310
500	19.4800	40.395	34.336	3.730	- 80.793	- 66.452
600	24.9000	52.178	31.987	6.114	- 78.968	- 63.653
700	24.9000	56.916	31.987	9.404	- 78.968	- 63.653
800	24.9000	62.274	31.987	13.584	- 78.968	- 63.653
900	24.9000	67.713	31.987	18.572	- 78.968	- 63.653
1000	24.9000	73.275	31.987	24.364	- 78.968	- 63.653
1100	24.9000	78.993	31.987	30.954	- 78.968	- 63.653
1200	24.9000	84.837	31.987	38.344	- 78.968	- 63.653
1300	24.9000	90.899	31.987	46.534	- 78.968	- 63.653
1400	24.9000	97.171	31.987	55.524	- 78.968	- 63.653
1500	24.9000	103.643	31.987	65.314	- 78.968	- 63.653
1600	24.9000	110.315	31.987	75.904	- 78.968	- 63.653
1700	24.9000	117.187	31.987	87.294	- 78.968	- 63.653
1800	24.9000	124.259	31.987	99.484	- 78.968	- 63.653
1900	24.9000	131.531	31.987	112.474	- 78.968	- 63.653
2000	24.9000	139.003	31.987	126.264	- 78.968	- 63.653
2100	24.9000	146.675	31.987	140.854	- 78.968	- 63.653
2200	24.9000	154.547	31.987	156.244	- 78.968	- 63.653
2300	24.9000	162.719	31.987	172.434	- 78.968	- 63.653
2400	24.9000	171.191	31.987	189.424	- 78.968	- 63.653
2500	24.9000	180.063	31.987	207.214	- 78.968	- 63.653
2600	24.9000	189.335	31.987	225.804	- 78.968	- 63.653
2700	24.9000	199.007	31.987	245.194	- 78.968	- 63.653
2800	24.9000	209.079	31.987	265.484	- 78.968	- 63.653
2900	24.9000	219.551	31.987	286.674	- 78.968	- 63.653
3000	24.9000	230.423	31.987	308.764	- 78.968	- 63.653

Lead Dichloride (PbCl₂) (Liquid)

Mol. Wt. = 278.12

ΔH_f^{298.15} = [-81.49] kcal. mole⁻¹S_{298.15}^o = [39.336] cal. deg.⁻¹ mole⁻¹T_m = 768°KΔH_m^o = 5.70 kcal. mole⁻¹T_b = 1226°KΔH_v^o = 26.81 ± 0.70 kcal. mole⁻¹

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy and Melting Data. C_p reported by M. Bizouard and P. Pauly, Compt. rend. 252, 51 (1961). T_m and ΔH_m^o obtained from M. Blanc and G. Petit, Compt. rend. 246, 1305 (1959). A glass transition temperature of 520°K. is assumed.

Vaporization Phenomena. T_b and ΔH_v^o calculated from ΔH_f^{298.15} and functions for condensed and gaseous states.

Lead Dichloride (PbCl₂)

(Ideal Gas) Mol. Wt. = 278.12

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	-0.000	-0.000	INFINITE	-3.486	-40.218	-40.218	INFINITE
100	11.084	64.077	2.502	-40.598	-41.504	-41.504	96.267
200	12.891	71.390	1.260	-40.510	-42.162	-42.162	46.070
298	13.370	76.630	-0.000	-40.610	-42.953	-42.953	31.484
300	13.377	76.713	-0.025	-40.612	-42.967	-42.967	31.300
400	13.599	80.596	1.375	-40.744	-43.733	-43.733	23.893
500	13.708	83.643	2.741	-40.904	-44.463	-44.463	19.434
600	13.769	86.148	4.115	-41.089	-45.156	-45.156	16.447
700	13.806	88.278	5.494	-41.286	-45.808	-45.808	14.245
800	13.827	90.029	6.875	-41.493	-46.419	-46.419	12.285
900	13.847	91.749	8.271	-41.709	-46.993	-46.993	10.585
1000	13.859	93.208	9.665	-43.118	-46.861	-46.861	9.241
1100	13.868	94.530	11.031	-43.328	-47.226	-47.226	8.382
1200	13.875	95.737	12.383	-43.522	-47.580	-47.580	7.853
1300	13.880	96.834	13.727	-43.702	-47.923	-47.923	7.526
1400	13.884	97.876	15.063	-43.870	-48.254	-48.254	7.268
1500	13.888	98.834	16.583	-44.134	-48.510	-48.510	7.068
1600	13.890	99.731	18.498	-44.340	-48.766	-48.766	6.865
1700	13.893	100.573	19.361	-44.549	-49.066	-49.066	6.607
1800	13.896	101.369	20.178	-44.752	-49.354	-49.354	6.392
1900	13.896	102.116	20.966	-44.955	-49.574	-49.574	6.202
2000	13.898	102.831	21.730	-45.213	-49.869	-49.869	5.943
2100	13.899	103.509	22.490	-45.520	-50.142	-50.142	5.685
2200	13.901	104.178	23.250	-45.874	-50.493	-50.493	5.429
2300	13.901	104.776	24.010	-46.284	-50.830	-50.830	5.173
2400	13.902	105.365	24.770	-46.750	-51.154	-51.154	4.917
2500	13.902	105.933	25.530	-47.270	-51.467	-51.467	4.661
2600	13.903	106.478	26.290	-47.846	-51.769	-51.769	4.405
2700	13.903	107.003	27.050	-48.474	-52.061	-52.061	4.149
2800	13.904	107.503	27.810	-49.154	-52.342	-52.342	3.893
2900	13.905	107.996	28.570	-49.886	-52.613	-52.613	3.637
3000	13.905	108.468	29.330	-50.670	-52.874	-52.874	3.381
3100	13.905	108.924	30.090	-51.504	-53.126	-53.126	3.125
3200	13.906	109.365	30.850	-52.388	-53.369	-53.369	2.869
3300	13.907	109.793	31.610	-53.322	-53.603	-53.603	2.613
3400	13.907	110.208	32.370	-54.306	-53.828	-53.828	2.357
3500	13.907	110.611	33.130	-55.340	-54.044	-54.044	2.101
3600	13.907	111.003	33.890	-56.424	-54.252	-54.252	1.845
3700	13.907	111.384	34.650	-57.558	-54.451	-54.451	1.589
3800	13.907	111.756	35.410	-58.742	-54.641	-54.641	1.333
3900	13.907	112.116	36.170	-59.976	-54.822	-54.822	1.077
4000	13.908	112.468	36.930	-61.260	-55.004	-55.004	0.821
4100	13.908	112.812	37.690	-62.594	-55.177	-55.177	0.565
4200	13.908	113.147	38.450	-63.978	-55.342	-55.342	0.309
4300	13.908	113.474	39.210	-65.412	-55.499	-55.499	0.053
4400	13.908	113.794	39.970	-66.896	-55.648	-55.648	-0.203
4500	13.908	114.107	40.730	-68.430	-55.790	-55.790	-0.459
4600	13.908	114.412	41.490	-69.994	-55.925	-55.925	-0.715
4700	13.908	114.703	42.250	-71.598	-56.054	-56.054	-0.971
4800	13.909	114.980	43.010	-73.242	-56.177	-56.177	-1.227
4900	13.909	115.251	43.770	-74.926	-56.294	-56.294	-1.483
5000	13.909	115.572	44.530	-76.650	-56.404	-56.404	-1.739
5100	13.909	115.847	45.290	-78.414	-56.507	-56.507	-1.995
5200	13.909	116.116	46.050	-80.218	-56.603	-56.603	-2.251
5300	13.909	116.382	46.810	-82.062	-56.693	-56.693	-2.507
5400	13.909	116.642	47.570	-83.946	-56.777	-56.777	-2.763
5500	13.909	116.898	48.330	-85.870	-56.856	-56.856	-3.019
5600	13.909	117.148	49.090	-87.834	-56.929	-56.929	-3.275
5700	13.909	117.395	49.850	-89.838	-57.004	-57.004	-3.531
5800	13.909	117.639	50.610	-91.882	-57.072	-57.072	-3.787
5900	13.909	117.874	51.370	-93.966	-57.134	-57.134	-4.043
6000	13.909	118.108	52.130	-96.090	-57.190	-57.190	-4.299

March 31, 1962

Cl₂Pb

Lead Dichloride (PbCl₂)

Mol. Wt. = 278.12

ΔH_f[°] 298.15 = -40.61 ± 0.70 kcal. mole⁻¹

S_{298.15}[°] = [76.630]

Point group C_{2v}

Vibrational Levels and Multiplicities

ω_e , cm.⁻¹

[240] (1)

[70] (1)

[300] (1)

Pb-Cl distance = 2.46 ± 0.02 Å Cl-Pb-Cl angle = 95°

$\sigma = 2$

I_A = 24.223 X 10⁻³⁹ g. cm.² I_B = 39.741 X 10⁻³⁹ g. cm.²

I_C = I_A + I_B = 62.970 X 10⁻³⁹ g. cm.²

Heat of Formation. Calculated from ΔH_f[°] 298.15 for PbCl₂(c) and ΔH_s[°] 298.15.

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the vibrational frequencies for the mercury dihalides.

Cl₂Pb

Point Group C_{2v} $\Delta H_f^\circ = -39.34 \pm 1.0 \text{ kcal/mol}$ $S_{298.15}^\circ = 67.36 \pm 0.5 \text{ gibbs/mol}$ $\Delta H_f^\circ = -39.34 \pm 1.0 \text{ kcal/mol}$ Silicon Dichloride (SiCl₂)
(Ideal Gas) GFW = 98.992

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log K _p
0	9.000	INF	INF	3.006	39.343	39.343	1.671
100	11.103	55.000	66.440	1.153	39.257	41.205	6.797
200	12.269	67.360	77.360	0.000	42.154	42.154	30.900
300	12.284	67.436	77.360	0.023	42.172	42.172	30.722
400	12.693	71.063	67.456	1.285	39.376	43.115	23.559
500	13.124	73.179	66.794	2.352	39.466	44.043	19.251
600	13.420	76.408	69.666	3.925	39.570	44.949	16.373
700	13.543	78.487	70.953	5.274	39.684	45.836	14.311
800	13.624	80.301	72.011	6.633	39.811	46.708	12.760
900	13.684	81.910	73.063	7.998	39.946	47.568	11.529
1000	13.726	83.334	74.065	9.366	40.083	48.400	10.578
1100	13.757	84.664	74.897	10.743	40.223	49.223	9.780
1200	13.781	85.862	75.562	12.120	40.421	50.031	9.112
1300	13.800	86.966	76.081	13.499	40.599	50.825	8.554
1400	13.815	87.969	77.360	14.880	40.787	51.604	8.056
1500	13.827	88.942	78.101	16.262	40.986	52.370	7.630
1600	13.837	89.635	78.607	17.645	41.196	53.122	7.256
1700	13.845	90.174	79.480	19.029	41.409	53.754	6.911
1800	13.852	91.466	80.124	20.414	41.585	54.300	6.599
1900	13.856	92.215	80.741	21.600	41.761	54.770	6.315
2000	13.859	93.426	81.333	23.100	41.940	55.170	6.076
2100	13.868	93.602	81.901	24.572	42.119	55.595	5.859
2200	13.872	94.248	82.448	25.959	42.300	55.937	5.638
2300	13.875	94.864	82.974	27.347	42.481	56.200	5.410
2400	13.879	95.455	83.482	28.735	42.664	56.487	5.185
2500	13.882	96.021	83.962	30.123	42.850	56.782	4.968
2600	13.885	96.566	84.446	31.511	43.037	57.071	4.753
2700	13.888	97.090	84.905	32.900	43.226	57.312	4.531
2800	13.893	97.593	85.349	34.289	43.418	57.542	4.310
2900	13.897	98.063	85.780	35.678	43.612	57.760	4.092
3000	13.902	98.504	86.196	37.068	43.808	57.951	3.875
3100	13.907	99.010	86.604	38.458	44.007	58.120	3.671
3200	13.914	99.480	86.999	39.850	44.207	58.280	3.477
3300	13.921	99.950	87.382	41.241	44.411	58.428	3.291
3400	13.928	100.266	87.756	42.634	44.615	58.561	3.110
3500	13.940	100.506	88.120	44.027	44.823	58.681	2.937
3600	13.952	101.092	88.475	45.422	45.037	58.792	2.770
3700	13.965	101.475	88.821	46.818	45.256	58.895	2.608
3800	13.980	101.847	89.159	48.215	45.481	58.990	2.450
3900	13.996	102.211	89.489	49.614	45.712	59.077	2.296
4000	14.015	102.565	89.812	51.014	45.949	59.156	2.145
4100	14.035	102.912	90.127	52.417	46.192	59.228	1.996
4200	14.058	103.250	90.435	53.822	46.441	59.293	1.850
4300	14.083	103.581	90.737	55.229	46.696	59.351	1.706
4400	14.109	103.905	91.033	56.638	46.957	59.402	1.563
4500	14.136	104.223	91.323	58.050	47.223	59.448	1.420
4600	14.169	104.534	91.606	59.466	47.494	59.489	1.277
4700	14.202	104.839	91.885	60.884	47.770	59.525	1.133
4800	14.237	105.138	92.156	62.307	48.051	59.557	1.000
4900	14.274	105.432	92.426	63.732	48.336	59.585	0.867
5000	14.313	105.721	92.689	65.161	48.625	59.609	0.733
5100	14.353	106.005	92.947	66.594	48.918	59.629	0.600
5200	14.396	106.284	93.201	68.032	49.215	59.645	0.467
5300	14.441	106.558	93.450	69.474	49.516	59.658	0.333
5400	14.487	106.826	93.693	70.920	49.821	59.668	0.200
5500	14.534	107.095	93.937	72.371	50.130	59.675	0.067
5600	14.583	107.357	94.174	73.827	50.445	59.679	-0.067
5700	14.633	107.616	94.408	75.288	50.765	59.679	-0.199
5800	14.685	107.871	94.637	76.754	51.090	59.675	-0.333
5900	14.738	108.122	94.864	78.225	51.420	59.668	-0.467
6000	14.791	108.371	95.087	79.701	51.755	59.658	-0.599

Dec. 31, 1960; Dec. 31, 1969

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	(1)	[28300]	(1)
[23000]	(3)	[29950]	(1)

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
513 (1)	[1901] (1)
502 (1)	

Bond Distance: Si-Cl = [2.04] Å

Bond Angle: Cl-Si-Cl = [106°]

Product of the Moments of Inertia: $I_A I_B I_C = [5.709 \times 10^{-114}] \text{ g}^3 \text{ cm}^6$ $\sigma = 2$

Heat of Formation

The adopted value is derived from $\Delta H_f^\circ = 78.5 \pm 2 \text{ kcal/mol}$ at 298.15 K for the reaction $\text{Si(c)} + \text{SiCl}_4(\text{g}) \rightarrow 2 \text{SiCl}_2(\text{g})$. JANAF analyses of equilibrium data for this reaction are summarized below. Three sets of data (1, 2, 3) yield average values of ΔH_f° (3rd law) which agree within 0.5 kcal/mol and values of ΔS_f° (2nd law) which are in reasonable agreement with the JANAF functions. Two of the equilibrium studies used flow techniques while the third used a static technique. A median value of ΔH_f° is adopted. Its uncertainty is estimated by assuming that the JANAF entropy for $\text{SiCl}_2(\text{g})$ may be too low by 0.7 gibbs/mol at 1400 K. The adopted value corresponds to ΔH_f° atom = 203.0 kcal/mol and an average bond energy of 101.5 kcal/mol.

Two other flow studies (3, 4) yield large entropy errors, suggesting that there are temperature-dependent errors in K_p . The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ichino (5) gave K_p values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but ΔH_f° (3rd law) is lower by 5 kcal/mol.

Source

Source	Date	Method	Input	Range	Entropy Test ^a	ΔH_f° , kcal/mol	
Schäfer (1)	1967	Flow	Equation	1273-1473	2nd Law	3rd Law	
Teichmann (2)	1966	Flow	Equation	1223-1573	1.6 ± 1	80.6 ± 1	78.35
					1.7 ± 0.8	80.8 ± 1.1	78.49
Chechenev (3)	1965	Flow	Data	1473-1573	36 ± 6	132 ± 9	76.4
Antipin (4)	1954	Flow	Data	1273-1573	26 ± 3	114 ± 4	75.4
Ichino (5)	1965	Static	Data	1448-1573	-2.1 ± 1.4	70.2 ± 2.1	73.4
Schäfer (6)	1953	Static	Equation	1400-1593	0.6 ± 0.9	79.8 ± 1.4	78.84

$\Delta G = \Delta S_f^\circ$ (2nd law) - ΔS_f° (JANAF functions); where equations are used as input, the uncertainties are those given by the original authors.

Heat Capacity and Entropy

The point group is assumed to be the same as that of CF_2 and SiF_2 . The Si-Cl bond length and Cl-Si-Cl bond angle are estimated to be intermediate between those in HSiCl_3 and H_2SiCl_2 . Comparisons with CF_2 , SiF_2 , H_2SiF_2 and H_2SiF_2 confirm that the estimated angle is reasonable. Further confirmation of the structure comes from analysis of isotopic splittings in the infrared spectra of matrix-isolated SiCl_2 . Milligan and Jacox (7) deduced angles of 90 to 120° from alternative assignments for the two stretching vibrations. Observations on argon matrices gave 502 and 513 cm⁻¹ for these vibrations, but it was not possible to decide which is the symmetric mode. Principal moments of inertia are $I_A = 31.25 \times 10^{-39}$, $I_B = 5.035 \times 10^{-39}$, and $I_C = 36.29 \times 10^{-39}$ g cm².

Milligan and Jacox (7) also observed an unstructured absorption in the ultraviolet spectrum. This is the region in which gas-phase emission studies (8) showed features tentatively ascribed to SiCl_2 . Vibrational spacings of about 250 and 540 cm⁻¹ were associated (8) with the ground state; however, this analysis should be reviewed in the light of the matrix spectra. Meanwhile, we estimate that the bending mode should be similar to that in H_2SiCl_2 , probably 190 ± 40 cm⁻¹.

The ground state is assumed to be 3A_1 , as suggested by Hückel-molecular-orbital calculations (9). Singlet excited states

(8, 10) are included near 28000 and 30000 cm⁻¹, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie et al. (10) that the continuous spectrum near 23000 cm⁻¹ is due to a triplet excited state.

References

- H. Schäfer, H. Brudersack and B. Morcher, *Z. Anorg. Allg. Chem.* **352**, 122 (1967).
- K. Schumann and E. Wolf, *ibid.*, **357**, 145 (1966).
- V. M. Teichmann and V. A. Kiselev, *Dokl. Akad. Nauk SSSR*, **170**, 120 (1966).
- P. F. Antipin and V. V. Sargarev, *Russ. J. Appl. Chem. (English trans.)* **27**, 737 (1954).
- T. Ichino, A. Matsumoto and S. Yamagishi, *Kogyo Kagaku Zasshi* **58**, 262 (1955).
- H. Schäfer and J. Nickl, *Z. Anorg. Allg. Chem.* **274**, 250 (1953).
- D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **43**, 1338 (1965).
- R. M. Asundi, R. Karim and K. Samuel, *Proc. Phys. Soc.* **50**, 581 (1969).
- J. W. Hastie, R. H. Hauge and J. L. Margrave, *J. Mol. Spectrosc.* **29**, 152 (1969).



GFW = 118.806

(CRYSTAL)

TITANIUM DICHLORIDE (TiCl_2)

Titanium Dichloride (TiCl_2)

(Crystal) GFW = 118.806

$\Delta H_f^\circ = -123.0 \pm 4.0$ kcal/mol

$S_{298.15}^\circ = 20.88 \pm 1.0$ gibbs/mol

$T_b = [59.4]^\circ\text{K}$

$\Delta H_{298.15}^\circ = -123.2 \pm 4.0$ kcal/mol

$\Delta H_s^\circ = [59.4]$ kcal/mol

Heat of Formation

The heat of formation of $\text{TiCl}_2(\text{c})$ has been measured calorimetrically. The chosen value of ΔH_{298}° is the average of two such determinations. Values of ΔH_{298}° are also calculated from the heats of reaction for the processes (A) $2\text{TiCl}_3(\text{c}) = \text{TiCl}_2(\text{c}) + \text{TiCl}_4(\text{g})$, (B) $3\text{TiCl}_2(\text{c}) = 2\text{TiCl}_3(\text{g}) + \text{Ti}(\text{c})$, and (C) $2\text{TiCl}_2(\text{c}) = \text{TiCl}_4(\text{g}) + \text{Ti}(\text{c})$. These heats of reaction are combined with auxiliary JANAF values for the heats of formation of $\text{TiCl}_3(\text{c})$, $\text{TiCl}_3(\text{g})$, $\text{TiCl}_4(\text{g})$, and $\text{Ti}(\text{c})$. The following table summarizes the data used to calculate ΔH_{298}° .

Source	Reac.	Method	No. Pts.	Range $^\circ\text{K}$	Second Law	Third Law	Drift eu	ΔH_{298}° kcal/mol
Clifton and MacLeod (1)		Calorimetric			$\Delta H_{298.15}^\circ$			
Krievie et al. (2)	A	Calorimetric	11	615-732	36.021.4	38.9	4.222.1	-123.4
Farber and Darnell (3)	A	Effusion	22**	593-720	35.620.8	39.6	6.121.3	-123.7
Sanderson and MacLeod (4)	A	Knudsen	13***	679-821	39.520.5	35.9	-3.420.7	-123.0
Sanderson and MacLeod (4)	A	Static	13	798-893	94.421.9	112.6	21.422.2	-126.7
Farber and Darnell (5)	B	Effusion	11	798-893	51.521.4	63.0	13.621.7	-123.1
Farber and Darnell (5)	C	Effusion	11	798-893	51.521.4	63.0	13.621.7	-127.7
Hartman and Rinds (6)	A	Effusion	20	815-974	38.820.5	35.7	-3.320.5	-126.9
Skinner and Ruehrwein (7)	A	Manometric	5	802-928	37.520.5	36.0	-1.920.6	-126.9

*Calculated values based on third law $\Delta H_{298.15}^\circ$.

**Four points rejected due to failure of a statistical test.

***Two points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The heat capacity of $\text{TiCl}_2(\text{c})$ has been measured by Kim and Stout (8) over the range 5° to 300°K . They calculated the adopted value of S_{298}° from their measurements based on $S_{298}^\circ = 0.017$ eu. The heat capacity above 300°K is estimated by graphical extrapolation. The large uncertainty on S_{298}° is due to the possibility of sizeable electronic contributions to the heat capacity below 5°K which would account for the rather low value of S_{298}° reported by Kim and Stout (8).

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of $\text{TiCl}_2(\text{c})$ and $\text{TiCl}_2(\text{g})$. The temperature of sublimation is taken as the point at which $\Delta G^\circ = 0$ for the process $\text{TiCl}_2(\text{c}) = \text{TiCl}_2(\text{g})$. These values are hypothetical since TiCl_2 would be decomposed to $\text{TiCl}_3(\text{g})$ and $\text{TiCl}_4(\text{g})$ below this temperature.

References

1. D. G. Clifton and G. E. MacLeod, J. Phys. Chem. **60**, 311 (1956).
2. W. F. Krievie, S. P. Vango and D. M. Mason, J. Chem. Phys. **25**, 519 (1956).
3. M. Farber and A. J. Darnell, J. Phys. Chem. **59**, 156 (1955).
4. B. S. Sanderson and G. E. MacLeod, J. Phys. Chem. **60**, 316 (1956).
5. H. Farber and A. J. Darnell, J. Chem. Phys. **25**, 526 (1956).
6. H. Hartman and G. Rinck, Z. Physik, Chem. **11**, 213 (1957).
7. G. B. Skinner and R. A. Ruehrwein, J. Phys. Chem. **59**, 113 (1955).
8. S. Kim and J. W. Stout, private communication, University of Chicago, 1967.



Titanium Dichloride (TiCl₂)

(Ideal Gas) GFW = 118.806

Point Group [D_{2h}]

(IDEAL GAS)

GFW = 118.806

 $\Delta H_f^\circ = -56.6 \pm 3$ kcal/mol $\Delta H_{298.15}^\circ = -56.7 \pm 3$ kcal/mol $S_{298.15}^\circ = [66.5 \pm 3.0]$ g/bbs/mol

Ground State Quantum Weight = 3

T, °K	C _p ^a	g/bbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log Kp
0	-0.000	-0.000	INFINITE	3.237	-56.591	-56.591	INFINITE
100	9.629	53.355	77.684	1.261	-56.634	-57.261	125.185
200	12.686	61.206	67.759	1.305	-56.673	-57.869	63.236
298	13.743	66.500	66.500	1.305	-56.700	-58.455	42.648
300	13.756	66.505	66.500	1.029	-56.701	-58.466	42.592
400	14.216	70.614	67.046	1.427	-56.747	-59.047	32.262
500	14.452	73.614	68.091	2.462	-56.811	-59.615	26.056
600	14.595	76.492	69.271	4.314	-56.894	-60.169	21.917
700	14.698	79.277	70.456	7.247	-56.935	-60.530	18.520
800	14.776	82.014	72.725	10.200	-56.973	-60.734	14.991
900	14.833	84.614	75.774	13.200	-57.012	-60.892	13.599
1000	14.863	87.086	78.666	16.256	-57.056	-60.984	12.455
1100	14.882	89.436	81.422	19.366	-57.100	-61.010	11.467
1200	14.897	91.679	84.082	22.530	-57.144	-61.054	10.527
1300	14.907	93.822	86.654	25.750	-57.188	-61.100	9.639
1400	14.917	95.875	89.142	29.020	-57.232	-61.146	8.799
1500	14.926	97.846	91.574	32.350	-57.276	-61.192	7.914
1600	14.934	99.740	93.962	35.740	-57.320	-61.238	7.074
1700	14.941	101.574	96.310	39.190	-57.364	-61.284	6.274
1800	14.947	103.358	98.622	42.700	-57.408	-61.330	5.514
1900	14.952	105.092	100.900	46.270	-57.452	-61.376	4.774
2000	14.956	106.786	103.154	49.900	-57.496	-61.422	4.054
2100	14.959	108.440	105.394	53.590	-57.540	-61.468	3.354
2200	14.961	110.054	107.614	57.340	-57.584	-61.514	2.674
2300	14.962	111.638	109.814	61.150	-57.628	-61.560	2.014
2400	14.963	113.192	111.994	65.020	-57.672	-61.606	1.374
2500	14.963	114.716	114.144	68.950	-57.716	-61.652	0.754
2600	14.962	116.210	116.274	72.940	-57.760	-61.698	0.154
2700	14.960	117.684	118.384	77.000	-57.804	-61.744	-0.446
2800	14.957	119.138	120.474	81.130	-57.848	-61.790	-1.046
2900	14.953	120.572	122.544	85.330	-57.892	-61.836	-1.646
3000	14.948	122.000	124.594	89.600	-57.936	-61.882	-2.246
3100	14.942	123.414	126.624	93.940	-57.980	-61.928	-2.846
3200	14.935	124.814	128.634	98.350	-58.024	-61.974	-3.446
3300	14.927	126.200	130.624	102.830	-58.068	-62.020	-4.046
3400	14.918	127.574	132.594	107.380	-58.112	-62.066	-4.646
3500	14.908	128.938	134.534	111.990	-58.156	-62.112	-5.246
3600	14.897	130.292	136.444	116.670	-58.200	-62.158	-5.846
3700	14.885	131.636	138.324	121.420	-58.244	-62.204	-6.446
3800	14.872	132.970	140.174	126.240	-58.288	-62.250	-7.046
3900	14.858	134.294	142.004	131.130	-58.332	-62.296	-7.646
4000	14.843	135.608	143.814	136.090	-58.376	-62.342	-8.246
4100	14.827	136.912	145.604	141.020	-58.420	-62.388	-8.846
4200	14.810	138.206	147.374	146.020	-58.464	-62.434	-9.446
4300	14.792	139.490	149.124	151.090	-58.508	-62.480	-10.046
4400	14.773	140.764	150.854	156.230	-58.552	-62.526	-10.646
4500	14.753	142.028	152.574	161.440	-58.596	-62.572	-11.246
4600	14.732	143.282	154.274	166.720	-58.640	-62.618	-11.846
4700	14.710	144.526	155.954	172.070	-58.684	-62.664	-12.446
4800	14.687	145.760	157.614	177.490	-58.728	-62.710	-13.046
4900	14.663	146.984	159.254	182.980	-58.772	-62.756	-13.646
5000	14.638	148.200	160.884	188.540	-58.816	-62.802	-14.246
5100	14.612	149.406	162.514	194.170	-58.860	-62.848	-14.846
5200	14.585	150.602	164.084	199.870	-58.904	-62.894	-15.446
5300	14.557	151.788	165.594	205.640	-58.948	-62.940	-16.046
5400	14.528	152.964	167.144	211.480	-58.992	-62.986	-16.646
5500	14.498	154.130	168.724	217.390	-59.036	-63.032	-17.246
5600	14.467	155.286	170.334	223.370	-59.080	-63.078	-17.846
5700	14.435	156.432	171.974	229.420	-59.124	-63.124	-18.446
5800	14.402	157.568	173.644	235.540	-59.168	-63.170	-19.046
5900	14.368	158.694	175.344	241.730	-59.212	-63.216	-19.646
6000	14.333	159.810	177.074	248.000	-59.256	-63.262	-20.246

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[3]
[7000]	[6]
[17000]	[8]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	g_i
[279] (1)	[1]
[136] (2)	[2]
[439] (1)	[1]

Bond Distance: Ti-Cl = [2.31] Å

Bond Angle: Cl-Ti-Cl = [100°]

Rotational Constant: B₀ = [0.0449] cm⁻¹

σ = 2

Heat of Formation

Gross and Levi (1) have measured the equilibrium $2\text{TiCl}_3(\text{g}) + \text{Ti}(\text{c}) \rightarrow 3\text{TiCl}_2(\text{g})$ at 1723°K and obtain $\Delta G_{1723}^\circ = 21.7$ kcal/mol from four measurements. This yields $\Delta H_{298}^\circ(\text{TiCl}_2, \text{g}) = -56.7 \pm 3$ kcal/mol. They discuss the measurements of Farber and Darnell (2), on the vapor pressure of $\text{TiCl}_2(\text{c})$, and show that the results are probably in error due to disproportionation of $\text{TiCl}_3(\text{g})$ on condensation. In the work of Skinner and Ruhwain (3) on the reaction $2\text{NaCl}(\text{g}) + \text{Ti}(\text{c}) = 2\text{Na}(\text{g}) + \text{TiCl}_2(\text{g})$, Gross and Levi indicate that the basic assumption, of conversion to TiCl_2 only, is erroneous. In the third law analysis of both these data sets significant drifts are obtained which tends to confirm the above arguments.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $\text{TiCl}_2(\text{c})$ reported by Benzinger and Rundle (4). The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to correspond to the inverted states of $\text{NiCl}_2(\text{g})$ (5). The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear (6, 7, 8, 9).

References

1. P. Gross and D. L. Levi, 16e Cong. Intern. Chim. Pure et Appl. 628, (1958).
2. M. Farber and A. J. Darnell, J. Chem. Phys. 25, 526 (1956).
3. G. B. Skinner and R. A. Ruhwain, J. Phys. Chem. 59, 113 (1965).
4. H. C. Benzinger and R. E. Rundle, Acta Cryst. 1, 274 (1949).
5. C. W. DeKock and D. M. Guen, J. Chem. Phys. 44, 4387 (1966).
6. R. A. Berg and O. Sinanoglu, J. Chem. Phys. 32, 1082 (1960).
7. J. T. Hougen, G. E. Laro, and T. C. James, J. Chem. Phys. 31, 1670 (1961).
8. G. E. Laro, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. 36, 2879 (1962).
9. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. 40, 3471 (1964).

Tungsten Dichloride (WCl₂)
(Crystal)

GFV = 254.756

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H _T ^o	ΔH _T ^o	ΔG _T ^o	Log K _p
0						
100						
200						
298	18.600	31.200	31.200	0.000	- 61.500	- 52.587
300	18.610	31.315	31.200	- 0.34	- 61.492	- 52.532
400	19.133	36.740	31.937	1.922	- 61.023	- 49.616
500	19.656	41.065	33.344	3.861	- 60.538	- 46.819
600	20.179	44.696	34.941	5.853	- 60.026	- 44.123
700	20.702	47.644	36.553	7.894	- 59.494	- 41.481
800	21.225	50.044	38.172	9.993	- 58.944	- 38.989
900	21.750	51.974	39.783	12.142	- 58.287	- 36.534
1000	22.273	53.493	41.343	14.343	- 57.634	- 34.153
1100	22.796	54.640	42.853	16.586	- 56.982	- 31.839
1200	23.319	55.416	44.319	18.880	- 56.241	- 29.588
1300	23.842	55.933	45.749	21.200	- 55.411	- 27.400
1400	24.365	56.319	46.112	23.670	- 54.632	- 25.274
1500	24.888	56.508	47.596	26.133	- 53.783	- 23.205
1600	25.411	56.641	48.736	28.648	- 52.899	- 21.196
1700	25.934	56.714	49.544	31.200	- 51.944	- 19.244
1800	26.457	56.694	50.097	33.816	- 51.001	- 17.346
1900	26.980	56.619	51.025	36.507	- 49.994	- 15.502
2000	27.503	56.536	52.021	39.231	- 48.950	- 13.712

TUNGSTEN DICHLORIDE (WCl₂)

(CRYSTAL)

GFV = 254.756



ΔH_f^o = Unknown

ΔH_f^o_{298.15} = -61.5 ± 3 kcal/mol

S_{298.15}^o = [31.2] gibbs/mol

Td = 862°K

Heat of Formation.

The heat of formation, ΔH_f^o (WCl₂, c) = -61.5 ± 3 kcal/mol, is derived from the heat of combustion, ΔH_c^o = -140 ± 3 kcal/mol for WCl₂(c) + 3/2 O₂(g) → WO₃(c) + Cl₂(g), reported by S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kov, A. V. Suvorov, N. V. Andreeva, E. N. Sharupin, and A. K. Baev, Zhur. Khim. 5, 1650 (1960). The value of ΔH_c^o was determined calorimetrically, but no further information about the combustion process was given in the paper.

Heat Capacity and Entropy.

CP₂₉₈ = 6.2 gibbs/g-atom and CP₉₀₀ = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York, 1958. Between 298° and 900°, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy, S₂₉₈^o = 31.2 eu, is estimated by the method of W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, 1952. S. A. Shchukarev et al., loc. cit., have estimated ΔS_r^o = -30 eu for W(c) + Cl₂(g) = WCl₂(c) which leads to S₂₉₈^o (WCl₂, c) = 31.1 eu, using JANAF auxiliary data.

Temperature of Decomposition.

The decomposition temperature is obtained by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by S. A. Shchukarev, G. I. Novikov, and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz. i Khim., No. 2, 78 (1959). Decomposition pressure data for Cl:W ratios less than two suggest that the decomposition reaction is not simple.

Point Group [D_{∞h}]
S_{298.15} = [74] gibbs/mol
Ground State Quantum Weight = [5]
 $\Delta H_f^\circ = [-3 \pm 25]$ kcal/mol
 $\Delta H_c^\circ = [-3 \pm 25]$ kcal/mol
 $\Delta H_{298.15}^\circ = [-3 \pm 25]$ kcal/mol

Electronic Levels and Quantum Weights

ϵ_i cm ⁻¹	g_i
0	[5]
[5600]	[10]
[8900]	[10]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	
[360]	(1)
[60]	(2)
[423]	(1)

Bond Distance: W-Cl = [2.26] Å
Bond Angle: Cl-W-Cl = [180]°
Rotational Constant: B₀ = [0.04655] cm⁻¹
σ = [2]

Heat of Formation.

The value of $\Delta H_{298}^\circ(\text{WCl}_2, g) = -3 \pm 25$ kcal/mol is calculated from the heat of formation of the crystal plus the heat of sublimation, $\Delta H_{298}^\circ = 58.5 \pm 25$ kcal/mol. The latter is estimated from the heats of sublimation of TiCl₂, CrCl₂, MnCl₂, FeCl₂, CoCl₂, NiCl₂ given by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).

The uncertainty covers the difference between the heats of sublimation among the above compounds and also the possible error in transference from the first row transition metal dichlorides to tungsten dichloride.

S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Beev, Zh. Neorg. Khim. 5, 1650 (1960), have also estimated the heat of sublimation as 102 kcal/mol.

Heat Capacity and Entropy.

The molecular configuration of WCl₂(g) is assumed to be linear. The bond distance is estimated to be the same as that in WCl₆(g). The ground state configuration (Σ), the low lying electronic levels and their quantum weights are assumed to be the same as those for CrCl₂(g), observed by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The vibrational frequencies are calculated from a valence force field model. The stretching force constant, K₁, is estimated to be the same as that of HgCl₂(g), 2.7 millidynes/Å. The bending force constant is assumed to be one hundredth of the stretching force constant. The moment of inertia is I = 6.013 x 10⁻³⁶ g cm².

Sept. 30, 1962; Dec. 31, 1966



GFW = 162.126

(CRYSTAL)

ZIRCONIUM DICHLORIDE (ZrCl_2)

Zirconium Dichloride (ZrCl_2)

(Crystal) GFW = 162.126

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_{298.15}^\circ = [-103.0 \pm 10] \text{ kcal/mol}$

$\Delta H_m^\circ = [6.4 \pm 3] \text{ kcal/mol}$

$\Delta H_{298.15}^\circ = [58.5 \pm 10] \text{ kcal/mol}$

$S_{298.15}^\circ = [26.3 \pm 3] \text{ gibbs/mol}$

$T_m = [1000]^\circ\text{K}$

Heat of Formation

The value of $\Delta H_{298}^\circ(\text{ZrCl}_2, c) = -103.0 \text{ kcal/mol}$ is calculated from the estimated $\Delta H_{298}^\circ = 58.5 \text{ kcal/mol}$ for $\text{ZrCl}_2(c) + \text{ZrCl}_2(g)$, using $\Delta H_{298}^\circ(\text{ZrCl}_2, g) = -44.5 \text{ kcal/mol}$ (1). The estimated ΔH_{298}° is obtained as an average of the heats of sublimation at 298°K for TiCl_2 , VCl_2 , CrCl_2 , MnCl_2 , FeCl_2 , CoCl_2 , NiCl_2 given by L. Brewer, G. R. Somayajulu and E. Brackett (2).

Heat Capacity and Entropy

The heat capacities of $\text{ZrCl}_2(c)$ are estimated based on the assumption that $C_p(\text{ZrCl}_2, c) = 1/2[C_p(\text{ZrCl}_4, c) + C_p(\text{Zr}, c)]$. The entropy, S_{298}° , is also estimated in a manner similar to that of the heat capacity.

Melting Data

The melting point was estimated to be 1000°K by L. Brewer (3) and the heat of melting was also estimated by A. Glassner (4).

References

1. JANAF $\text{ZrCl}_2(g)$ table dated Dec. 31, 1969.
2. L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963).
3. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw-Hill Book Company, New York, 1949.
4. A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K ," ANL Report 5750, Argonne National Laboratory.

T, °K	C_p°	$-\frac{\text{gibbs/mol}}{S^\circ}$	$-\frac{(G^\circ - H^\circ_{298})/T}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100	17.350	26.300	26.300	0.000	92.176	67.567
200	17.378	26.407	26.300	0.032	92.109	67.101
300	18.168	31.521	26.992	1.612	88.529	66.370
400	18.700	35.634	28.323	3.656	85.034	37.168
500	19.130	39.082	29.836	5.548	81.608	29.726
600	19.550	42.002	31.175	7.451	78.522	20.468
700	19.868	44.692	32.678	9.491	75.422	14.952
800	20.204	47.052	34.324	11.495	71.648	17.399
900	20.536	49.199	35.706	13.493	68.414	14.952
1000						
1100	20.700	51.165	37.023	15.356	65.215	12.957
1200	20.900	52.942	38.178	17.098	62.041	10.961
1300	21.080	54.656	39.478	19.737	58.787	9.682
1400	21.180	56.222	40.615	21.650	55.617	8.682
1500	21.250	57.686	41.705	23.971	52.483	7.647
1600	21.300	59.059	42.787	26.009	49.383	6.745
1700	21.350	60.322	43.765	27.745	46.324	5.954
1800	21.400	61.573	44.702	30.169	43.271	5.254
1900	21.450	62.732	45.620	32.511	40.254	4.630
2000	21.500	63.833	46.504	34.659	37.284	4.072

Zirconium Dichloride (ZrCl₂)

(Liquid) GFW = 162.126

T, °K	C _p	$\frac{\text{gkcal/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
100							
200							
250	21.750	29.278	29.278	.000	- 98.372	- 88.436	64.025
300	21.750	29.413	29.278	.040	- 98.358	- 88.374	64.361
400	21.750	35.670	30.132	2.215	- 97.636	- 85.157	66.528
500	21.750	40.523	31.743	6.390	- 96.965	- 82.116	35.093
600	21.750	46.489	33.566	6.565	- 96.337	- 79.206	26.451
700	21.750	47.881	35.325	8.740	- 95.746	- 76.398	23.053
800	21.750	50.766	37.102	10.915	- 95.190	- 73.673	20.126
900	21.750	53.307	38.763	13.090	- 94.667	- 71.015	17.285
1000	21.750	55.599	40.334	15.265	- 94.175	- 68.414	14.952
1100	21.750	57.672	41.817	17.440	- 93.714	- 65.860	13.085
1200	21.750	59.564	43.218	19.615	- 93.296	- 63.296	11.528
1300	21.750	61.305	44.544	21.790	- 93.556	- 60.750	10.213
1400	21.750	62.917	45.799	23.965	- 92.990	- 58.247	9.093
1500	21.750	64.418	46.991	26.140	- 92.437	- 55.785	8.128
1600	21.750	65.822	48.125	28.315	- 91.888	- 53.359	7.289
1700	21.750	67.140	49.205	30.490	- 91.370	- 50.965	6.552
1800	21.750	68.383	50.236	32.665	- 90.856	- 48.605	5.901
1900	21.750	69.559	51.222	34.840	- 90.354	- 46.270	5.322
2000	21.750	70.675	52.167	37.015	- 89.866	- 43.963	4.808

ZIRCONIUM DICHLORIDE (ZrCl₂)

(LIQUID)

GFW = 162.126

$$S^\circ_{298.15} = [29.278] \text{ gibbs/mol}$$

$$\Delta H^\circ_{298.15} = [-98.372] \text{ kcal/mol}$$

$$T_m = [1000]^\circ\text{K}$$

$$\Delta H_m^\circ = [6.4 \pm 3] \text{ kcal/mol}$$

$$T_b = [1565.3]^\circ\text{K}$$

$$\Delta H_v^\circ = [45.0] \text{ kcal/mol}$$

Heat of Formation

The $\Delta H^\circ_{298}(\text{ZrCl}_2, l)$ is calculated from $\Delta H^\circ_{298}(\text{ZrCl}_2, c)$ by adding ΔH_m° and the difference between $H_{1000} - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7.25 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The melting point was estimated to be 1000°K by L. Brewer (1), and the heat of melting was also estimated by A. Glasner (2).

Vaporization Data

T_b is the temperature at which the Gibbs energy change approaches zero for the process $\text{ZrCl}_2(l) \rightarrow \text{ZrCl}_2(g)$. The difference between ΔH° for $\text{ZrCl}_2(l)$ and $\text{ZrCl}_2(g)$ at T_b is ΔH_v° .

References

1. L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Goull, Ed., McGraw-Hill Book Company, New York, 1949.
2. A. Glasner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500°K," ANL Report 5750, Argonne National Laboratory.

GFW = 162.126

(IDEAL GAS)

ZIRCONIUM DICHLORIDE (ZrCl₂)Point Group = [D_{∞h}] $\Delta H_f^\circ = -144.4 \pm 5 \text{ kcal/mol}$ $\Delta H_f^\circ_{298.15} = -144.5 \pm 5 \text{ kcal/mol}$ $S^\circ_{298.15} = [69.9 \pm 3] \text{ gibbs/mol}$

Ground State Quantum Weight = [3]

Zirconium Dichloride (ZrCl₂)

(Ideal Gas)

GFW = 162.126

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	10.000	56.357	INF	2.500	44.852	6.115
100	12.856	64.565	71.132	1.313	44.458	50.213
200	13.785	66.896	69.896	1.000	44.500	34.213
300	13.706	68.081	69.081	1.006	44.500	34.012
400	14.231	70.017	71.845	1.252	44.500	34.012
500	14.457	71.219	71.489	2.665	44.618	21.032
600	14.587	70.668	72.671	4.318	44.712	48.609
700	14.668	82.123	73.865	5.781	44.833	15.449
800	14.724	84.085	75.022	6.750	44.983	13.697
900	14.765	85.418	76.146	7.715	45.146	11.230
1000	14.803	87.380	77.176	10.268	45.384	51.385
1100	14.841	88.792	78.169	11.686	45.596	17.779
1200	14.885	90.066	79.109	13.172	45.706	9.560
1300	14.937	91.279	80.000	14.663	45.811	8.905
1400	14.987	92.435	80.850	16.160	45.914	8.484
1500	15.067	93.425	81.650	17.663	46.012	8.153
1600	15.146	94.400	82.417	19.173	46.168	7.425
1700	15.232	95.321	83.149	20.692	46.296	7.045
1800	15.323	96.195	83.850	22.250	46.429	6.707
1900	15.418	97.018	84.525	23.847	46.566	6.405
2000	15.516	97.818	85.166	25.504	46.705	6.129
2100	15.613	98.578	85.787	26.860	46.847	5.881
2200	15.709	99.306	86.385	28.426	46.996	5.634
2300	15.803	100.007	86.962	30.002	47.153	5.407
2400	15.893	100.687	87.520	31.680	47.319	5.199
2500	15.980	101.332	88.059	33.460	47.496	5.002
2600	16.062	101.960	88.582	34.783	47.684	4.822
2700	16.140	102.568	89.089	36.393	47.886	4.656
2800	16.215	103.156	89.581	38.010	48.100	4.500
2900	16.287	103.726	90.058	39.641	48.326	4.353
3000	16.346	104.279	90.524	41.287	48.562	4.220
3100	16.407	104.816	90.976	42.904	48.808	4.093
3200	16.463	105.338	91.417	44.548	49.066	3.974
3300	16.514	105.846	91.846	46.217	49.336	3.862
3400	16.561	106.341	92.264	47.910	49.618	3.758
3500	16.614	106.820	92.674	49.510	49.910	3.656
3600	16.660	107.289	93.074	51.174	50.212	3.561
3700	16.702	107.746	93.464	52.892	50.526	3.472
3800	16.739	108.192	93.846	54.664	50.852	3.387
3900	16.783	108.627	94.219	56.490	51.190	3.305
4000	16.821	109.053	94.585	57.871	51.533	3.229
4100	16.857	109.469	94.943	59.209	51.884	3.156
4200	16.892	109.875	95.294	61.242	52.250	3.084
4300	16.923	110.274	95.630	63.074	52.623	3.013
4400	16.950	110.663	95.954	64.708	52.999	2.943
4500	16.992	111.044	96.305	66.325	53.378	2.875
4600	17.023	111.418	96.630	68.026	53.760	2.807
4700	17.053	111.784	96.948	69.730	54.146	2.741
4800	17.083	112.142	97.250	71.436	54.536	2.676
4900	17.110	112.496	97.544	73.146	54.930	2.612
5000	17.137	112.842	97.870	74.858	55.327	2.537
5100	17.163	113.182	98.167	76.571	55.728	2.468
5200	17.188	113.515	98.459	78.293	56.133	2.400
5300	17.213	113.843	98.750	80.011	56.542	2.333
5400	17.235	114.166	99.039	81.730	56.955	2.267
5500	17.256	114.481	99.307	83.458	57.372	2.201
5600	17.276	114.792	99.561	85.185	57.798	2.135
5700	17.295	115.098	99.850	86.913	58.228	2.069
5800	17.313	115.399	100.137	88.641	58.662	2.003
5900	17.330	115.695	100.417	90.369	59.099	1.937
6000	17.345	115.987	100.635	92.109	59.540	1.869

June 30, 1962; Dec. 31, 1969

Electronic Levels and Quantum Weights

E_e, cm^{-1}	g_e
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}
[346] (1)
[92] (2)
[461] (1)

Bond Distance: Zr-Cl = [2.3] Å

Bond Angle: Cl-Zr-Cl = [180]°

Rotational Constant: $B_0 = [0.04934] \text{ cm}^{-1}$ $\sigma = [2]$

Heat of Formation

Potter (1) investigated mass spectrometrically the gaseous equilibria among ZrCl , ZrCl_2 , ZrCl_3 and ZrCl_4 . Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equilibrium constants for the reaction $\text{ZrCl}_4(g) + \text{ZrCl}_2(g) \rightleftharpoons 2\text{ZrCl}_3(g)$ in the temperature range 1873-2110°K, second and third law analyses give the heat of reaction at 298°K as -15.8 and +1.7 kcal/mol, respectively. The third law drift is 8.9 ± 3.7 eu. Based on the third law heat of reaction and $\Delta H_f^\circ(\text{ZrCl}_4, g) = -207.77 \text{ kcal/mol}$ (2) and $\Delta H_f^\circ(\text{ZrCl}_3, g) = -125.3 \text{ kcal/mol}$ (3), we obtain $\Delta H_f^\circ(\text{ZrCl}_2, g) = -44.5 \text{ kcal/mol}$ which is adopted in the tabulation.

Farber et al. (4) also studied mass spectrometrically the reaction (a) $\text{Zr}(c) + \text{ZrCl}_4(g) \rightleftharpoons 2\text{ZrCl}_2(g)$ and the reaction (b) $\text{Zr}(c) + \text{ZrCl}_2(g) \rightleftharpoons \text{ZrCl}_3(g)$. They reported second law heats of reaction as $\Delta H_{298}^\circ = 28.8 \pm 1.8 \text{ kcal/mol}$ for reaction (a); and $-141.1 \pm 2.2 \text{ kcal/mol}$ for reaction (b). Third law analysis of the equilibrium constants which were calculated from their ion intensities of run 3 (the only available values) gives $\Delta H_f^\circ(\text{ZrCl}_2, g) = -43.4 \text{ kcal/mol}$. See JANAF $\text{ZrCl}_3(g)$ table (3) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that other transition metal dichlorides are linear (5, 6, 7, 8, 9, 10) even though some fluorides are bent (11). The bond distance is assumed to be the same as that of $\text{ZrCl}_4(g)$. The electronic levels and quantum weights are estimated to be the same as those of $\text{TiCl}_2(g)$ (12).

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 2.5 millidynes/Å and the bending force constant 0.05 millidynes/Å. The moment of inertia is $52.2817 \times 10^{-39} \text{ g cm}^2$.

References

1. N. D. Potter, Aeronutronic Div., Philco-Ford, Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF $\text{ZrCl}_4(g)$ table dated Dec. 31, 1969.
3. JANAF $\text{ZrCl}_3(g)$ table dated Dec. 31, 1969.
4. M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL-TR-67-244, Contract F0441-67-C-0010, Nov. 1967.
5. R. A. Berg and G. Sinanoglu, J. Chem. Phys. **32**, 1082 (1960).
6. J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1870 (1961).
7. G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. **38**, 2879 (1962).
8. A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).
9. M. E. Jacox and D. E. Milligan, J. Chem. Phys. **51**, 4143 (1969).
10. K. R. Thompson and K. D. Carlson, J. Chem. Phys. **49**, 4379 (1968).
11. J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Chem. Phys. **51**, 2648 (1969).
12. JANAF $\text{TiCl}_2(g)$ table dated Dec. 31, 1969.

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg ⁻¹	H° - H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	∞	6.865	61.789	INFINITE	INFINITE
100	21.780	71.100	105.304	2.860	61.817	61.789	6.073
200	21.780	105.304	105.304	2.860	61.817	61.789	6.073
298	20.773	102.631	102.631	∞	61.800	61.489	44.794
300	20.795	102.815	102.815	∞	61.800	61.488	33.539
400	30.621	111.515	108.065	3.091	61.810	61.394	28.761
500	31.028	118.397	108.065	6.166	61.853	61.271	22.273
600	31.256	124.007	108.067	9.281	61.940	61.148	16.047
700	31.396	128.905	111.171	12.434	62.059	61.005	10.623
800	31.488	133.104	113.656	15.559	62.215	60.848	6.664
900	31.552	136.817	116.027	18.671	62.399	60.664	3.224
1000	31.598	140.144	118.275	21.809	62.616	60.462	11.067
1100	31.632	143.157	120.402	25.030	62.858	60.234	10.925
1200	31.657	145.910	122.415	28.189	63.131	59.986	9.227
1300	31.678	148.445	124.321	31.361	63.430	59.710	8.462
1400	31.694	150.793	126.129	34.550	63.756	59.407	7.769
1500	31.707	152.980	127.847	37.760	64.109	59.078	7.100
1600	31.717	155.027	129.483	40.971	64.483	58.729	6.456
1700	31.726	156.950	131.043	44.203	64.872	58.367	5.832
1800	31.733	158.764	132.532	47.456	65.276	57.992	5.226
1900	31.740	160.460	133.959	50.730	65.697	57.605	4.637
2000	31.745	162.108	135.326	54.024	66.136	57.207	4.060
2100	31.750	163.657	136.638	57.339	66.594	56.797	3.495
2200	31.754	165.134	137.900	60.674	67.070	56.374	2.941
2300	31.757	166.546	139.115	64.030	67.561	55.939	2.397
2400	31.760	167.897	140.286	67.406	68.066	55.494	1.862
2500	31.763	169.194	141.417	70.802	68.584	55.040	1.337
2600	31.765	170.440	142.509	74.218	69.114	54.577	0.821
2700	31.767	171.638	143.566	77.654	69.656	54.107	0.314
2800	31.769	172.784	144.590	81.110	70.210	53.631	-0.184
2900	31.771	173.889	145.581	84.586	70.776	53.150	-0.686
3000	31.773	174.956	146.544	88.082	71.353	52.664	-1.192
3100	31.774	176.028	147.478	91.597	71.941	52.163	-1.701
3200	31.775	177.036	148.386	95.130	72.540	51.657	-2.211
3300	31.776	178.014	149.269	98.682	73.150	51.146	-2.721
3400	31.777	178.963	150.129	102.253	73.770	50.630	-3.231
3500	31.778	179.884	150.966	105.844	74.400	50.109	-3.741
3600	31.779	180.779	151.782	109.456	75.040	49.584	-4.251
3700	31.780	181.650	152.577	113.088	75.690	49.054	-4.761
3800	31.781	182.497	153.353	116.740	76.350	48.519	-5.271
3900	31.782	183.323	154.111	120.402	77.020	47.979	-5.781
4000	31.782	184.128	154.852	124.074	77.690	47.434	-6.291
4100	31.783	184.912	155.575	127.756	78.360	46.889	-6.801
4200	31.783	185.678	156.283	131.448	79.040	46.344	-7.311
4300	31.784	186.426	156.975	135.150	79.730	45.799	-7.821
4400	31.784	187.157	157.653	138.862	80.430	45.254	-8.331
4500	31.785	187.871	158.317	142.584	81.140	44.709	-8.841
4600	31.785	188.570	158.967	146.316	81.860	44.164	-9.351
4700	31.786	189.253	159.604	150.058	82.590	43.619	-9.861
4800	31.786	189.923	160.229	153.810	83.330	43.074	-10.371
4900	31.787	190.578	160.841	157.532	84.080	42.529	-10.881
5000	31.787	191.220	161.442	161.264	84.840	41.984	-11.391
5100	31.787	191.850	162.033	165.006	85.610	41.439	-11.901
5200	31.787	192.467	162.612	168.768	86.390	40.894	-12.411
5300	31.788	193.072	163.181	172.540	87.180	40.349	-12.921
5400	31.788	193.667	163.740	176.322	87.980	39.804	-13.431
5500	31.788	194.250	164.289	180.114	88.790	39.259	-13.941
5600	31.788	194.823	164.830	183.916	89.610	38.714	-14.451
5700	31.789	195.385	165.361	187.730	90.440	38.169	-14.961
5800	31.789	195.938	165.883	191.552	91.280	37.624	-15.471
5900	31.789	196.480	166.396	195.384	92.130	37.079	-15.981
6000	31.789	197.010	166.903	199.226	92.990	36.534	-16.491

Mar. 31, 1966

Point Group D_{3h}S_{298.15} = [102.63] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[100](1)	350 (2)
[150](1)	[300](2)
[250](1)	[60](2)
[200](1)	[60](2)

Bond Distance: Cu-Cl = 2.16 Å

Bond Angle: Cl-Cu-Cl = 150°

Product of the Moments of Inertia: I_AI_BI_C = 2.02847 X 10⁻¹¹¹ g.³ cm.⁶

Heat of Formation.

The heat of sublimation was determined by second and third law analysis of the following vapor pressure data. D. W. Magee, Doctoral Thesis, Ohio State University (1955), measured both vapor pressure by torsion effusion and vapor density in the range 533-644°K. and found only trimer present. The 2nd and 3rd law analyses gave ΔH_f⁰ 298 = 37.37 ± 0.04 and 37.24 ± 0.02 kcal. mole⁻¹ with a drift of -0.25 ± 0.07 cal. deg⁻¹ mole⁻¹. R. A. J. Shelton, Trans. Faraday Soc. 57, 2113 (1961) using Knudsen effusion in the range 547-657°K. obtained ΔH_f⁰ 298 = 40.35 ± 1.4 and 37.42 ± 0.4 kcal. mole⁻¹ with a drift of -4.9 cal. deg⁻¹ mole⁻¹. P. I. Fedorov and M. N. Shakhov, Izv. Vysishikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. 4, 550 (1961), using transport methods obtained vapor pressures over the liquid from 751-1057°K. Using 2nd and 3rd law analysis these gave ΔH_f⁰ 298 = 38.6 ± 1.0 and 39.27 ± 0.5 kcal. mole⁻¹.

L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950) obtained equilibrium constants for the reaction 3Cu(c) + 3HCl(g) → Cu₃Cl₃(g) + 1.5 H₂(g). Second and third law analysis of these constants gave ΔH_r⁰ 298 = 3.9 ± 0.6 and 4.39 ± 0.3 kcal. mole⁻¹ which leads to ΔH_f⁰ = -61.8 ± 0.5 kcal. mole⁻¹. This was the value adopted since it is dependent only on HCl(g) and does not involve three times the uncertainty of CuCl(c) as do the sublimation experiments, which yield values in good agreement but of larger uncertainty.

Heat Capacity and Entropy.

The structure of the trimer has been investigated by C-R. Wong and V. Schomaker, J. Phys. Chem. 61, 358 (1957). They conclude that the molecule is planar with D_{3h} symmetry and a Cu-Cl bond length of 2.16 Å. They also state that a very large amplitude of the symmetric in-plane bending appears plausible from the diffraction pattern. The infra-red spectrum has been investigated by W. Klemperer, S. A. Rice and R. S. Berry, J. Am. Chem. Soc. 79, 1810 (1957). They observed one strong absorption with a maximum at 350 cm⁻¹ they attribute this to bond stretching motion of type E'. They also suggest that the broad absorption may involve another mode of approximately equal frequency.

In order to estimate the remaining frequencies we assumed that the other infra-red active E' mode would be close to the observed 350 cm⁻¹ and this was estimated as 300 cm⁻¹. The in-plane bending is the third E' mode and since this has a very large amplitude it was estimated as 60 cm⁻¹. By analogy with other D_{3h} rings the A₂' mode was assumed to be in the same region as the E' stretches and was taken to be 250 cm⁻¹. The 2A₁' stretches were estimated as 100 and 150 cm⁻¹, while the out of plane A₂" was taken as 200 cm⁻¹ and the E" as 80 cm⁻¹. These values gave calculated entropies in excellent agreement with the equilibrium data and thus support the estimates.

The individual moments of inertia were I_A=I_B = 100.472 X 10⁻³⁹ g. cm.², I_C = 200.944 X 10⁻³⁹ g. cm.²

Trichlorofluorosilane (FSiCl₃)
(Ideal Gas) Mol. Wt. = 153.461

INTERIM TABLE

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹	S ^o	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	13.167	61.098	INFINITE	-	0.592	-200.480	-200.480	INFINITE
100	13.167	61.098	67.416	-	3.432	-200.986	-194.197	831.136
200	13.483	72.211	82.191	-	1.926	-201.063	-195.354	213.462
298.15	13.530	76.295	86.295	-	1.000	-201.000	-192.555	141.147
300	21.545	80.428	80.295	0.040	-200.909	-192.512	-192.512	140.236
400	21.025	80.552	81.161	2.294	-200.900	-192.512	-192.512	140.236
500	21.371	82.068	82.439	4.625	-200.785	-186.910	-186.910	81.694
600	24.398	96.491	84.758	7.040	-200.662	-184.146	-184.146	67.072
700	24.743	100.279	86.711	9.498	-200.538	-181.404	-181.404	56.634
800	24.980	103.600	88.619	11.985	-200.418	-178.679	-178.679	48.811
900	25.125	106.544	90.484	14.500	-200.300	-175.976	-175.976	42.667
1000	25.272	109.206	92.195	17.043	-200.182	-173.291	-173.291	37.667
1100	25.366	111.622	93.653	19.545	-200.075	-170.587	-170.587	33.891
1200	25.418	113.832	95.428	22.085	-199.972	-167.909	-167.909	30.579
1300	25.485	115.761	97.423	24.632	-199.876	-165.241	-165.241	27.776
1400	25.527	117.525	99.498	26.740	-199.780	-162.587	-162.587	25.301
1500	25.577	119.152	101.648	28.420	-199.684	-159.930	-159.930	23.101
1600	25.608	121.177	103.990	32.299	-199.601	-157.280	-157.280	21.482
1700	25.613	122.730	107.223	34.861	-211.621	-154.526	-154.526	19.865
1800	25.673	124.583	104.535	30.992	-211.300	-151.827	-151.827	18.205
1900	25.688	126.901	105.620	42.560	-211.261	-149.455	-149.455	16.768
2000	25.702	128.154	106.664	45.130	-211.146	-147.130	-147.130	15.689
2100	25.713	129.350	107.668	47.701	-211.032	-137.820	-137.820	13.690
2200	25.733	130.588	108.570	52.285	-210.821	-134.493	-134.493	12.779
2300	25.741	132.639	110.471	55.419	-210.706	-131.177	-131.177	11.177
2400	25.748	133.649	111.344	57.993	-210.602	-124.546	-124.546	10.469
2500	25.754	134.621	112.188	60.568	-210.501	-121.237	-121.237	9.813
2600	25.759	135.527	113.106	63.144	-210.402	-117.933	-117.933	9.205
2700	25.769	137.335	114.569	68.297	-210.213	-111.336	-111.336	8.111
2800	25.773	138.180	115.317	70.674	-210.122	-108.040	-108.040	7.616
2900	25.777	138.998	116.045	73.452	-210.034	-104.747	-104.747	7.154
3000	25.780	139.741	116.752	76.039	-209.950	-101.459	-101.459	6.719
3100	25.786	141.309	118.113	81.186	-209.786	-94.860	-94.860	5.925
3200	25.789	142.035	118.767	83.765	-304.685	-91.137	-91.137	5.532
3300	25.791	142.742	119.405	86.344	-304.546	-85.207	-85.207	5.033
3400	25.793	143.428	120.028	88.923	-304.416	-79.282	-79.282	4.559
3500	25.798	144.100	120.637	91.503	-304.216	-73.362	-73.362	4.085
3600	25.799	144.753	121.232	94.082	-304.160	-67.439	-67.439	3.665
3700	25.799	145.390	121.814	96.662	-304.035	-61.523	-61.523	3.279
3800	25.801	146.011	122.382	99.242	-303.914	-55.604	-55.604	2.893
3900	25.803	146.619	122.939	101.822	-303.797	-49.701	-49.701	2.526
4000	25.805	147.192	123.481	104.401	-303.681	-43.800	-43.800	2.175
4100	25.807	147.742	124.018	106.983	-303.569	-37.890	-37.890	1.840
4200	25.808	148.269	124.541	109.564	-303.459	-31.982	-31.982	1.519
4300	25.808	148.774	125.053	112.144	-303.351	-26.081	-26.081	1.213
4400	25.809	149.256	125.556	114.725	-303.247	-20.182	-20.182	0.919
4500	25.810	149.719	126.053	117.306	-303.148	-14.286	-14.286	0.637
4600	25.811	150.151	126.533	119.887	-303.055	-8.389	-8.389	0.367
4700	25.812	151.022	127.008	122.468	-302.950	-2.503	-2.503	0.107
4800	25.813	151.523	127.475	125.050	-302.856	3.300	3.300	0.142
4900	25.813	152.005	127.923	127.631	-302.765	9.281	9.281	0.363
5000	25.815	152.471	128.368	130.212	-302.676	15.262	15.262	0.587
5100	25.815	152.971	128.827	132.792	-302.590	21.244	21.244	0.817
5200	25.816	153.436	129.262	135.375	-302.509	26.933	26.933	1.051
5300	25.816	153.883	129.690	137.957	-302.430	32.621	32.621	1.258
5400	25.816	154.304	130.104	140.539	-302.357	38.309	38.309	1.450
5500	25.816	154.783	130.526	143.120	-302.277	44.000	44.000	1.638
5600	25.816	155.217	130.934	145.702	-302.207	50.450	50.450	1.838

December 31, 1960.



TRICHLOROFUROSILANE (FSiCl₃)

MOL. WT. = 153.461

Point Group C_{3v}

ΔH_f^o 298.15 = [-201 ± 15] kcal mole⁻¹

S_{298.15}^o = [80.3 ± 4] cal deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm⁻¹
[925] (1)
[350] (1)
[500] (2)
[270] (2)
[200] (2)

Product of the Moments of Inertia: I_AI_BI_C = [142,900 × 10⁻¹¹⁷] g³ cm⁶ σ = 3

All data from C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.



T, °K.	C _p	S°	$\frac{S^\circ - (F^\circ - H_{298}^\circ)}{T}$	$\frac{\text{kcal. mole}^{-1}}{T}$	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	-0.000	-0.000	INFINITE	-	4.710	- 95.804	-	INFINITE
100	13.923	13.127	52.582	-	3.946	- 96.194	- 95.804	197.957
200	20.607	25.303	36.055	-	2.150	- 95.902	- 85.055	92.040
298	23.100	34.019	34.019	-	0.000	- 95.460	- 79.824	56.510
300	23.150	34.162	34.020	+0.43	-	- 95.451	- 79.727	56.078
400	25.500	41.141	34.055	2.675	-	- 94.890	- 74.567	40.739
500	28.650	47.131	36.000	5.165	-	- 94.154	- 69.564	30.405
600	30.900	51.532	36.970	8.047	-	- 93.306	- 64.726	23.575
700	32.700	54.765	37.925	11.076	-	- 92.356	- 60.074	18.164
800	34.100	57.060	38.845	14.179	-	- 91.277	- 55.676	13.754
900	35.100	58.494	39.724	17.351	-	- 90.015	- 51.026	10.300
1000	35.800	59.291	40.547	20.547	-	- 88.618	- 46.669	7.819
1100	36.200	60.000	41.311	23.747	-	- 87.038	- 42.363	6.416
1200	36.400	60.600	42.000	26.947	-	- 85.338	- 38.142	5.122
1300	36.500	61.100	42.600	30.147	-	- 83.572	- 34.042	3.976
1400	36.600	61.600	43.200	33.347	-	- 81.722	- 29.841	3.068
1500	36.700	62.100	43.800	36.547	-	- 79.834	- 25.614	2.361

$$\Delta H_f^\circ 0 = -95.80 \pm 0.20 \text{ kcal. mole}^{-1}$$
$$\Delta H_f^\circ 298.15 = -95.46 \pm 0.20 \text{ kcal. mole}^{-1}$$
$$\Delta H_m^\circ = 10.30 \text{ kcal. mole}^{-1}$$
$$\Delta H_m^\circ (\text{to dimer}) = 34.52 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 34.019 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$T_m = 577^\circ \text{K.}$$

Heat of Formation.

The enthalpy change, $\Delta H_f^\circ 298.15 = -24.49 \pm 0.07 \text{ kcal. mole}^{-1}$, for the reaction $\text{Fe}(\text{ }) + 3(\text{HCl} \cdot 12.751 \text{ H}_2\text{O})(\text{l}) + 1/2(\text{H}_2\text{O}_2 \cdot 12.580 \text{ H}_2\text{O})(\text{l}) = \text{FeCl}_3(\text{c}) + 45.483 \text{ H}_2\text{O}(\text{l})$ was determined by M. P. Koehler and J. P. Coughlin, J. Phys. Chem. **63**, 605 (1959). This leads to $\Delta H_f^\circ 298.15 = -95.46 \pm 0.20 \text{ kcal. mole}^{-1}$ for $\text{FeCl}_3(\text{c})$, using $\Delta H_f^\circ 298.15 = -38.9 \pm 0.05$ and $-45.68 \pm 0.01 \text{ kcal. mole}^{-1}$ for hydrochloric acid and hydrogen peroxide solution, respectively, obtained from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, National Bureau of Standards Circular 500, 1952. From $\Delta H_f^\circ 298.15 = -38.0 \pm 0.2 \text{ kcal. mole}^{-1}$ for the reaction $\text{FeCl}_3(\text{c}) = \text{Fe}^{+++}(\text{aq.})$ reported by J. C. M. Li and N. V. Gregory, J. Am. Chem. Soc. **74**, 4670 (1952), the value of $\Delta H_f^\circ 298.15$ (FeCl_3, c) was calculated as $-95.26 \pm 0.2 \text{ kcal. mole}^{-1}$. The former $\Delta H_f^\circ 298.15$ value is adopted.

The equilibrium pressures of the reaction $2 \text{FeCl}_2(\text{c}) + \text{Cl}_2(\text{g}) = 2\text{FeCl}_3(\text{c})$, in the temperature range of 435.7-482.2°K., were measured by H. Schäfer and E. Oehler, Z. anorg. allgem. Chem. **271**, 206 (1953). Using the reported partial pressures for $\text{Cl}_2(\text{g})$, the enthalpy change ($\Delta H_f^\circ 298.15$) of the reaction was evaluated as -27.49 ± 0.44 and $-27.21 \text{ kcal. mole}^{-1}$ by the second and third law methods, respectively. Based on the third law value for $\Delta H_f^\circ 298.15$, the value of $\Delta H_f^\circ 298.15$ (FeCl_3, c) was derived to be $-95.36 \pm 0.12 \text{ kcal. mole}^{-1}$ which is in good agreement with the adopted value.

Heat Capacity and Entropy.

The low temperature (51-298.15°K.) heat capacities and high temperature (339.6-560.9°K.) heat content of $\text{FeCl}_3(\text{c})$ were determined by S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. **73**, 4184 (1951). The low temperature C_p and the derived high temperature C_p were plotted. The two C_p curves were joined smoothly at 298°K. The C_p values above 560.9°K. were obtained by graphical extrapolation. The value of $S_{298.15}^\circ$ was derived from the low temperature data reported by S. S. Todd and J. P. Coughlin, loc. cit., using $S_{51}^\circ = 6.29 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$. The value of $S_{298.15}^\circ$ was selected to make the second and third law values of ΔH_f° , derived from the equilibrium data reported by H. Schäfer and E. Oehler, loc. cit., in good agreement. The difference in S_{51}° between the selected value, 6.29, and the reported value, 4.50 cal. deg. $^{-1} \text{ mole}^{-1}$, by S. S. Todd and J. P. Coughlin, loc. cit., is assumed to be the magnetic entropy remaining at 51°K. which was unaccounted for in the report.

Melting Data.

T_m and ΔH_m° were obtained from S. S. Todd and J. P. Coughlin, loc. cit.

Heat of Sublimation.

The difference between $\Delta H_f^\circ 298.15$ for $\text{Fe}_2\text{O}_3(\text{g})$ and $2\text{FeCl}_3(\text{c})$ is the heat of sublimation at 298.15°K. The former is obtained by the second and third law analyses of related equilibrium data. See $\text{Fe}_2\text{O}_3(\text{g})$ table for details.

Iron Trichloride (FeCl₃)
(Liquid) Mol. Wt. = 162.206



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100						
200						
298	32.000	47.955	47.955	0.000	- 86.713	- 75.232
300	32.000	48.153	47.956	0.050	- 86.687	- 75.161
400	32.000	57.259	49.211	3.4250	- 85.358	- 71.522
500	32.000	64.299	54.221	6.4221	- 82.936	- 68.202
600	32.000	70.334	58.235	9.659	- 82.946	- 65.138
700	32.000	75.266	56.896	12.859	- 81.852	- 62.257
800	32.000	79.539	59.465	16.059	- 80.849	- 59.529
900	32.000	83.309	61.809	19.259	- 79.960	- 56.918
1000	32.000	86.600	64.221	22.459	- 79.258	- 54.399
1100	32.000	89.730	66.403	25.659	- 78.779	- 51.931
1200	32.000	92.514	68.465	28.859	- 78.092	- 49.526
1300	32.000	95.076	70.415	32.059	- 77.068	- 47.188
1400	32.000	97.447	72.252	35.259	- 76.063	- 44.926
1500	32.000	99.655	74.015	38.459	- 75.075	- 42.758

IRON TRICHLORIDE (FeCl₃)

(LIQUID)

MOL. WT. = 162.206

S_{298.15} = 47.955 cal. deg.⁻¹ mole⁻¹
 ΔH_f^o 298.15 = -86.713 kcal. mole⁻¹
 ΔH_m^o = 10.30 kcal. mole⁻¹
 ΔH_v^o (to dimer) = 10.46 kcal. mole⁻¹
 T_m = 577°K.
 T_b = 805°K.

Heat of Formation.

The value of ΔH_f^o 298.15 (FeCl₃, l) was obtained from ΔH_f^o 298.15 (FeCl₃, c) by adding ΔH_m^o and the difference between H_m^o - H_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeCl₃(l) was taken from S. S. Todd and J. P. Coughlin, J. Am. Chem. Soc. 73, 4184 (1951) and assumed as constant between 298.15° and 1500°K. The entropy (S_{298.15}) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH_m^o were reported by S. S. Todd and J. P. Coughlin, loc. cit.

Vaporization Data.

The boiling point (T_b) is determined as the temperature at which the free energy change (ΔG_p^o) of the reaction 2FeCl₃(l) = Fe₂Cl₆(g) approaches zero. The corresponding enthalpy change at T_b is the heat of vaporization (ΔH_v^o).



T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(H°-H° ₂₉₈)/T	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	13.511	64.204	97.744	3.345	60.487	60.487	INFINITE
200	17.298	75.058	84.910	3.345	60.487	60.487	131.425
298	18.572	82.243	82.243	∞.000	60.487	60.487	65.197
300	18.586	82.358	82.243	∞.034	60.487	60.487	43.150
400	19.117	87.787	82.980	1.923	60.487	60.487	32.134
500	19.379	92.084	84.166	3.849	60.487	60.487	25.524
600	19.526	95.432	85.073	5.705	60.487	60.487	21.114
700	19.616	98.049	87.752	7.562	60.487	60.487	17.957
800	19.675	101.272	90.126	9.417	60.487	60.487	15.563
900	19.716	103.592	92.067	11.687	60.487	60.487	13.727
1000	19.746	105.671	93.011	13.660	60.487	60.487	12.233
1100	19.767	107.554	93.840	15.346	62.580	65.348	10.906
1200	19.784	109.278	94.497	16.813	63.125	66.673	9.957
1300	19.797	110.859	95.000	18.102	63.322	67.649	9.071
1400	19.807	112.326	95.418	19.253	63.536	68.393	8.309
1500	19.816	113.693	95.761	20.304	63.767	68.947	7.647
1600	19.823	114.972	96.033	21.256	64.015	69.327	7.045
1700	19.828	116.174	96.267	22.116	64.272	69.549	6.499
1800	19.833	117.308	96.461	22.891	64.547	69.713	5.987
1900	19.837	118.380	96.618	23.581	64.831	69.811	5.499
2000	19.841	119.398	96.744	24.196	65.125	69.856	5.021
2100	19.844	120.366	96.844	24.737	65.429	69.941	4.559
2200	19.846	121.289	96.917	25.202	65.742	70.063	4.113
2300	19.848	122.171	96.965	25.592	66.063	70.213	3.681
2400	19.850	123.016	96.987	25.907	66.399	70.387	3.253
2500	19.852	123.827	97.000	26.147	66.750	70.583	2.839
2600	19.854	124.605	97.015	26.312	67.116	70.799	2.439
2700	19.856	125.355	97.031	26.402	67.496	71.033	2.053
2800	19.857	126.077	97.047	26.416	67.889	71.283	1.681
2900	19.857	126.773	97.062	26.354	68.294	71.546	1.323
3000	19.858	127.447	97.075	26.216	68.709	71.821	0.979
3100	19.859	128.098	97.087	26.002	69.134	72.106	0.650
3200	19.860	128.728	97.097	25.712	69.568	72.400	0.336
3300	19.861	129.330	97.106	25.347	70.011	72.702	0.036
3400	19.862	129.932	97.114	24.907	70.463	73.011	-0.259
3500	19.862	130.508	97.121	24.392	70.924	73.326	-0.556
3600	19.863	131.058	97.126	23.802	71.394	73.647	-0.863
3700	19.863	131.612	97.129	23.137	71.872	73.972	-1.179
3800	19.864	132.142	97.130	22.407	72.358	74.302	-1.504
3900	19.864	132.658	97.130	21.611	72.851	74.636	-1.838
4000	19.865	133.161	97.130	20.750	73.350	74.974	-2.180
4100	19.865	133.651	97.130	19.824	73.854	75.316	-2.529
4200	19.865	134.130	97.130	18.833	74.363	75.661	-2.883
4300	19.866	134.597	97.130	17.776	74.876	76.009	-3.241
4400	19.866	135.054	97.130	16.653	75.393	76.359	-3.602
4500	19.866	135.500	97.130	15.465	75.914	76.711	-3.966
4600	19.867	135.937	97.130	14.211	76.439	77.064	-4.333
4700	19.867	136.364	97.130	12.892	76.967	77.418	-4.702
4800	19.867	136.782	97.130	11.508	77.498	77.772	-5.072
4900	19.867	137.192	97.130	10.059	78.031	78.126	-5.443
5000	19.867	137.594	97.130	8.544	78.565	78.480	-5.814
5100	19.868	137.987	97.130	6.964	79.100	78.833	-6.185
5200	19.868	138.373	97.130	5.319	79.635	79.185	-6.556
5300	19.868	138.751	97.130	3.618	80.170	79.536	-6.927
5400	19.868	139.123	97.130	1.861	80.704	79.886	-7.297
5500	19.868	139.487	97.130	0.048	81.237	80.235	-7.667
5600	19.869	139.845	97.130	-1.716	81.769	80.583	-8.036
5700	19.869	140.197	97.130	-3.469	82.300	80.929	-8.405
5800	19.869	140.542	97.130	-5.216	82.829	81.272	-8.774
5900	19.869	140.882	97.130	-6.957	83.356	81.614	-9.142
6000	19.869	141.216	97.130	-8.692	83.881	81.950	-9.509

June 30, 1965

IRON TRICHLORIDE (FeCl₃)

(IDEAL GAS)

MOL. WT. = 162.206

Point Group [D_{3h}]ΔH_f⁰ = -80.5 ± 1.2 kcal. mole⁻¹S_{298.15} = [82.243] cal. deg⁻¹ mole⁻¹ΔH_f⁰ 298.15 = -80.5 ± 1.2 kcal. mole⁻¹

Ground State Quantum Weight = [6]

Vibrational Frequencies and Degeneracies

 ω , cm⁻¹
 [350] (1)
 [180] (1)
 [310] (2)
 [130] (2)

Bond Distance: Fe-Cl = [2.17] Å

Bond Angle: Cl-Fe-Cl = [120]°

Product of the Moments of Inertia: I_AI_BI_C = [1.43769 × 10⁻¹¹²] g.³ cm.⁶σ⁻ = [6]

Heat of Formation.

The equilibrium pressures for the reaction Fe₂O₃(g) = 2FeCl₃(g) were determined by Kangro and Bernstorff¹ and Schüfer², respectively. Using their vapor pressure data the corresponding values of ΔH_f⁰ 298.15 for that reaction were evaluated by both the second and third law methods. Based on the third law values for ΔH_f⁰ 298.15, the heats of formation (ΔH_f⁰ 298.15) for FeCl₃(g) were derived. The results obtained are presented as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	ΔH _f ⁰ 298.15, kcal. mole ⁻¹
Kangro and Bernstorff ¹	760.2-1044.2	34.99 ± 0.44	35.75	-60.34 ± 0.30
Schüfer ²	675.2-1073.2	34.81 ± 0.02	34.93	-60.74 ± 0.20

¹ W. Kangro and H. Bernstorff, Z. anorg. allgem. Chem. **283**, 316 (1950).

² H. Schüfer, Z. anorg. allgem. Chem. **259**, 53 (1949).

 The adopted value of ΔH_f⁰ 298.15(FeCl₃ g) is -80.5 ± 1.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that of AlCl₃(g) due to the similarities in structure between Fe₂O₃(g) and Al₂O₃(g). The Fe-Cl bond distance was estimated by comparison with those for Fe₂Cl₆(g) reported by E. Z. Zasorin, N. O. Rambidi and P. A. Akishin, Zh. Strukt. Khim., **4**, 910 (1963) and O. Hassel and H. Viervoll, Acta Chem. Scand., **1**, 149 (1947). Both the ground state quantum weight and vibrational frequencies were estimated so that the second and third law values of ΔH_f⁰ 298.15, derived from the vapor pressure data, for the reaction Fe₂O₃(g) = 2FeCl₃(g) are in reasonable agreement. The three principal moments of inertia are: I_AI_BI_C = 4.15794 × 10⁻³⁸ and I_C = 8.31588 × 10⁻³⁸ g. cm.²

Cl₃Fe

Trichlorosilane (HSiCl₃)

(Ideal Gas) Mol. Wt. = 135.469

INTERIM TABLE

T, °K.	C _p ^o	S ^o - (R° - H ₃₀₀ °)/T	H ^o - H ₃₀₀ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	11.000	191.000	3.859	-110.800	-110.800	191.000
100	11.149	92.274	2.958	-110.800	-109.230	21.711
200	15.113	64.274	1.636	-111.730	-106.936	116.848
298	16.041	74.892	1.000	-112.000	-104.524	76.614
300	16.084	75.084	0.933	-112.005	-104.477	76.108
400	17.990	100.961	0.033	-112.005	-104.477	133.333
500	21.234	127.073	4.011	-112.306	-99.359	33.028
600	22.099	127.073	6.180	-112.363	-96.763	35.244
700	22.737	127.073	8.423	-112.360	-94.162	39.397
800	23.163	127.073	10.810	-112.363	-91.560	43.512
900	23.420	127.073	13.243	-112.363	-88.958	47.582
1000	23.634	127.073	15.714	-112.363	-86.357	51.615
1100	23.800	127.073	18.221	-112.360	-83.751	55.615
1200	23.924	127.073	20.761	-112.360	-81.145	59.580
1300	24.000	127.073	23.331	-112.360	-78.539	63.512
1400	24.034	127.073	25.931	-112.360	-75.933	67.412
1500	24.034	127.073	28.561	-112.360	-73.327	71.280
1600	24.000	127.073	31.221	-112.360	-70.721	75.112
1700	23.934	127.073	33.911	-112.360	-68.115	78.912
1800	23.834	127.073	36.631	-112.360	-65.509	82.680
1900	23.694	127.073	39.381	-112.360	-62.903	86.412
2000	23.514	127.073	42.161	-112.360	-60.297	90.112
2100	23.294	127.073	44.971	-112.360	-57.691	93.780
2200	23.034	127.073	47.811	-112.360	-55.085	97.412
2300	22.734	127.073	50.681	-112.360	-52.479	100.912
2400	22.394	127.073	53.581	-112.360	-49.873	104.380
2500	22.014	127.073	56.511	-112.360	-47.267	107.812
2600	21.594	127.073	59.471	-112.360	-44.661	111.212
2700	21.134	127.073	62.461	-112.360	-42.055	114.580
2800	20.634	127.073	65.481	-112.360	-39.449	117.912
2900	20.094	127.073	68.531	-112.360	-36.843	121.212
3000	19.514	127.073	71.611	-112.360	-34.237	124.480
3100	18.894	127.073	74.721	-112.360	-31.631	127.712
3200	18.234	127.073	77.861	-112.360	-29.025	130.912
3300	17.534	127.073	81.031	-112.360	-26.419	134.080
3400	16.794	127.073	84.231	-112.360	-23.813	137.212
3500	16.014	127.073	87.461	-112.360	-21.207	140.312
3600	15.194	127.073	90.721	-112.360	-18.601	143.380
3700	14.334	127.073	94.011	-112.360	-16.000	146.412
3800	13.434	127.073	97.331	-112.360	-13.394	149.412
3900	12.494	127.073	100.681	-112.360	-10.788	152.380
4000	11.514	127.073	104.061	-112.360	-8.182	155.312
4100	10.494	127.073	107.471	-112.360	-5.576	158.212
4200	9.434	127.073	110.911	-112.360	-2.970	161.080
4300	8.334	127.073	114.381	-112.360	-0.364	163.912
4400	7.194	127.073	117.881	-112.360	2.242	166.712
4500	6.014	127.073	121.411	-112.360	4.848	169.480
4600	4.794	127.073	124.961	-112.360	7.454	172.212
4700	3.534	127.073	128.531	-112.360	10.060	174.912
4800	2.234	127.073	132.121	-112.360	12.666	177.580
4900	0.894	127.073	135.731	-112.360	15.272	180.212
5000	-0.484	127.073	139.361	-112.360	17.878	182.812
5100	-1.804	127.073	143.011	-112.360	20.484	185.380
5200	-3.084	127.073	146.681	-112.360	23.090	187.912
5300	-4.324	127.073	150.371	-112.360	25.696	190.412
5400	-5.524	127.073	154.081	-112.360	28.302	192.880
5500	-6.684	127.073	157.811	-112.360	30.908	195.312
5600	-7.804	127.073	161.561	-112.360	33.514	197.712
5700	-8.884	127.073	165.331	-112.360	36.120	200.080
5800	-9.924	127.073	169.121	-112.360	38.726	202.412
5900	-10.924	127.073	172.931	-112.360	41.332	204.712
6000	-11.884	127.073	176.761	-112.360	43.938	207.012

December 31, 1960.

Cl₃HSi

Trichlorosilane (HSiCl₃)

(Ideal Gas)

Mol. Wt. = 135.469

ΔH_f^o 298.15 = -119.6 kcal. mole⁻¹

S_{298.15} = 74.924 cal. deg.⁻¹ mole⁻¹

Point Group C_{3v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

, cm.⁻¹

2274 (1) 810 (2)

497 (1) 600 (2)

250 (1) 179 (2)

Si-H dist. = 1.48 all angles = [109° 28']

Si-Cl dist. = 2.02 = 3

Product of Moments of Inertia: I_AI_BI_C = 75.642 X 10⁻¹¹ g.³ cm.⁶

Heat of Formation. ΔH_f^o 298.15 was calculated from heats of reaction reported by E. Wolf, Z. Anorg. u. Allgem. Chem. 313, 228 (1961) for the equation

SiHCl₃(g) + 5NaOH(c) = Na₂SiO₃(c) + 3NaCl(c) + 2H₂O(l)

Heat Capacity and Entropy. Molecular constants were found in Janz and Mikawa, Bull. Chem. Soc. Japan 34, 1495 (1961). Vibrational frequencies can also be found in Henderson and Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data," January, 1960.

Cl₃HSi

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	g°	(H°-H ₂₉₈)/T	cal. mole ⁻¹	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-	4.872	-	238.400	-	INFINITE	
100	13.939	59.759	98.842	3.910	-	237.515	-	237.515	
200	20.151	71.324	82.331	2.201	-	235.539	-	257.780	
298	24.380	80.223	80.223	0.000	-	240.134	-	234.000	
300	24.441	80.374	80.223	0.045	-	240.144	-	233.953	
400	26.595	87.916	81.279	2.668	-	240.653	-	229.421	
500	28.462	93.979	81.107	5.406	-	243.423	-	224.321	
600	29.376	99.255	85.420	8.301	-	243.972	-	226.446	
700	29.969	103.831	87.731	11.270	-	244.420	-	223.491	
800	30.372	107.861	90.000	15.289	-	244.807	-	220.476	
900	30.653	111.453	92.248	19.348	-	245.136	-	217.412	
1000	30.855	114.697	94.279	23.418	-	245.497	-	214.311	
1100	31.021	117.646	96.272	27.512	-	245.812	-	211.177	
1200	31.142	120.321	98.167	31.621	-	246.117	-	208.017	
1300	31.232	122.848	100.000	35.750	-	246.409	-	204.830	
1400	31.297	125.238	101.773	39.902	-	246.666	-	201.619	
1500	31.333	127.498	103.527	44.141	-	246.891	-	198.391	
1600	31.424	129.354	104.891	48.466	-	247.232	-	195.142	
1700	31.466	131.260	106.386	52.886	-	247.632	-	191.894	
1800	31.501	133.060	107.859	57.341	-	248.091	-	188.639	
1900	31.526	134.792	109.312	61.740	-	248.610	-	185.379	
2000	31.556	136.382	110.512	66.142	-	249.197	-	182.104	
2100	31.578	137.922	111.781	70.543	-	249.854	-	178.814	
2200	31.598	139.362	113.003	74.945	-	250.581	-	175.509	
2300	31.614	140.797	114.181	79.348	-	251.379	-	172.189	
2400	31.622	142.134	115.317	83.752	-	252.248	-	168.854	
2500	31.624	143.434	116.417	88.157	-	253.189	-	165.504	
2600	31.624	144.675	117.480	92.562	-	254.202	-	162.139	
2700	31.624	145.870	118.510	96.967	-	255.288	-	158.759	
2800	31.622	147.022	119.507	101.372	-	256.448	-	155.364	
2900	31.618	148.134	120.464	105.777	-	257.683	-	151.954	
3000	31.609	149.207	121.415	110.182	-	259.004	-	148.529	
3100	31.606	150.247	122.349	114.587	-	260.411	-	145.089	
3200	31.702	151.253	123.217	118.992	-	261.904	-	141.634	
3300	31.708	152.229	124.081	123.397	-	263.483	-	138.164	
3400	31.713	153.174	124.914	127.802	-	265.148	-	134.679	
3500	31.717	154.093	125.744	132.207	-	266.900	-	131.179	
3600	31.722	154.988	126.540	136.612	-	268.739	-	127.664	
3700	31.726	155.857	127.324	141.017	-	270.666	-	124.134	
3800	31.729	156.694	128.086	145.422	-	272.683	-	120.589	
3900	31.731	157.504	128.824	149.827	-	274.791	-	117.029	
4000	31.736	158.331	129.558	154.232	-	276.990	-	113.454	
4100	31.739	159.115	130.270	158.637	-	279.281	-	109.864	
4200	31.741	159.880	130.965	163.042	-	281.664	-	106.259	
4300	31.744	160.627	131.647	167.447	-	284.141	-	102.639	
4400	31.746	161.354	132.314	171.852	-	286.714	-	99.004	
4500	31.748	162.070	132.967	176.257	-	289.384	-	95.354	
4600	31.751	162.768	133.607	180.662	-	292.151	-	91.689	
4700	31.752	163.451	134.235	185.067	-	295.016	-	88.009	
4800	31.754	164.119	134.851	189.472	-	297.981	-	84.314	
4900	31.756	164.774	135.454	193.877	-	301.046	-	80.604	
5000	31.758	165.415	136.047	198.282	-	304.211	-	76.879	
5100	31.759	166.044	136.629	202.687	-	307.476	-	73.139	
5200	31.760	166.661	137.201	207.092	-	310.841	-	69.389	
5300	31.761	167.266	137.763	211.497	-	314.306	-	65.629	
5400	31.763	167.854	138.314	215.902	-	317.871	-	61.859	
5500	31.764	168.433	138.857	220.307	-	321.536	-	58.079	
5600	31.765	169.015	139.390	224.712	-	325.301	-	54.279	
5700	31.767	169.577	139.915	229.117	-	329.166	-	50.459	
5800	31.768	170.139	140.439	233.522	-	333.131	-	46.619	
5900	31.769	170.691	140.954	237.927	-	337.196	-	42.759	
6000	31.769	171.207	141.459	242.332	-	341.361	-	38.879	

June 30, 1962

Lithium Chloride, Trimeric (LiCl)₃ (Ideal Gas)

Mol. Wt. = 127.19
ΔH_f^o 298.15 = -240.134 + 5 kcal. mole⁻¹
S_{298.15}^o = 80.223 cal. deg.⁻¹ mole⁻¹
Point Group = D_{3h}

Vibrational Levels and Multiplicities
 ω_e , cm.⁻¹
 $\left[\begin{smallmatrix} 650 \\ 550 \end{smallmatrix} \right] \left\{ \begin{smallmatrix} 8 \\ 6 \end{smallmatrix} \right\}$

Bond distances and angles Li-Cl distance = [2.2] Å
LiClLi angle [120°]
Plane cyclic structure σ = 8

Moment of Inertia I_AI_BI_C = 2.675 × 10⁻¹¹² g.³ cm.⁶

Heat of Formation. The heat of sublimation at 298° was chosen so as to give the correct ratio of monomer, dimer and trimer at 870°K. The value used was 52.6 kcal. mole⁻¹, which compares very well with the value 53.6 kcal. mole⁻¹ obtained from a third law analysis of the data of An. N. Nemesyov and L. A. Sazonov, Zhur. Neorg. Khim. 4, 231 (1960) in conjunction with the relative concentrations of monomer, dimer, and trimer at 870°K from the work of R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1950).

Heat Capacity and Entropy. The postulated structure, bond lengths and frequencies were all taken from D. L. Hildenbrand, A. M. Saul P. R. Basford, S. E. Stephenson, L. Larson and A. Uyehara, Aero-nutronics Renth Quarterly Report on Contract NORD 17960 Report C-898 (1960).

Phosphoryl Chloride (POCl_3)
(Ideal Gas) Mol. Wt. = 153.346

T, °K.	C_p°	$\text{cal. mole}^{-1}\text{deg.}^{-1}$	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	$\log K_p$
0	0	0	0	0	0	0	0
100	11.934	60.000	1.973	128.714	128.714	128.714	INFINITE
200	17.410	70.215	3.362	129.302	129.302	129.302	276.026
298	20.296	77.767	4.666	129.545	129.545	129.545	134.613
300	20.335	77.893	4.700	129.631	129.631	129.631	87.998
400	22.979	83.984	6.038	129.831	129.831	129.831	87.412
500	24.007	89.011	7.260	129.842	129.842	129.842	63.803
600	24.650	93.270	8.250	129.850	129.850	129.850	49.638
700	24.913	96.960	9.104	129.850	129.850	129.850	40.199
800	25.028	100.110	9.759	129.850	129.850	129.850	33.459
900	25.079	102.728	10.261	129.850	129.850	129.850	28.313
1000	25.095	105.728	10.626	129.850	129.850	129.850	25.313
1100	25.079	108.111	10.841	129.850	129.850	129.850	21.684
1200	25.151	110.298	10.941	129.850	129.850	129.850	18.721
1300	25.228	112.336	10.967	129.850	129.850	129.850	16.256
1400	25.283	114.255	10.915	129.850	129.850	129.850	14.175
1500	25.412	115.946	10.781	129.850	129.850	129.850	12.415
1600	25.441	117.587	10.587	129.850	129.850	129.850	10.855
1700	25.507	119.132	10.346	129.850	129.850	129.850	9.510
1800	25.579	120.597	10.066	129.850	129.850	129.850	8.326
1900	25.627	121.973	9.751	129.850	129.850	129.850	7.256
2000	25.592	123.285	9.402	129.850	129.850	129.850	6.305
2100	25.614	124.534	9.036	129.850	129.850	129.850	5.495
2200	25.633	125.726	8.664	129.850	129.850	129.850	4.735
2300	25.649	126.867	8.286	129.850	129.850	129.850	4.044
2400	25.665	127.958	7.901	129.850	129.850	129.850	3.415
2500	25.678	129.006	7.511	129.850	129.850	129.850	2.831
2600	25.689	130.013	7.117	129.850	129.850	129.850	2.294
2700	25.697	130.971	6.716	129.850	129.850	129.850	1.824
2800	25.709	131.890	6.316	129.850	129.850	129.850	1.374
2900	25.717	132.780	5.916	129.850	129.850	129.850	0.945
3000	25.725	133.642	5.516	129.850	129.850	129.850	0.529
3100	25.732	134.475	5.116	129.850	129.850	129.850	0.130
3200	25.738	135.282	4.716	129.850	129.850	129.850	0.455
3300	25.743	136.061	4.316	129.850	129.850	129.850	0.826
3400	25.749	136.813	3.916	129.850	129.850	129.850	1.202
3500	25.754	137.660	3.516	129.850	129.850	129.850	1.529
3600	25.758	138.365	3.116	129.850	129.850	129.850	1.763
3700	25.762	139.071	2.716	129.850	129.850	129.850	1.984
3800	25.769	140.407	2.316	129.850	129.850	129.850	2.192
3900	25.774	141.610	1.916	129.850	129.850	129.850	2.392
4000	25.773	141.771	1.771	129.850	129.850	129.850	2.476
4100	25.776	141.736	1.636	129.850	129.850	129.850	2.580
4200	25.776	142.357	1.502	129.850	129.850	129.850	2.760
4300	25.776	142.978	1.368	129.850	129.850	129.850	2.931
4400	25.775	143.599	1.234	129.850	129.850	129.850	3.094
4500	25.775	144.136	1.100	129.850	129.850	129.850	3.249
4600	25.776	144.703	1.054	129.850	129.850	129.850	3.398
4700	25.776	145.258	1.008	129.850	129.850	129.850	3.540
4800	25.776	145.803	0.962	129.850	129.850	129.850	3.676
4900	25.773	146.332	0.916	129.850	129.850	129.850	3.807
5000	25.775	146.853	0.870	129.850	129.850	129.850	3.932
5100	25.776	147.364	0.824	129.850	129.850	129.850	4.052
5200	25.776	147.865	0.778	129.850	129.850	129.850	4.167
5300	25.776	148.366	0.732	129.850	129.850	129.850	4.276
5400	25.776	148.867	0.686	129.850	129.850	129.850	4.381
5500	25.802	149.312	0.640	129.850	129.850	129.850	4.487
5600	25.803	149.777	0.594	129.850	129.850	129.850	4.586
5700	25.804	150.234	0.548	129.850	129.850	129.850	4.681
5800	25.806	150.686	0.502	129.850	129.850	129.850	4.773
5900	25.806	151.124	0.456	129.850	129.850	129.850	4.861
6000	25.807	151.558	0.410	129.850	129.850	129.850	4.947

June 30, 1962



MOL. WT. = 153.346

(IDEAL GAS)

PHOSPHORYL CHLORIDE (POCl_3)

$\Delta H_f^\circ 298.15 = -129.7 \pm 0.4 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = 77.77 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ 0 = -129.7 \pm 0.4 \text{ kcal. mole}^{-1}$
 Point Group C_{3v}

Vibrational Levels and Multiplicities		
ω , cm.^{-1}	ω , cm.^{-1}	ω , cm.^{-1}
1290 (1)	486 (1)	337 (1)
581 (2)	267 (2)	193 (2)

P-O distance = $1.99 \pm 0.02 \text{ \AA}$
 $I_A = 422.3 \times 10^{-40} \text{ g. cm.}^2$
 $I_B = 412.2 \times 10^{-40} \text{ g. cm.}^2$
 $I_C = 576.7 \times 10^{-40} \text{ g. cm.}^2$
 $\sigma = 3$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ for $\text{POCl}_3(\text{g})$ was derived from the $\Delta H_f^\circ 298.15$ of $\text{POCl}_3(\text{l})$ and the $\Delta H_v^\circ 298.15$ of the $\text{POCl}_3(\text{l})$ was calculated from the heat of hydrolysis observed by T. Charnley and H. A. Skinner, J. Chem. Soc., 450, (1953) for the reaction:



The auxiliary thermochemical data, on the heats of formation of water and aqueous solutions of HCl and of H_3PO_4 , were taken from the National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Circular 500, and were adjusted for consistency with JANAF tables. The heat of vaporization was measured and corrected to 298.15°K by J. B. Ott and W. P. Glaueque, J. Am. Chem. Soc., 82, 1308 (1960). A correction was made for the change in phosphorus reference state [white (α) \rightarrow red (γ)].

Heat Capacity and Entropy.

The molecular constants are from the microwave spectral data of Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys., 20, 164 (1952). In order to determine the structure Williams et al. (loc. cit.) assumed the P-Cl distance equal to 1.99 \AA . This was the smallest value allowed ($2.02 \pm 0.03 \text{ \AA}$) by the electron diffraction work of L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc., 60, 1836 (1938).

Ott and Glaueque (loc. cit.) have given the moments of inertia obtained from a weighted average of the isotopic species. I_A , I_B due to isotopic loss of symmetry. The $S_{298.15}^\circ$ calculated from calorimetric data by Ott and Glaueque (loc. cit.) was $77.75 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ and the $S_{298.15}^\circ$ calculated from the spectral data was $77.77 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.



Point Group C_{3v}
S_{298.15} = 74.47 ± 0.10 gibbs/mol
Ground State Quantum Weight = 1
ΔH_f⁰ = -84.5 ± 1.3 kcal/mol
ΔH_f^{298.15} = -64.8 ± 1.3 kcal/mol

Phosphorus Trichloride (PCl₃)
(Ideal Gas) GFW = 137.3328

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	ΔH ^o	kcal/mol	ΔG ^o	Log Kp
0	1.000	INFINITE	INFINITE	2.608	-84.455	-	-84.455	INFINITE
100	11.106	59.007	66.146	-2.914	-84.696	-	-83.675	1.39,161
200	13.065	68.027	75.976	-1.590	-84.779	-	-82.614	48.421
298	17.108	74.467	84.667	-1.000	-84.800	-	-81.545	48.114
300	17.135	74.673	84.667	-1.032	-84.800	-	-81.525	48.821
400	16.173	79.461	75.154	1.403	-84.807	-	-80.432	33.019
500	16.731	83.782	76.480	3.651	-84.809	-	-79.338	25.936
600	19.057	87.226	77.992	5.541	-84.823	-	-78.243	21.215
700	19.263	90.162	79.326	6.458	-84.856	-	-77.144	17.694
800	19.497	92.055	80.858	7.227	-84.915	-	-76.045	14.619
900	19.566	97.113	83.823	11.337	-85.161	-	-74.946	12.106
1000	19.618	99.980	85.117	15.250	-84.814	-	-73.847	10.420
1100	19.656	100.689	86.345	17.214	-84.843	-	-72.748	9.017
1200	19.674	101.074	86.616	18.616	-84.856	-	-71.649	7.819
1300	19.714	101.724	86.616	21.151	-84.304	-	-70.550	6.819
1400	19.734	105.085	89.659	23.124	-84.136	-	-69.451	5.942
1500	19.751	106.359	90.673	25.098	-83.971	-	-68.352	5.177
1600	19.764	107.557	91.631	26.074	-83.807	-	-67.253	4.502
1700	19.776	108.689	92.539	27.049	-83.643	-	-66.154	3.917
1800	19.786	109.756	93.425	28.025	-83.481	-	-65.055	3.417
1900	19.794	110.771	94.266	31.008	-83.327	-	-63.956	2.991
2000	19.801	111.737	95.077	34.968	-83.169	-	-62.857	2.658
2100	19.807	112.659	95.855	38.968	-83.017	-	-61.758	2.385
2200	19.811	113.539	96.597	42.968	-82.869	-	-60.659	2.159
2300	19.814	114.383	97.328	46.931	-82.717	-	-59.560	1.979
2400	19.818	115.192	98.027	42.913	-82.572	-	-58.461	1.837
2500	19.822	115.969	98.702	44.895	-82.431	-	-57.362	1.726
2600	19.826	116.718	99.355	46.878	-82.293	-	-56.263	1.635
2700	19.829	117.436	100.000	48.861	-82.158	-	-55.164	1.554
2800	19.831	118.125	100.642	50.844	-82.028	-	-54.065	1.481
2900	19.833	118.800	101.292	52.826	-81.903	-	-52.966	1.418
3000	19.837	119.460	101.958	54.809	-81.782	-	-51.867	1.363
3100	19.839	119.458	101.776	56.811	-81.666	-	-50.768	1.315
3200	19.841	120.058	102.339	58.795	-81.555	-	-49.669	1.273
3300	19.843	120.591	102.819	60.764	-81.445	-	-48.570	1.236
3400	19.845	121.061	103.219	62.749	-81.342	-	-47.471	1.202
3500	19.846	121.466	103.548	64.733	-81.243	-	-46.372	1.171
3600	19.848	122.825	104.443	66.718	-81.146	-	-45.273	1.141
3700	19.849	122.869	104.937	68.702	-81.054	-	-44.174	1.111
3800	19.850	123.014	105.380	70.686	-80.969	-	-43.075	1.081
3900	19.851	124.014	105.880	72.673	-80.887	-	-41.976	1.051
4000	19.852	124.516	106.348	74.659	-80.806	-	-40.877	1.021
4100	19.853	125.007	106.797	76.644	-80.731	-	-39.778	0.991
4200	19.854	125.485	107.236	78.628	-80.656	-	-38.679	0.961
4300	19.855	125.954	107.664	80.615	-80.586	-	-37.580	0.931
4400	19.856	126.409	108.087	82.600	-80.519	-	-36.481	0.901
4500	19.856	126.855	108.499	84.586	-80.451	-	-35.382	0.871
4600	19.857	127.291	108.903	86.572	-80.387	-	-34.283	0.841
4700	19.858	127.718	109.299	88.558	-80.325	-	-33.184	0.811
4800	19.859	128.136	109.688	90.543	-80.264	-	-32.085	0.781
4900	19.859	128.546	110.068	92.529	-80.203	-	-30.986	0.751
5000	19.859	128.947	110.441	94.515	-80.144	-	-29.887	0.721
5100	19.860	129.340	110.808	96.501	-80.085	-	-28.788	0.691
5200	19.860	129.726	111.169	98.486	-80.026	-	-27.689	0.661
5300	19.861	130.107	111.526	100.471	-79.972	-	-26.590	0.631
5400	19.861	130.475	111.869	102.456	-79.915	-	-25.491	0.601
5500	19.861	130.840	112.211	104.440	-79.859	-	-24.392	0.571
5600	19.862	131.198	112.547	106.426	-79.803	-	-23.293	0.541
5700	19.862	131.550	112.876	108.411	-79.748	-	-22.194	0.511
5800	19.862	131.895	113.200	110.396	-79.693	-	-21.095	0.481
5900	19.863	132.234	113.522	112.381	-79.642	-	-20.000	0.451
6000	19.863	132.568	113.836	114.366	-79.592	-	-18.901	0.421

Dec. 31, 1960, Sept. 30, 1962, June 30, 1970

Neale and Williams (1) measured the heat of hydrolysis of liquid phosphorus trichloride and reported a ΔH_p = -87.5 ± 0.3 kcal/mol for the following reaction:
PCl₃(l) + (X₂ + 3) H₂O + H₃PO₃(aq) + 3 HCl(aq)
with X₂ in range 4500 to 7500. Combining this result with heat of formation data for aqueous H₃PO₃, -229.4 kcal/mol (2, 5, 16), H₂O (2), and aqueous HCl (2) we derive ΔH_f⁰(PCl₃, l) = -76.7 kcal/mol. Chamley and Skinner (3) made an independent investigation of the hydrolysis of liquid phosphorus trichloride and obtained enthalpy data in very good agreement with Neale and Williams' results. Their results lead to ΔH_f⁰(PCl₃, l) = -76.5 kcal/mol when combined with heat of formation data (2, 5, 16).
Neale and Williams (4) also investigated the hydrolysis of liquid phosphorus trichloride in aqueous bromine solution with the formation of phosphoric acid rather than phosphorous acid which results when hydrolysis occurs in water. They reported a ΔH_p = -137.9 kcal/mol for the following reaction:
PCl₃(l) + Br₂(aq) + (X₂ + 4) H₂O + H₃PO₄(aq) + 3 HBr(aq) + 2 HBr(aq)
with X₂ in range 3500 to 8300. Combining this result with the following heat of formation data:
ΔH_f⁰(H₃PO₄·1/2 H₂O) = -308.4 ± 0.5 kcal/mol (5)
ΔH_f⁰(Br₂(aq)) = -0.2 kcal/mol (6)
HCl(aq) and HBr(aq) (2)
along with dilution data for H₃PO₄(aq) (2), we derive ΔH_f⁰(PCl₃, l) = -77.0 kcal/mol.

The heat of formation from white phosphorus of gaseous PCl₃, ΔH_f⁰(PCl₃, g) = -89.0 ± 1.1 kcal/mol, is calculated from the heat of formation of the liquid, ΔH_f⁰(PCl₃, l) = -76.7 ± 1.0 kcal/mol, an average value of the three results given above, and the heat of vaporization of PCl₃. The heat of vaporization of the liquid, ΔH_v⁰ = 7.7 ± 0.1 kcal/mol, is determined from a second law analysis of the combined vapor pressure data of Misel von and Saryakov (7) and Regnault (8). The smoothed vapor pressure data of Regnault as reported by Stull (9) were used. Converting to the P_{red}, V standard state with a ΔH_{trans} = 4.2 ± 0.2 kcal/mol (10), we derive ΔH_f⁰(PCl₃, g) = -84.8 ± 1.3 kcal/mol.
An independent value for the heat of formation can be obtained from the work of Duss and Mykytiuk (12) on the reaction
1.5CaF₂ + PCl₃(g) + 1.5CaCl₂ + PF₃(g). The authors report ΔH₃₀ = -2.97 kcal. From a reexamination of their technique we believe that this heat evolution is likely to be too small, perhaps by 100%. The analytical results indicate that the reaction is 99% complete or better; thus, we can use this with JANAF entropies to calculate ΔH₂₉₈⁰ = -3.55 kcal. Finch et al. (13) have reported ΔH_f⁰(CaF₂, o) - ΔH_f⁰(CaCl₂, c) = -100.87 ± 0.02 kcal/mol; thus, we obtain ΔH_f⁰(PCl₃, g) = -70.1 ± 2.0 kcal/mol from ΔH₂₉₈⁰(PF₃, g) = -224.9 ± 0.9 kcal/mol. This value is not adopted because of the lack of calorimeter calibration, but it offers an attractive possibility for further study.

Heat Capacity and Entropy
The molecular structure and bond length given above for PCl₃ are from the electron diffraction studies of Hedberg and Iwamide (11). The adopted values are in good agreement within experimental error with the following structural data reported by Klatuk and Townes (12) from microwave studies: P-Cl = 2.043 ± 0.003 Å, the angle Cl-P-Cl = 100° ± 20'. The vibrational frequencies are from the recent infrared and Raman studies of Frankiss and Miller (13) and are in excellent agreement with those of Miller et al. (14) and Davis and Oetjen (15). Individual moments of inertia calculated from the electron diffraction data are: I_A = I_B = 32.393 × 10⁻³⁹ g cm², and I_C = 57.673 × 10⁻³⁹ g cm².

References
1. E. Neale and L. T. D. Williams, *J. Chem. Soc.*, **1952**, 4535.
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. T. Chamley and H. A. Skinner, *J. Chem. Soc.*, **1953**, 450.
4. E. Neale and L. T. D. Williams, *J. Chem. Soc.*, **1954**, 2156.
5. C. H. Wu, H. M. Sipsky, and L. G. T. Faraday Soc., **53**, 252 (1957).
6. L. A. Niselson and G. V. Saryakov, *Russ. J. Inorg. Chem. (English Transl.)*, **5**, 548 (1960).
7. H. V. Regnault, *Mém. Paris*, **25**, 339 (1862).
8. D. Stull, *Ind. Eng. Chem.*, **39**, 617 (1947).
9. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., June 30, 1961.
10. E. Neale and L. T. D. Williams, *J. Chem. Soc.*, **1952**, 4535.
11. P. Klatuk and C. Townes, *J. Chem. Phys.*, **35**, 589 (1962).
12. S. G. Frankiss and F. A. Miller, *Spectrochim. Acta*, **21**, 235 (1965).
13. A. Miller, E. Niecke, B. Krebs, and O. Glomser, *Z. Naturforsch.*, **23b**, 588 (1968).
14. P. W. Davis and R. A. Oetjen, *J. Mol. Spectroscopy*, **2**, 253 (1958).
15. A. Finch, P. J. Gardner, K. S. Hussain and K. K. Sen Gupta, *Chem. Commun.*, **872** (1968).
16. H. C. Duss and D. P. Mykytiuk, *J. Chem. Eng. Data*, **9**, 585 (1964).
17. A. Finch, P. J. Gardner and C. J. Steadman, *Can. J. Chem.*, **46**, 3447 (1968).

Thiophosphoryl Chloride (PCl₃)
(Ideal Gas) Mol. Wt. = 169.412

INTERIM TABLE

T. °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
100	12.000	INFINITE	0.000	0.000	0.000	86.135	86.135	INFINITE
200	12.573	61.566	61.566	1.980	86.673	86.295	86.295	92.109
300	21.474	80.604	80.604	0.000	86.800	83.100	83.100	60.911
400	21.513	80.737	80.608	0.040	86.802	83.076	83.076	60.516
500	23.034	82.412	83.149	4.631	87.876	80.335	80.335	35.113
600	24.469	96.827	95.071	7.054	88.215	78.794	78.794	26.699
700	24.807	100.626	97.028	9.519	88.500	77.178	77.178	24.095
800	25.036	103.955	98.940	12.012	88.744	75.522	75.522	22.434
900	25.194	106.716	100.716	14.524	88.941	73.727	73.727	18.727
1000	25.313	109.574	102.575	17.050	89.100	72.161	72.161	15.770
1100	25.401	111.991	94.196	19.585	89.230	70.357	70.357	13.357
1200	25.469	114.205	97.764	22.129	89.325	68.325	68.325	11.350
1300	25.522	116.245	97.262	24.679	89.375	66.075	66.075	9.657
1400	25.568	118.138	96.686	27.233	89.409	63.586	63.586	8.209
1500	25.606	119.993	100.082	29.781	89.424	60.958	60.958	6.958
1600	25.627	121.556	101.336	32.353	89.496	58.145	58.145	5.865
1700	25.650	123.111	102.571	34.916	89.496	55.145	55.145	4.904
1800	25.670	124.577	103.754	37.482	89.496	52.075	52.075	4.052
1900	25.686	125.964	104.874	40.050	89.496	48.942	48.942	3.290
2000	25.701	127.284	105.974	42.620	89.496	45.756	45.756	2.608
2100	25.713	128.538	107.019	45.190	89.496	42.522	42.522	1.992
2200	25.724	129.734	108.024	47.762	89.496	39.242	39.242	1.433
2300	25.733	130.878	108.993	50.335	89.496	35.915	35.915	0.923
2400	25.740	131.978	109.928	52.908	89.496	32.542	32.542	0.458
2500	25.749	133.024	110.831	55.483	89.496	29.118	29.118	0.031
2600	25.755	134.034	111.704	58.058	89.496	25.645	25.645	0.363
2700	25.761	135.006	112.559	60.634	89.496	22.118	22.118	0.726
2800	25.766	135.943	113.398	63.211	89.496	18.542	18.542	1.063
2900	25.770	136.843	114.218	65.786	89.496	14.915	14.915	1.375
3000	25.775	137.721	114.993	68.365	89.496	11.238	11.238	1.666
3100	25.778	138.566	115.742	70.942	89.496	7.508	7.508	1.938
3200	25.782	139.385	116.410	73.520	89.496	3.722	3.722	2.192
3300	25.785	140.178	117.118	76.099	89.496	0.000	0.000	2.431
3400	25.788	140.946	117.805	78.677	89.496	-3.722	-3.722	2.655
3500	25.791	141.696	118.460	81.256	89.496	-7.445	-7.445	2.865
3600	25.793	142.422	119.135	83.836	89.496	-11.168	-11.168	3.064
3700	25.795	143.129	119.774	86.415	89.496	-14.891	-14.891	3.251
3800	25.797	143.817	120.387	88.995	89.496	-18.614	-18.614	3.428
3900	25.799	144.487	120.974	91.574	89.496	-22.337	-22.337	3.596
4000	25.801	145.140	121.602	94.154	89.496	-26.060	-26.060	3.755
4100	25.802	145.777	122.164	96.735	89.496	-29.783	-29.783	3.906
4200	25.804	146.399	122.753	99.315	89.496	-33.506	-33.506	4.049
4300	25.806	147.006	123.310	101.895	89.496	-37.229	-37.229	4.186
4400	25.808	147.598	123.839	104.475	89.496	-40.952	-40.952	4.316
4500	25.808	148.180	124.339	107.057	89.496	-44.675	-44.675	4.440
4600	25.809	148.747	124.813	109.637	89.496	-48.398	-48.398	4.558
4700	25.810	149.302	125.266	112.218	89.496	-52.121	-52.121	4.672
4800	25.811	149.845	125.699	114.800	89.496	-55.844	-55.844	4.780
4900	25.812	150.378	126.312	117.382	89.496	-59.567	-59.567	4.884
5000	25.813	150.899	126.907	119.962	89.496	-63.290	-63.290	4.983
5100	25.814	151.410	127.382	122.543	89.496	-67.013	-67.013	5.079
5200	25.815	151.911	127.869	125.125	89.496	-70.736	-70.736	5.171
5300	25.815	152.403	128.308	127.706	89.496	-74.459	-74.459	5.258
5400	25.816	152.886	128.691	130.287	89.496	-78.182	-78.182	5.343
5500	25.817	153.359	129.201	132.869	89.496	-81.905	-81.905	5.424
5600	25.817	153.825	129.637	135.451	89.496	-85.628	-85.628	5.502
5700	25.818	154.282	130.065	138.033	89.496	-89.351	-89.351	5.578
5800	25.819	154.731	130.487	140.615	89.496	-93.074	-93.074	5.651
5900	25.820	155.176	130.909	143.197	89.496	-96.797	-96.797	5.720
6000	25.820	155.606	131.309	145.778	89.496	-100.520	-100.520	5.786

Dec. 31, 1960, Sept. 30, 1962

Thiophosphoryl Chloride (PCl₃)
(Ideal Gas)
Mol. Wt. = 169.412
ΔH°_f 298.15 = [-86.8] kcal. mole⁻¹
S°_{298.15} = 80.60 cal. deg⁻¹ mole⁻¹
Point Group C_{3v}

Vibrational Frequencies and Degeneracies

ω _v , cm ⁻¹	ω _v , cm ⁻¹	ω _v , cm ⁻¹
169 (2)	[247] (2)	247 (1)
431 (1)	540 (2)	751 (1)

Bond distance P-S = 1.65 ± 0.02 Å P-Cl = 2.02 ± 0.01 Å σ = 3
Cl-P-Cl angle = 100.5° ± 1° I_AI_BI_C = 2.0690 × 10⁻¹¹² g. cm.⁶
Heat of Formation. ΔH°_f 298 was estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corporation, Alexandria, Virginia, "Survey of Thermochemical Data," January 1960. Henderson and Scheffee (loc. cit.) use white(α) phosphorus as a reference state. Their estimated ΔH°_f 298 was adjusted to the Red (V) phosphorus reference state [see White(α) phosphorus sheet.]

Heat Capacity and Entropy. J. S. Ziomek and E. A. Piotrowski, J. Chem. Phys. 34, 1087 (1961) have chosen the most probable values for the wave numbers from the infrared spectral data of G. Cilento, D. A. Ramsey, and R. N. Jones, J. Am. Chem. Soc. 71, 2753 (1949), and the Raman spectral data of A. Simon and G. Schulze, Naturwissenschaften 25, 669 (1937); V. N. Matthe, Nature 139, 469 (1935); H. Gerding and R. Westrick, Rec. trav. chim. 61, 842 (1942); and M. Delvaux and F. Francos, Compt. Rend. 220, 817 (1945). Ziomek and Piotrowski (loc. cit.) found their normal coordinate treatments gave the listed wave numbers as fundamentals and lent support for the 247 cm⁻¹ band missing from the Raman spectral data. The structure, (bond distances and angles) was determined from microwave data by Q. Williams, J. Sheridan, and W. Gordy, J. Chem. Phys. 20, 164 (1952).

Silicon Trichloride (SiCl₃)

(Ideal Gas) GFW = 134.445

Point Group C_{3v} $\Delta H_f^\circ = -95.7 \pm 10$ kcal/mol $S_{298.15}^\circ = 76.17 \pm 1.5$ gibbs/mol $\Delta H_f^\circ = -96 \pm 10$ kcal/mol

Ground State Quantum Weight = 12

T, °K	Cp ^a	gibbs/mol S ^b - (C ^a - H ²⁹⁸)/T	H ^c - H ²⁹⁸ kcal/mol	ΔG ^d	Log Kp
0	11.920	107.916	3.807	95.747	INFINITE
100	11.920	60.746	2.000	95.154	207.967
200	16.916	69.798	1.573	94.346	103.096
298	16.916	76.168	1.000	93.536	68.564
300	16.958	76.272	0.931	93.521	68.130
400	18.023	85.407	3.422	92.455	50.944
500	18.975	88.836	5.503	91.869	40.156
600	19.200	91.779	7.413	91.008	33.164
700	19.350	94.353	9.245	90.227	28.525
800	19.446	96.693	11.006	89.404	24.825
900	19.513	98.856	12.711	88.546	21.181
1000	19.590	100.857	14.367	87.651	17.574
1200	19.634	102.264	17.144	86.015	15.064
1300	19.689	103.437	19.114	85.091	14.138
1400	19.746	104.415	21.053	84.167	13.211
1500	19.811	105.257	22.953	83.241	12.283
1600	19.873	105.978	24.825	82.315	11.357
1700	19.932	106.592	26.678	81.389	10.432
1800	19.988	107.100	28.513	80.463	9.507
1900	20.041	107.503	30.331	79.537	8.582
2000	20.091	107.813	32.135	78.611	7.657
2100	20.138	108.034	33.910	77.685	6.732
2200	20.182	108.175	35.660	76.759	5.807
2300	20.223	108.235	37.390	75.833	4.882
2400	20.261	108.215	39.095	74.907	3.957
2500	20.296	108.115	40.775	73.981	3.032
2600	20.328	107.937	42.430	73.055	2.107
2700	20.358	107.682	44.060	72.129	1.182
2800	20.385	107.350	45.665	71.203	0.257
2900	20.410	106.950	47.245	70.277	-0.668
3000	20.433	106.500	48.800	69.351	-1.593
3100	20.453	106.000	50.330	68.425	-2.518
3200	20.470	105.460	51.740	67.500	-3.443
3300	20.485	104.880	53.030	66.575	-4.368
3400	20.498	104.260	54.290	65.650	-5.293
3500	20.509	103.600	55.520	64.725	-6.218
3600	20.518	102.910	56.720	63.800	-7.143
3700	20.525	102.190	57.890	62.875	-8.068
3800	20.530	101.440	59.030	61.950	-8.993
3900	20.534	100.670	60.140	61.025	-9.918
4000	20.537	100.000	61.220	60.100	-10.843
4100	20.539	99.320	62.270	59.175	-11.768
4200	20.540	98.640	63.300	58.250	-12.693
4300	20.541	97.960	64.310	57.325	-13.618
4400	20.542	97.280	65.300	56.400	-14.543
4500	20.543	96.600	66.270	55.475	-15.468
4600	20.544	95.820	67.220	54.550	-16.393
4700	20.545	95.040	68.150	53.625	-17.318
4800	20.546	94.260	69.060	52.700	-18.243
4900	20.547	93.480	69.950	51.775	-19.168
5000	20.548	92.700	70.820	50.850	-20.093
5100	20.549	91.920	71.670	49.925	-21.018
5200	20.550	91.140	72.500	49.000	-21.943
5300	20.551	90.360	73.310	48.075	-22.868
5400	20.552	89.580	74.100	47.150	-23.793
5500	20.553	88.800	74.870	46.225	-24.718
5600	20.554	88.020	75.620	45.300	-25.643
5700	20.555	87.240	76.350	44.375	-26.568
5800	20.556	86.460	77.060	43.450	-27.493
5900	20.557	85.680	77.750	42.525	-28.418
6000	20.558	84.900	78.420	41.600	-29.343

Dec. 31, 1969

Vibrational Frequencies and Degeneracies

$\frac{\omega}{\text{cm}^{-1}}$	$\frac{g}{\text{cm}^{-1}}$
470 (1)	582 (2)
[240] (1)	[175] (2)

Bond Distance: Si-Cl = (2.02 ± 0.02) ÅBond Angle: Cl-Si-Cl = 110.9° Product of the Moments of Inertia: $I_A I_B I_C = [7.5469 \times 10^{-113}] \text{ g cm}^6$ $\sigma = 3$

Heat of Formation

The adopted value is derived from an average bond energy of $\Delta H_{\text{atom}}^\circ/3 = 96 \pm 3$ kcal/mol. This value is estimated by comparison of average bond energies for SiH_n where $M = \text{C or Si}$, $X = \text{F or Cl}$, and $n = 2, 3$ or 4 . These comparisons suggest that the average bond energy for SiCl_3 should be bracketed by those for SiCl_4 and SiCl_2 , i.e. 94.3 and 101.5 kcal/mol, respectively. Alternative estimates from linear plots of $\Delta H_f^\circ(\text{SiCl}_n)$ versus ΔH_f° for SiF_n , CCl_n , and CF_n yield -98, -96, and -86 kcal/mol for ΔH_f° of SiCl_3 at 298.15°K. These agree with the adopted value of -96 \pm 10 kcal/mol, which corresponds to $\Delta H_{\text{atom}}^\circ = 288 \pm 10$ kcal/mol.

Kerr et al. (1) reported relative rates for several reactions of SiCl_3 , but the authors state that no absolute activation energies are known for reactions of this radical. This precludes derivation of thermochemical values from the kinetic studies. Recently, however, Vurzel et al. (4) reported studies of the decomposition of SiCl_4 by adiabatic compression. Rate constants, as reported in Chemical Abstracts, led to an activation energy of 86 ± 5 kcal/mol for $\text{SiCl}_4 \rightarrow \text{SiCl}_3 + \text{Cl}$. The activation energy for recombination should be very close to zero, so $\Delta H_r = 86 \pm 5$ compared with the adopted result of 86 ± 10 at room temperature. Steele et al. (2) derived an average value of $D(\text{Cl}_3\text{Si-H}) = 93 \pm 4$ kcal/mol from an interpretation of electron impact studies on several molecules. Using $\Delta H_f^\circ(\text{Cl}_3\text{SiH}, g) = -122.6$ kcal/mol (3), we calculate $\Delta H_f^\circ(\text{SiCl}_3, g) = -82$ kcal/mol and estimate the uncertainty as about 10 kcal/mol.

Heat Capacity and Entropy

Jacob and Milligan (5) studied the formation of SiCl_3 by photolysis of HSiCl_3 trapped in matrices of argon, nitrogen and CO. The two stretching fundamentals were assigned from the infrared spectra. Isotopic splittings were found to be consistent with an angle of $72 \pm 5^\circ$ between the threefold axis and each of the Si-Cl bonds. This yields a bond angle of 110.9° which is similar to that of HSiCl_3 . Non-planarity of SiCl_3 is consistent with the electron-spin-resonance studies of Roncin (6).

We adopt the results of Jacob (5) and estimate the bond length and two bending vibrations by analogy with HSiCl_3 . Similar analogies are reliable for SiF_3 and CF_3 . The ground state quantum weight is taken as two, but excited electronic levels are neglected. Jacob (5) observed unstructured absorptions corresponding to excitation energies of 30000-34500 cm^{-1} and 41000-46000 cm^{-1} . Principal moments of inertia are $I_A = 65.18 \times 10^{-39}$ and $I_B = I_C = 34.03 \times 10^{-39} \text{ g cm}^2$.

References

1. J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson and J. C. Youngs, *J. Chem. Soc. A*, 1968, 510.
2. W. C. Steele, L. D. Nichols and F. G. A. Stone, *J. Amer. Chem. Soc.*, **84**, 4441 (1962).
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. F. B. Vurzel, L. S. Polak and V. S. Shchepachev, *Kinet. Katal.*, **7** (6), 1068 (1966); *Chem. Abstr.*, **57**, 59296 (1967).
5. M. E. Jacob and D. E. Milligan, *J. Chem. Phys.*, **48**, 3130 (1968).
6. J. Roncin, *Mol. Cryst.*, **3** (1), 117-44 (1967); *Chem. Abstr.*, **58**, 64560 (1968).



Titanium Trichloride (TiCl₃)

(Crystal)

GFW = 154.259

T, °K	C _p ^o	S ^o - (C _p ^o - H ^o)/T	H ^o - H ^o ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	13.011	16.000	INFINITE	-173.057	-173.057	INFINITE
100	24.361	25.626	54.440	-173.619	-167.710	366.529
200	24.361	25.626	35.436	-173.344	-161.669	176.860
298	23.222	33.401	0.000	-172.500	-156.442	113.875
300	23.230	33.245	-0.043	-172.491	-156.343	113.896
400	23.452	46.286	34.318	-172.009	-151.034	82.521
500	24.638	45.606	36.062	-171.550	-145.843	63.748
600	24.390	50.020	36.031	-171.098	-140.748	51.466
700	24.558	53.115	40.959	-170.724	-135.742	42.723
800	24.558	56.071	43.406	-170.204	-130.743	36.723
900	25.235	60.711	43.406	-169.766	-125.858	30.563
1000	25.503	62.744	45.568	-169.334	-121.005	26.446
1100	25.769	65.187	47.242	-168.902	-116.191	23.085
1200	26.567	67.235	51.783	-168.467	-111.507	19.585
1300	26.567	67.235	51.783	-168.467	-106.847	16.045
1400	26.559	71.493	51.787	-168.309	-101.796	15.491
1500	26.620	73.338	53.162	-167.744	-97.065	14.142

TITANIUM TRICHLORIDE (TiCl₃)

(CRYSTAL)

GFW = 154.259

ΔH_f^o = -173.1 ± 1.0 kcal/mol
 ΔH_f^o_{298.15} = -172.5 ± 1.0 kcal/mol
 ΔH_f^o = 0 kcal/mol
 ΔH_s^o = [39.71] kcal/mol

S_{298.15} = 33.4 ± 0.3 gibbs/mol

T_m = 220.1°K

T_s = [1104.1]°K

Heat of Formation

The heat of formation, ΔH_f^o₂₉₈, of TiCl₃(c) has been measured by several investigators. The results of these measurements are as follows.

Investigators

Investigator	Method	ΔH _f ^o , Kcal/mol
Schaffer et al. (1954) (1)	Calorimetric, TiCl ₄ + Hg = TiCl ₃ + 1/2Hg ₂ Cl ₂	-171.9, -172.4
Clifton and MacWood (1956) (2)	Solution calorimetric	-172.4
Johnson et al. (1956) (3)	Calorimetric, TiCl ₄ (l) + Hl(g) = TiCl ₃ (c) + HCl(g) + 1/2I ₂	-172.5
Krievie et al. (1956) (4)	Solution calorimetric	-171.3
Krievie and Mason (1956) (5)	Equilibrium, TiCl ₃ (c) + HCl(g) = TiCl ₄ (g) + 1/2H ₂ (g)	-172.9
Altman et al. (1956) (6)	Equilibrium, 2TiCl ₃ (c) + 3TiCl ₄ (g) = 4TiCl ₃ (c)	-189.4, -171.0
Head (1960) (7)	Equilibrium, 2TiCl ₄ (2) + H ₂ (g) = 2TiCl ₃ (c) + 2HCl(g)	-172.3
	TiCl ₄ (l) + Hg(l) = 1/2Hg ₂ Cl ₂ (c) + TiCl ₃ (c)	
	TiCl ₄ (l) + Ag(c) = AgCl(c) + TiCl ₃ (c)	

The chosen value of -172.5 ± 1.0 kcal/mol is that reported by Johnson et al. (3).

Heat Capacity and Entropy

The heat capacity and entropy of TiCl₃(c) has been measured over the temperature range 54° to 1000°K by King et al. (8). The value of S₂₉₈^o is calculated from these data based on S₂₁^o = 4.29 eu.

Transition Data

A second order transition at 220.1°K was observed by King et al. (8). The heat capacity at this temperature is in excess of 146.8 gibbs/mol. King et al. measured the value of H₂₄₀^o - H₂₀₀^o as 1.213 kcal/mol.

Heat of Sublimation

The heat of sublimation is calculated from the heats of formation of TiCl₃(c) and TiCl₃(g) at the sublimation temperature. The sublimation temperature is taken as the point at which ΔGr = 0 for the process TiCl₃(c) = TiCl₃(g).

References

1. H. Schaffer, G. Breil, and G. Pfeffer, Z. Anorg. Chem. **276**, 325 (1954).
2. D. G. Clifton and G. E. MacWood, J. Phys. Chem. **60**, 309 (1956).
3. W. H. Johnson, A. A. Gilliland, and E. T. Prosen, J. Res. Natl. Bur. Std. **64A**, 515 (1956).
4. W. F. Krievie, S. F. Vango, and D. M. Mason, J. Chem. Phys. **25**, 89 (1956).
5. W. F. Krievie and D. M. Mason, J. Chem. Phys. **25**, 524 (1956).
6. D. Altman, M. Farber, and D. M. Mason, J. Chem. Phys. **25**, 531 (1956).
7. R. B. Head, Aust. J. Chem. **13**, 332 (1960).
8. E. G. King et al., U. S. Bur. Mines RI5799, 1961.



Titanium Trichloride (TiCl₃)

(Ideal Gas) GFw = 154.259

Point Group = C_{3v}

S_{298.15}° = [75.7 ± 1.0] gibbs/mol

ΔH_f° = -128.1 ± 1.5 kcal/mol

ΔH_f°_{298.15} = -128.9 ± 1.5 kcal/mol

T, °K	Cp*	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔG _f °	Log Kp
0	.000	.000	INFINITE	-3.675	-126.132	-126.132	INFINITE
100	10.054	60.959	90.124	2.627	-126.462	-126.462	276.921
200	14.601	75.703	77.771	3.769	-126.953	-126.953	181.644
250	17.334	79.703	75.703	.000	-126.900	-125.355	91.961
300	17.380	75.811	75.704	-.032	-126.901	-125.433	91.378
400	18.796	61.027	76.405	1.649	-126.948	-124.249	67.897
500	19.531	65.309	77.771	3.769	-126.953	-123.097	53.806
600	19.924	66.900	79.335	5.744	-126.946	-121.927	44.412
700	20.139	67.997	80.929	7.748	-126.947	-120.756	37.702
800	20.261	69.495	82.485	9.769	-126.965	-119.568	32.670
900	20.333	67.066	83.977	11.799	-129.006	-118.412	28.754
1000	20.377	65.231	85.397	13.634	-129.075	-117.234	25.621
1100	20.406	101.175	64.744	15.873	-129.171	-116.048	23.056
1200	20.424	102.951	66.022	17.915	-130.231	-114.808	20.099
1300	20.437	104.566	69.234	19.956	-130.255	-113.522	19.085
1400	20.445	106.101	90.365	22.002	-130.266	-112.234	17.520
1500	20.450	107.512	91.461	24.047	-130.355	-110.942	16.164
1600	20.452	108.632	92.524	26.092	-130.435	-109.644	14.977
1700	20.453	110.072	93.520	28.137	-130.516	-108.340	13.926
1800	20.452	111.241	94.673	30.183	-130.662	-107.033	12.996
1900	20.450	112.346	95.364	32.228	-130.612	-105.714	12.160
2000	20.448	113.395	96.259	34.273	-135.436	-104.236	11.390
2100	20.445	114.393	97.099	36.317	-135.616	-102.672	10.685
2200	20.443	115.344	97.907	38.362	-135.768	-101.100	10.043
2300	20.440	116.253	98.685	40.406	-135.983	-99.517	9.456
2400	20.437	117.122	99.435	42.450	-136.170	-97.926	8.917
2500	20.434	117.957	100.159	44.493	-136.383	-96.330	8.421
2600	20.431	118.758	100.859	46.536	-136.557	-94.725	7.962
2700	20.429	119.529	101.537	48.579	-136.756	-93.112	7.537
2800	20.426	120.272	102.193	50.622	-136.960	-91.491	7.141
2900	20.423	120.989	102.829	52.665	-137.187	-89.863	6.772
3000	20.421	121.681	103.445	54.707	-137.379	-88.230	6.428
3100	20.418	122.351	104.045	56.749	-137.595	-86.587	6.104
3200	20.416	122.999	104.627	58.790	-137.817	-84.941	5.801
3300	20.413	123.627	105.193	60.832	-138.043	-83.282	5.516
3400	20.410	124.236	105.744	62.873	-138.272	-81.617	5.246
3500	20.407	124.828	106.281	64.914	-138.508	-79.952	4.992
3600	20.404	125.403	106.804	66.954	-240.373	-78.010	4.746
3700	20.401	125.962	107.315	68.995	-240.588	-73.497	4.501
3800	20.398	126.506	107.812	71.035	-240.820	-68.984	3.961
3900	20.395	127.036	108.299	73.074	-241.070	-64.453	3.612
4000	20.392	127.552	108.774	75.114	-241.338	-59.922	3.274
4100	20.388	128.055	109.238	77.153	-241.620	-55.384	2.952
4200	20.384	128.547	109.692	79.191	-241.920	-50.841	2.646
4300	20.381	129.026	110.136	81.230	-242.233	-46.290	2.353
4400	20.377	129.495	110.570	83.267	-242.561	-41.724	2.078
4500	20.373	129.953	110.996	85.305	-242.903	-37.159	1.805
4600	20.369	130.400	111.413	87.342	-243.255	-32.579	1.546
4700	20.366	130.836	111.822	89.379	-243.621	-27.994	1.302
4800	20.363	131.267	112.222	91.415	-243.999	-23.406	1.066
4900	20.359	131.687	112.615	93.451	-244.387	-18.805	.839
5000	20.351	132.098	113.001	95.486	-244.784	-14.197	.621
5100	20.347	132.501	113.379	97.521	-245.190	-9.578	.410
5200	20.342	132.896	113.751	99.555	-245.606	-4.953	.208
5300	20.338	133.284	114.116	101.589	-246.030	-.328	.014
5400	20.333	133.664	114.474	103.623	-246.462	4.316	.175
5500	20.329	134.037	114.827	105.656	-246.899	9.666	.356
5600	20.324	134.403	115.173	107.689	-247.344	13.616	.531
5700	20.319	134.763	115.513	109.721	-247.795	16.280	.701
5800	20.314	135.116	115.846	111.752	-248.251	22.957	.865
5900	20.310	135.463	116.176	113.784	-248.713	27.633	1.024
6000	20.305	135.805	116.502	115.814	-249.179	32.320	1.177

Dec. 31, 1960; Mar. 31, 1964; June 30, 1968; Dec. 31, 1968

Electronic Levels and Quantum Weights			
ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies			
ω_i , cm ⁻¹		ω_i , cm ⁻¹	
[275] (1)	[530] (1)	[590] (2)	
[275] (1)	[260] (2)		

Bond Distance: Ti-Cl = [2.3] Å
Bond Angle: Cl-Ti-Cl = [100°]
Products of the Moments of Inertia: I_AI_BI_C = [1.33 × 10⁻¹¹²] g³ cm⁶ σ = 3

Heat of Formation

The heat of formation of TiCl₃(g) is calculated from the heats of reaction for the processes, (A) 3TiCl₂(g) + Ti(c) = 4TiCl₃(g) and (B) TiCl₂(c) = TiCl₃(g), combined with auxiliary JANAF heats of formation for TiCl₂(g), TiCl₂(c) and Ti(c). Equilibrium measurements of reaction (A) have been reported by Gross and Levi (1). Vapor pressure measurements for reaction (B) have been reported by Sanderson and Macdonald (2) and by Farber and Darnell (3). Second and third law analyses of these data yield the following results.

Source	Reaction	No. Points	Range, °K	ΔH _f °, kcal/mol	Second Law	Third Law	Drift, eu	ΔH _f °298*
Gross and Levi (1)	A	3	1223			31.6 ± 2.0		-126.5
Sanderson and Macdonald (2)	B	9**	628-823		42.8 ± 1.1	42.8	-0.1 ± 1.5	-129.3
Farber and Darnell	B	8	636-732		45.3 ± 2.1	45.8	0.8 ± 3.1	-126.2

*Calculation based on third law ΔH_f°298.

**One point rejected due to failure of statistical test.

The chosen value of ΔH_f°298 is -128.9 kcal/mol. This value is the average of the first two determinations.

Heat Capacity and Entropy

The interatomic distance is estimated from that of the solid, given as 2.46 Å by Matte et al. (4), and from comparisons of bond distances of crystal and gas phase tetrahalides of titanium. The pyramidal bond angle is estimated assuming TiCl₃(g) similar to the group V trihalides. The principal moments of inertia are I_A = 4.29 × 10⁻³⁸ g cm² and I_C = 7.26 × 10⁻³⁸ g cm². The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti³⁺ (5).

References

1. P. Gross and D. L. Levi, Congres International de Chimie Pure et Appliquees, 16e Congres, Paris, 1957; Memoires presentes a la Section de Chemie Minerale, 627 (1959).
2. B. S. Sanderson and G. E. Macdonald, J. Phys. Chem. 50, 314 (1956).
3. M. Farber and A. J. Darnell, J. Phys. Chem. 59, 156 (1955).
4. G. Matte, P. Corradini, and G. Allegria, J. Polym. Sci. 51, 399 (1961).
5. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.



GFW = 197.579

(CRYSTAL)

ZIRCONIUM TRICHLORIDE (ZrCl_3)

Zirconium Trichloride (ZrCl_3)

GFW = 197.579

(Crystal)

$\Delta H_f^\circ = \text{Unknown}$

$\Delta H_f^\circ_{298.15} = [-170.7 \pm 15] \text{ kcal/mol}$

$\Delta H_f^\circ_{298.15} = [45.4] \text{ kcal/mol}$

$S^\circ_{298.15} = [34.8 \pm 3] \text{ gibbs/mol}$

$T_s = [1045.9]^\circ\text{K}$

Heat of Formation

Turnbull and Watts (1) determined the equilibrium pressures for the disproportionation of $\text{ZrCl}_3(\text{c})$ in the temperature range from 613°K to 723°K by a modified dew point technique. Third law and second law analyses of their vapor pressure-temperature equation give the same heat of reaction $\Delta H_{298}^\circ = 30.7 \text{ kcal/mol}$ for $2\text{ZrCl}_3(\text{c}) \rightarrow \text{ZrCl}_2(\text{c}) + \text{ZrCl}_4(\text{g})$. The adopted value, $\Delta H_f^\circ(\text{ZrCl}_3, \text{c}) = -170.7 \text{ kcal/mol}$, is calculated from the heat of reaction at 298°K, and $\Delta H_f^\circ(\text{ZrCl}_4, \text{g}) = -207.77 \text{ kcal/mol}$ (2) and $\Delta H_{298}^\circ(\text{ZrCl}_2, \text{c}) = -103 \text{ kcal/mol}$ (3). The assigned uncertainty, $\pm 15 \text{ kcal/mol}$ is mainly due to the uncertainty in the heat of formation of $\text{ZrCl}_2(\text{c})$, and also the dew point technique used.

Heat Capacity and Entropy

The heat capacities of $\text{ZrCl}_3(\text{c})$ are estimated from the Cp values of $\text{ZrCl}_4(\text{c})$ by deduction of one Cl atom Cp contributions which are calculated as $1/4(\text{Cp}(\text{ZrCl}_4, \text{c}) - \text{Cp}(\text{Zr}, \text{c}))$. The S_{298}° is calculated as 34.85 eu based on the assumption that $S_{298}^\circ(\text{ZrCl}_3, \text{c}) = S_{298}^\circ(\text{ZrCl}_4, \text{c}) - 1/4(S_{298}^\circ(\text{ZrCl}_4, \text{c}) - S_{298}^\circ(\text{Zr}, \text{c}))$.

Heat of Sublimation

The heat of sublimation is calculated from the difference in the heats of formation of gas and crystal at 298°K. The sublimation temperature is taken as the point at which $\Delta G^\circ = 0$ for $\text{ZrCl}_3(\text{c}) = \text{ZrCl}_3(\text{g})$.

References

1. A. G. Turnbull and J. A. Watts, Aust. J. Chem. **16**, 947 (1963).
2. JANAF $\text{ZrCl}_4(\text{g})$ table dated Dec. 31, 1969.
3. JANAF $\text{ZrCl}_2(\text{c})$ table dated Dec. 31, 1969.

T, °K	Cp°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
100							
200							
298	22.990	34.850	34.850	.000	-170.700	-154.481	111.238
300	23.019	34.992	34.850	.043	-170.691	-154.381	112.466
400	24.069	41.768	35.767	2.400	-170.201	-149.017	81.419
500	24.730	47.212	37.529	4.841	-169.691	-143.779	62.846
600	25.235	51.767	39.533	7.340	-169.173	-138.646	50.502
700	25.664	55.690	41.567	9.886	-168.651	-133.599	41.712
800	26.064	59.143	43.553	12.472	-168.126	-128.628	35.140
900	26.433	62.234	45.400	15.097	-167.598	-123.722	30.044
1000	26.768	65.036	47.279	17.759	-167.067	-118.877	25.981
1100	27.050	67.604	49.012	20.451	-166.537	-114.083	22.444
1200	27.300	69.968	50.661	23.168	-166.006	-109.287	19.904
1300	27.550	72.163	52.232	25.911	-165.470	-104.516	17.371
1400	27.800	74.215	53.730	28.679	-164.933	-99.800	15.579
1500	28.000	76.139	55.160	31.469	-164.748	-95.134	13.461
1600	28.200	77.953	56.528	34.279	-164.028	-90.517	12.344
1700	28.370	79.668	57.840	37.108	-163.301	-85.942	11.089
1800	28.550	81.295	59.098	39.954	-162.571	-81.415	9.885
1900	28.750	82.841	60.307	42.814	-161.840	-76.924	8.848
2000	28.750	84.313	61.471	45.684	-161.114	-72.475	7.920



Zirconium Trichloride (ZrCl₃)

GFW = 197.579

Point Group: [C_{3v}]

$$\Delta H_f^\circ = -124.9 \pm 5 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -125.3 \pm 5 \text{ kcal/mol}$$

$$S_{298.15}^\circ = (81.0 \pm 3) \text{ gibbs/mol}$$

$$\text{Ground State Quantum Weight} = [2]$$

T, °K	Cp	S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	ΔH ^o	Log Kp
100	12.920	63.812	196.111E	6.210	-124.998	196.111E
200	16.648	74.068	82.691	1.119	-125.278	125.278
298	18.170	81.070	0.000	0.000	-125.300	90.060
300	18.189	81.182	0.034	0.034	-125.300	89.494
400	18.949	86.531	1.794	1.695	-125.307	66.673
500	19.487	90.823	3.165	3.819	-125.313	52.960
600	19.874	94.412	4.675	5.768	-125.326	43.650
700	20.189	97.496	6.389	7.791	-125.346	37.328
800	20.431	100.168	8.313	9.967	-125.369	32.640
900	20.591	102.618	10.433	12.229	-125.392	28.563
1000	20.669	104.760	12.826	14.682	-125.416	25.063
1100	20.756	106.784	15.499	17.329	-125.441	22.089
1200	20.847	108.573	18.457	20.176	-125.466	19.599
1300	20.941	110.148	21.695	23.250	-125.492	17.507
1400	20.989	111.768	25.235	26.583	-125.517	15.767
1500	20.970	113.230	29.003	29.340	-125.477	14.391
1600	20.915	114.579	33.000	28.431	-125.476	13.239
1700	20.824	115.854	37.223	26.823	-125.466	12.253
1800	20.711	117.053	41.683	24.523	-125.446	11.423
1900	20.591	118.173	46.385	21.549	-125.419	10.733
2000	20.465	119.245	51.348	18.795	-125.403	10.173
2100	20.342	120.265	56.582	16.264	-125.370	9.733
2200	20.226	121.236	62.101	13.972	-125.326	9.399
2300	20.117	122.158	67.907	11.926	-125.276	9.166
2400	20.014	123.030	73.999	9.142	-125.222	9.026
2500	20.000	123.901	80.481	5.625	-125.155	8.975
2600	20.000	124.717	87.452	2.407	-125.076	8.999
2700	20.000	125.482	94.917	-0.587	-124.984	9.076
2800	20.000	126.197	102.877	-3.643	-124.879	9.206
2900	20.000	126.862	111.342	-6.766	-124.762	9.386
3000	20.000	127.477	120.317	-9.947	-124.633	9.616
3100	20.000	128.042	129.792	-13.184	-124.491	9.899
3200	20.000	128.557	139.767	-16.477	-124.336	10.236
3300	20.000	129.022	150.242	-19.824	-124.169	10.626
3400	20.000	129.437	161.217	-23.224	-123.991	11.066
3500	20.000	129.802	172.692	-26.674	-123.799	11.556
3600	20.000	130.117	184.667	-30.174	-123.594	12.096
3700	20.000	130.382	197.142	-33.724	-123.376	12.686
3800	20.000	130.597	210.117	-37.324	-123.146	13.326
3900	20.000	130.762	223.592	-40.974	-122.896	14.016
4000	20.000	130.877	237.567	-44.674	-122.626	14.756
4100	20.000	130.942	252.042	-48.424	-122.336	15.546
4200	20.000	130.957	267.017	-52.224	-122.026	16.386
4300	20.000	130.922	282.492	-56.074	-121.696	17.276
4400	20.000	130.837	298.467	-60.074	-121.346	18.216
4500	20.000	130.702	314.942	-64.224	-120.976	19.206
4600	20.000	130.517	331.917	-68.524	-120.586	20.246
4700	20.000	130.282	349.392	-72.974	-120.176	21.336
4800	20.000	130.007	367.367	-77.574	-119.746	22.476
4900	20.000	129.682	385.842	-82.324	-119.286	23.666
5000	20.000	129.307	404.817	-87.224	-118.796	24.906
5100	20.000	128.882	424.292	-92.274	-118.276	26.196
5200	20.000	128.407	444.267	-97.474	-117.726	27.536
5300	20.000	127.882	464.742	-102.824	-117.146	28.926
5400	20.000	127.307	485.717	-108.324	-116.536	30.366
5500	20.000	126.682	507.192	-113.974	-115.896	31.856
5600	20.000	126.007	529.167	-119.774	-115.226	33.396
5700	20.000	125.282	551.642	-125.724	-114.526	34.986
5800	20.000	124.507	574.617	-131.824	-113.796	36.626
5900	20.000	123.682	598.092	-138.074	-113.036	38.316
6000	20.000	122.807	622.067	-144.474	-112.246	40.056

June 30, 1961; Dec. 31, 1961; June 30, 1964; Dec. 31, 1969

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	ϵ_2
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[490] (1)	[333] (2)
[185] (1)	[131] (2)

$$\text{Bond Distance: Zr-Cl} = [2.3] \text{ \AA}$$

$$\text{Bond Angle: Cl-Zr-Cl} = [100^\circ]$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = [1.5104 \times 10^{-112}] \text{ g}^3 \text{ cm}^6$$

$$\sigma = [3]$$

Heat of Formation

Potter (1) investigated mass spectrometrically the equilibrium $\text{CaCl}_2(\text{g}) + \text{ZrCl}_4(\text{g}) \rightleftharpoons \text{ZrCl}_2(\text{g}) + \text{ZrCl}_3(\text{g})$ in the temperature range 1163-1577°K. Ion intensities were measured 2.5 eV above threshold and they were used in the calculation of equilibrium constants. Using the reported equilibrium constants, the heats of reaction at 298°K are evaluated by the third law and second law methods as -3.69 and -16.67 kcal/mol, respectively. The third law drift is 9.31 ± 1.25 eu. Using the third law $\Delta H_f^\circ = -3.69$ kcal/mol, $\Delta H_f^\circ(\text{ZrCl}_4, \text{g}) = -207.77$ kcal/mol (2), $\Delta H_f^\circ(\text{CaCl}_2, \text{g}) = -28.8$ kcal/mol (3) and $\Delta H_f^\circ(\text{ZrCl}_2, \text{g}) = -115.0$ kcal/mol (4), we obtain $\Delta H_f^\circ(\text{ZrCl}_3, \text{g}) = -125.3$ kcal/mol, which is adopted in the tabulation.

Farber et al. (5) also studied mass spectrometrically the reaction $\text{Zr}(\text{c}) + 3\text{ZrCl}_2(\text{g}) \rightleftharpoons 4\text{ZrCl}_3(\text{g})$ in the temperature range from 1579°K to 1729°K. They reported a second law heat of reaction as $\Delta H_f^\circ = 59.2 \pm 1.6$ kcal/mol. Since the attainment of equilibrium was questionable in their studies, the heat of reaction obtained from the third law method is generally more reliable. Using their reported ion intensities of run 3 (temperature range from 1667°K to 1898°K, five points), we have calculated the equilibrium constants $K_1 = (I_{\text{ZrCl}_3})^2 / (I_{\text{ZrCl}_2})^3$ for reaction (1) $\text{ZrCl}_3(\text{g}) + \text{ZrCl}_3(\text{g}) \rightleftharpoons 2\text{ZrCl}_2(\text{g})$, and $K_2 = (I_{\text{ZrCl}_3})^2 / (I_{\text{ZrCl}_4})^2$ for reaction (2) $\text{ZrCl}_3(\text{g}) + \text{ZrCl}_4(\text{g}) \rightleftharpoons 2\text{ZrCl}_2(\text{g})$. Third law analyses of the equilibrium constants give $\Delta H_f^\circ = -11.0$ kcal/mol for reaction (1) and its drift 4.1 ± 1.7 eu; and $\Delta H_f^\circ = 1.4$ kcal/mol for reaction (2) and its drift 21.1 ± 1.2 eu. Using the third law heats of reaction, and $\Delta H_f^\circ(\text{ZrCl}_2, \text{g}) = 49.1$ kcal/mol (6) and $\Delta H_f^\circ(\text{ZrCl}_4, \text{g}) = -207.77$ kcal/mol (2), we obtain $\Delta H_f^\circ(\text{ZrCl}_3, \text{g}) = -124.9$ kcal/mol and $\Delta H_f^\circ(\text{ZrCl}_2, \text{g}) = -43.4$ kcal/mol which are in good agreement with the values adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be a pyramid similar to the group VA trichlorides. The bond distance is assumed to be the same as that of $\text{ZrCl}_4(\text{g})$. The three principal moments of inertia are $I_A = I_B = 45.9145 \times 10^{-39}$ and $I_C = 72.6247 \times 10^{-39} \text{ g cm}^2$. The electronic levels are estimated as three times higher than those of $\text{TiCl}_3(\text{g})$, based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by C. E. Moore (7). The quantum weights are assumed to be the same as those of $\text{TiCl}_3(\text{g})$.

Vibrational frequencies are calculated from the estimated force constants by the valence force method (8). The force constants are estimated from those of PCl_3 , AsCl_3 and SbCl_3 listed by Herzberg (8).

References

1. N. D. Potter, Aeronautics Div., Philco-Ford Corp., Newport Beach, Calif., private communication, dated Dec. 4, 1969.
2. JANAF ZrCl₄(g) table, dated Dec. 31, 1969.
3. The heat of formation and the free energy functions of CaCl₂(g) are preliminary values calculated by the Thermal Laboratory, The Dow Chemical Company, Midland, Mich.
4. The heat of formation and the free energy functions of CaCl₂(g) are preliminary values calculated by the Thermal Laboratory, The Dow Chemical Company, Midland, Mich.
5. M. Farber, H. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRL-TR-67-244, Contract F04611-67-C-0010, Nov. 1967.
6. JANAF ZrCl₂(g) table, dated Dec. 31, 1969.
7. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std. Circ. 467.
8. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc. New York, 1945.



MAGNESIUM DICHLORIDE, DIMERIC (Mg_2Cl_4) (IDEAL GAS)

GFW = 190.436

Magnesium Dichloride, Dimeric (Mg_2Cl_4)

(Ideal Gas) GFW = 190.436

Point Group: $[D_{2h}]$

$\Delta H_f^\circ = -228.11 \pm 7 \text{ kcal/mol}$

$\Delta H_{298.15}^\circ = -228.10 \pm 7 \text{ kcal/mol}$

$S_{298.15}^\circ = [100.098 \pm 5] \text{ gibbs/mol}$

Ground State Quantum Weight = 1

T, °K	C_p	S°	$-(G^\circ - H^\circ_{298})/T$	ΔH_f°	$H^\circ - H^\circ_{298}$	kcal/mol	ΔG_f°	Log Kp
0	21.680	71.495	196.111E	-	5.787	-228.107	-228.107	196.111E
100	21.680	71.495	196.111E	-	5.787	-228.107	-228.107	463.945E
200	27.529	88.672	192.748	-	2.815	-228.411	-223.870	244.634
298	29.544	100.098	190.098	-	+0.00	-228.100	-221.569	162.370
300	29.547	100.281	190.099	-055	-228.097	-221.468	-221.468	161.339
400	30.658	108.924	191.271	3.064	-227.979	-219.379	-219.379	118.808
500	30.911	115.775	193.511	6.132	-227.898	-217.110	-217.110	84.899
600	31.170	121.435	196.040	9.237	-227.869	-214.959	-214.959	78.299
700	31.431	126.253	198.592	12.463	-227.885	-212.905	-212.905	66.481
800	31.676	130.444	201.144	15.846	-227.944	-210.946	-210.946	56.426
900	31.911	134.152	203.700	19.426	-228.046	-209.074	-209.074	50.426
1000	31.544	137.474	206.265	23.265	-228.195	-207.235	-207.235	45.003
1100	31.603	140.485	208.837	27.265	-228.334	-205.423	-205.423	40.380
1200	31.634	143.236	211.409	31.423	-228.458	-203.634	-203.634	36.523
1300	31.649	145.730	213.980	35.746	-228.568	-201.862	-201.862	33.529
1400	31.676	148.106	216.546	40.226	-228.664	-200.117	-200.117	30.509
1500	31.691	150.302	219.109	44.864	-228.748	-198.397	-198.397	27.435
1600	31.704	152.347	221.668	49.664	-228.820	-196.699	-196.699	24.315
1700	31.714	154.270	224.222	54.626	-228.880	-195.020	-195.020	21.145
1800	31.723	156.088	226.772	59.750	-228.928	-193.362	-193.362	17.925
1900	31.730	157.806	229.318	65.036	-228.964	-191.724	-191.724	14.655
2000	31.736	159.428	231.860	70.482	-228.988	-190.104	-190.104	11.335
2100	31.742	160.974	234.395	76.090	-228.999	-188.502	-188.502	8.065
2200	31.746	162.451	236.926	81.862	-228.998	-186.917	-186.917	4.845
2300	31.750	163.864	239.453	87.798	-228.984	-185.348	-185.348	1.675
2400	31.754	165.216	241.976	93.898	-228.958	-183.794	-183.794	-1.545
2500	31.757	166.510	244.492	100.162	-228.919	-182.254	-182.254	-2.765
2600	31.760	167.756	246.999	106.590	-228.868	-180.728	-180.728	-3.985
2700	31.763	168.954	249.498	113.182	-228.805	-179.215	-179.215	-5.205
2800	31.766	170.106	251.988	120.940	-228.730	-177.714	-177.714	-6.425
2900	31.769	171.224	254.468	128.864	-228.644	-176.224	-176.224	-7.645
3000	31.772	172.301	256.938	136.954	-228.548	-174.744	-174.744	-8.865
3100	31.770	173.343	259.400	145.120	-228.442	-173.274	-173.274	-10.085
3200	31.772	174.352	261.852	153.362	-228.326	-171.814	-171.814	-11.305
3300	31.774	175.328	264.296	161.686	-228.200	-170.364	-170.364	-12.525
3400	31.776	176.278	266.732	170.098	-228.064	-168.924	-168.924	-13.745
3500	31.778	177.199	269.160	178.598	-227.918	-167.494	-167.494	-14.965
3600	31.777	178.094	271.578	187.178	-227.762	-166.064	-166.064	-16.185
3700	31.778	178.965	273.982	195.838	-227.596	-164.634	-164.634	-17.405
3800	31.779	179.806	276.378	204.578	-227.420	-163.204	-163.204	-18.625
3900	31.779	180.636	278.762	213.398	-227.234	-161.774	-161.774	-19.845
4000	31.780	181.442	281.138	222.298	-227.038	-160.344	-160.344	-21.065
4100	31.781	182.227	283.502	231.278	-226.832	-158.914	-158.914	-22.285
4200	31.781	182.993	285.862	240.328	-226.616	-157.484	-157.484	-23.505
4300	31.782	183.738	288.218	249.448	-226.390	-156.054	-156.054	-24.725
4400	31.782	184.471	290.570	258.628	-226.154	-154.624	-154.624	-25.945
4500	31.783	185.186	292.918	267.868	-225.908	-153.194	-153.194	-27.165
4600	31.784	185.884	295.252	277.168	-225.652	-151.764	-151.764	-28.385
4700	31.784	186.568	297.582	286.528	-225.386	-150.334	-150.334	-29.605
4800	31.785	187.238	299.908	295.948	-225.110	-148.904	-148.904	-30.825
4900	31.785	187.892	302.230	305.428	-224.824	-147.474	-147.474	-32.045
5000	31.785	188.534	304.548	314.968	-224.528	-146.044	-146.044	-33.265
5100	31.786	189.164	306.858	324.568	-224.222	-144.614	-144.614	-34.485
5200	31.786	189.784	309.158	334.228	-223.906	-143.184	-143.184	-35.705
5300	31.787	190.394	311.458	343.948	-223.580	-141.754	-141.754	-36.925
5400	31.787	190.984	313.748	353.728	-223.244	-140.324	-140.324	-38.145
5500	31.787	191.564	316.028	363.568	-222.908	-138.894	-138.894	-39.365
5600	31.787	192.137	318.298	373.468	-222.562	-137.464	-137.464	-40.585
5700	31.787	192.699	320.558	383.428	-222.206	-136.034	-136.034	-41.805
5800	31.788	193.252	322.808	393.448	-221.840	-134.604	-134.604	-43.025
5900	31.788	193.796	325.048	403.528	-221.464	-133.174	-133.174	-44.245
6000	31.788	194.330	327.278	413.668	-221.078	-131.744	-131.744	-45.465

Vibrational Frequencies and Degeneracies

ω_1, cm^{-1}	ω_2, cm^{-1}	ω_3, cm^{-1}	ω_4, cm^{-1}
[500] (1)	[240] (1)	[130] (2)	
[400] (1)	[200] (1)	[100] (2)	
295 (1)	[150] (1)	[80] (2)	

Bond Distance: $\text{Mg}-\text{Cl} = [2.18] \text{ \AA}$, $\text{Mg}-\text{Cl}(\text{ring}) = [2.3] \text{ \AA}$

Bond Angles: $\text{Cl}'-\text{Mg}-\text{Cl}(\text{in ring}) = [90^\circ]$, $\text{Cl}-\text{Mg}-\text{Cl}' = [135^\circ]$

Product of the Moments of Inertia: $I_A I_B I_C = 1.3313 \times 10^{-111} \text{ g cm}^6$

Heat of Formation

References relative to the monomer-dimer ratio in magnesium chloride vapor are given in the discussion for monomeric ideal gas. The selected best value for the heat of dimerization at 900°K is -39.2 kcal/mol. Combined with heat of formation data for the monomer and the heat capacity of the dimer, this yields $\Delta H_{298.15}^\circ = -228.10 \text{ kcal/mol}$.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was assumed, with the outer $\text{Mg}-\text{Cl}$ distance the same as in MgCl_2 and the ring $\text{Mg}-\text{Cl}$ distance slightly larger. The ring was taken to be square, and the $\text{Cl}-\text{Mg}-\text{Cl}'$ angle 135° . This structure gives individual moments of inertia of $I_A = 31.12 \times 10^{-39} \text{ g cm}^2$, $I_B = 191.86 \times 10^{-39} \text{ g cm}^2$ and $I_C = I_A + I_B$.

A reasonable set of frequencies was estimated by comparison with MgCl_2 monomer and other dimer molecules. The single observed frequency is from A. Buchler and W. Klemperer, J. Chem. Phys. 29, 121 (1958), who erroneously ascribed it to the bending mode of the monomer. The estimated values were adjusted until the entropy of dimerization at 900°K was -29.9 gibbs/mol, as selected in the discussion for ideal monomeric gas. The calculated thermodynamic properties of monomer and dimer give total vapor pressures in good agreement with experiment and yield a boiling point for magnesium chloride of 1624°K at one atmosphere pressure.



Molybdenum Tetrachloride (MoCl₄)

(Crystal) GFW = 237.752

$$\Delta H_f^\circ = \text{Unknown}$$

$$\Delta H_{298.15}^\circ = -114 \pm 2 \text{ kcal/mol}$$

$$\Delta H_m^\circ = [4 \pm 2] \text{ kcal/mol}$$

$$S_{298.15}^\circ = [53.5 \pm 3] \text{ gibbs/mol}$$

$$T_m = 590^\circ\text{K}$$

Heat of Formation

The adopted $\Delta H_f^\circ = -114$ kcal/mol was determined by Shchukarev et al. (1) by solution calorimetry. The authors measured the heat of solution of MoCl₄ in the aqueous solvent FeCl₃ + HCl and obtained the heat of formation from a comparison with the heat of solution of MoCl₅ measured in the same solvent.

The decomposition pressures of 2MoCl₅(c) = 2MoCl₄(c) + Cl₂(g) (80 - 150°C) were measured manometrically by Saeki and Matsuzaki (2). From the reported data we evaluate the enthalpy change for the above reaction by third law analysis.

Based on ΔH_{298}° MoCl₅(c) = -126 kcal/mol and the third law $\Delta H_{298}^\circ = 24.132$ kcal/mol, we obtain ΔH_{298}° MoCl₄(c) = -113.94 kcal/mol, which is in very good agreement with the value reported by Shchukarev et al. (1).

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of WCl₄(c). The estimated $S_{298}^\circ = 53.5$ eu is based on the assumption that the entropy difference between MoCl₄(c) and MoCl₅(c) is about the same as that between WCl₄(c) and WCl₅(c). The entropy obtained from the second law analysis of the data of Saeki and Matsuzaki (2) agrees with the adopted one within the error of the vapor pressure data.

Melting Data

See liquid table.

References

1. S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Russ. J. Inorg. Chem. (English Transl.) 5, 802 (1960).
2. Y. Saeki and R. Matsuzaki, Denki Kagaku 33, 155-8 (1965).

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
0							
100							
200							
298	31.000	53.500	53.500	.000	-114.000	-96.136	70.470
300	31.000	53.492	53.501	.057	-113.984	-96.026	69.955
400	32.300	42.768	54.732	3.222	-113.069	-90.177	49.270
500	33.600	70.135	57.100	6.517	-112.096	-84.564	36.963
600	34.900	76.376	59.605	9.942	-111.040	-79.155	26.812
700	36.200	81.652	62.572	13.497	-109.684	-73.931	23.042
800	37.400	86.779	65.294	17.187	-108.618	-68.682	18.618
900	38.500	91.285	67.935	21.015	-107.428	-63.995	15.540
1000	39.900	95.436	70.481	24.956	-105.741	-59.273	12.984
1100	40.800	99.282	72.926	28.992	-104.173	-54.700	10.468
1200	41.600	102.668	75.276	33.113	-102.538	-50.276	9.156
1300	42.200	106.222	77.527	37.304	-100.852	-45.968	7.731
1400	42.700	109.368	79.690	41.549	-99.133	-41.832	6.530
1500	43.200	112.331	81.768	45.844	-97.387	-37.799	5.507

Molybdenum Tetrachloride (MoCl_4)
(Liquid) $\text{GFW} = 237.752$

T, °K	C_p°	S°	$-(C^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0							
100							
200							
298	35,000	58.682	58.682	0.000	-110.621	-64.302	69.125
300	35,000	58.699	58.683	0.065	-110.597	-94.202	68.626
400	35,000	66.967	60.055	3.565	-109.347	-88.927	48.566
500	35,000	76.777	62.648	7.065	-108.169	-83.959	36.698
600	35,000	83.158	62.251	10.082	-107.038	-79.223	28.487
700	35,000	86.358	61.935	13.098	-105.937	-74.258	23.115
800	35,000	88.228	61.672	16.065	-104.861	-70.285	19.201
900	35,000	89.350	61.445	19.065	-103.799	-66.024	16.03
1000	35,000	101.038	76.473	24.565	-102.753	-61.886	13.425
1100	35,000	104.373	78.660	28.068	-101.721	-57.868	11.493
1200	35,000	107.119	81.445	31.565	-100.707	-53.904	9.418
1300	35,000	110.220	83.247	35.065	-99.712	-50.046	8.414
1400	35,000	112.814	85.268	38.565	-98.738	-46.262	7.222
1500	35,000	115.229	87.186	42.065	-97.787	-42.546	6.199

MOLYBDENUM TETRACHLORIDE (MoCl_4)

(LIQUID)

$\text{GFW} = 237.752$



$S^\circ_{298.15} = [58.682] \text{ gibbs/mol}$

$\Delta H_f^\circ_{298.15} = [-110.621 \pm 2] \text{ kcal/mol}$

$T_m = 580^\circ\text{K}$

$\Delta H_m^\circ = [4 \pm 2] \text{ kcal/mol}$

$T_b = [580]^\circ\text{K}$

$\Delta H_v^\circ = [14.7] \text{ kcal/mol}$

Heat of Formation

The heat of formation is obtained from $\Delta H_f^\circ(c)$ by adding ΔH_m° and the difference between $H^\circ_{590} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7 gibbs/g-atom. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from V. Gutmann, "Halogen Chemistry," Vol. 3, Academic Press, New York, 1987. ΔH_m° is estimated such that the derived ΔG_f° for $\text{MoCl}_4(l)$ yields a reasonable boiling point which is expected to be between 600 and 700°K from comparisons with related compounds.

Vaporization Data

T_b is the temperature at which the Gibbs energy change (ΔG_r°) of the following process $\text{MoCl}_4(l) = \text{MoCl}_4(g)$ approaches zero. The difference between ΔH_f° for $\text{MoCl}_4(l)$ and $\text{MoCl}_4(g)$ at T_b is the heat of vaporization.

Molybdenum Tetrachloride (MoCl₄)

(Ideal Gas)

GFW = 237.752

Point Group T_d $\Delta H_f^\circ = -91.8 \pm 3 \text{ kcal/mol}$ $S_{298.15}^\circ = [88.9] \text{ gibbs/mol}$ $\Delta H_f^\circ = -92.0 \pm 3 \text{ kcal/mol}$

Ground State Quantum Weight = [3]

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	+000	INFINITE	INFINITE	5.321	-91.637	-91.637	INFINITE
100	16.547	66.724	108.140	-8.182	-92.167	-89.661	195.910
200	21.366	79.688	90.959	-2.214	-92.132	-87.116	95.196
298	23.448	86.669	+000	+000	-92.000	-84.661	52.073
300	23.473	89.014	86.669	+0.83	-91.998	-84.636	61.658
400	24.412	95.911	89.803	2.443	-91.444	-82.205	44.915
500	24.693	101.416	91.594	4.911	-91.702	-79.611	34.868
600	25.168	105.981	93.622	7.415	-91.567	-77.485	28.209
700	25.452	110.564	95.663	9.968	-91.468	-75.468	23.480
800	25.587	113.264	97.664	12.481	-91.378	-73.776	19.682
900	25.531	114.268	99.568	15.030	-91.213	-72.464	17.111
1000	25.587	118.961	101.375	17.567	-91.110	-69.167	14.898
1100	25.630	121.402	103.086	20.144	-91.017	-65.876	13.066
1200	25.691	123.693	104.243	22.800	-90.876	-61.319	10.309
1300	25.691	125.689	104.243	25.240	-90.876	-61.319	10.309
1400	25.714	127.594	107.701	27.650	-90.832	-59.047	9.218
1500	25.735	129.369	109.087	30.423	-90.808	-56.777	8.272
1600	25.756	131.030	110.407	32.997	-90.808	-54.509	7.446
1700	25.779	132.602	111.676	35.366	-90.808	-52.241	6.707
1800	25.799	134.066	112.870	38.134	-90.874	-49.968	6.067
1900	25.823	135.462	114.023	40.734	-90.942	-47.690	5.486
2000	25.844	136.787	115.128	43.317	-91.040	-45.414	4.963
2100	25.875	138.049	116.190	45.904	-91.159	-43.132	4.489
2200	25.913	139.253	117.217	48.491	-91.292	-40.852	4.062
2300	25.951	140.406	118.199	50.980	-91.432	-38.574	3.682
2400	25.987	141.510	119.143	53.680	-91.708	-36.232	3.299
2500	26.000	142.571	120.059	56.278	-91.977	-33.918	2.965
2600	26.035	143.591	120.945	58.680	-92.302	-31.567	2.665
2700	26.080	144.572	121.802	60.982	-92.674	-29.187	2.397
2800	26.101	145.524	122.637	63.194	-93.171	-26.687	2.099
2900	26.141	146.440	123.437	66.704	-93.800	-24.093	1.846
3000	26.177	147.326	124.219	69.322	-94.561	-21.874	1.594
3100	26.213	148.185	124.978	71.941	-95.454	-19.284	1.357
3200	26.248	149.020	125.717	74.564	-96.480	-16.604	1.134
3300	26.282	149.832	126.437	77.191	-97.640	-13.852	0.925
3400	26.315	150.611	127.135	79.821	-98.934	-11.055	0.727
3500	26.347	151.375	127.816	82.454	-101.927	-8.451	0.540
3600	26.378	152.117	128.481	85.090	-102.197	-5.977	0.363
3700	26.409	152.839	129.132	87.729	-102.743	-3.419	0.206
3800	26.439	153.540	129.763	90.372	-103.020	-2.076	0.116
3900	26.464	154.232	130.382	93.017	-103.432	-1.164	0.061
4000	26.490	154.903	130.996	95.664	-103.301	4.773	0.261
4100	26.514	155.557	131.578	98.315	-103.580	7.477	0.399
4200	26.539	156.206	132.126	100.962	-103.667	12.904	0.530
4300	26.563	156.842	132.653	103.608	-103.667	18.331	0.656
4400	26.586	157.432	133.277	106.279	-104.432	15.637	0.777
4500	26.599	158.029	133.921	108.934	-104.719	18.344	0.892
4600	26.617	158.614	134.553	111.599	-105.004	21.100	1.002
4700	26.639	159.187	135.168	114.275	-105.540	23.896	1.121
4800	26.664	160.297	135.991	119.591	-105.868	29.357	1.309
4900	26.677	160.836	136.384	122.258	-106.168	34.828	1.506
5000	26.689	161.384	136.869	124.926	-106.444	40.304	1.718
5100	26.699	161.941	137.346	127.594	-106.691	45.778	1.942
5200	26.712	162.501	137.813	130.264	-106.911	51.257	2.119
5300	26.723	163.068	138.273	132.934	-107.100	56.737	2.310
5400	26.721	162.691	138.273	135.611	-107.258	62.217	2.494
5500	26.730	163.381	138.725	138.284	-107.384	67.697	2.671
5600	26.739	163.663	139.169	140.961	-107.484	73.177	2.848
5700	26.748	164.001	140.037	143.633	-107.554	78.658	3.010
5800	26.753	164.309	140.961	146.309	-107.594	84.139	3.171
5900	26.759	164.589	141.759	148.985	-107.614	89.620	3.328
6000	26.765	164.709	142.478	151.661	-107.614	95.101	3.478

Dec. 31, 1968

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$

Electronic Levels and Quantum Weights

 $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ $\omega, \text{ cm}^{-1}$ </

Tungsten Oxytetrachloride (WOCl₄)

(Crystal) GFW = 341.6614

T, °K	Cp	gibbs/mol S° - (G° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
100						
200						
298	34,954	41,300	41,300	.000	-160.400	-131.305
300	35,000	41,516	41,301	.095	-160.383	-131.125
400	37,500	51,526	45,701	3.690	-159.162	-121.922
500	40,000	60,584	49,735	7.585	-158.160	-112.196
600	42,500	68,088	48,596	11.695	-156.756	-103.131
700	44,350	74,786	51,868	16.043	-155.174	-94.317
800	45,800	80,796	55,115	20.545	-153.476	-85.741
900	46,300	86,208	58,274	25.141	-151.709	-77.377
1000	46,900	91,118	61,317	29.801	-149.904	-69.215

(CRYSTAL)

S₂₉₈⁰.15 = [41.3 ± 4] gibbs/mol
Tm = 484°K
ΔHf₀⁰ = Unknown
ΔHf₂₉₈⁰.15 = -160.4 ± 2 kcal/mol
ΔHm⁰ = 10.846 ± 3 kcal/mol

Heat of Formation.

S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov¹ measured calorimetrically the heats of reaction (1) and (2) at 298°K as -131.5 ± 0.3 and -13.6 ± 0.1 kcal/mol, respectively. The reactions are given as follows:
(1) WOCl₄(c) + 6 NaOH(16.3 H₂O) → Na₂WO₄(190,000 H₂O) + 4 NaCl(50,000 H₂O) + 3 H₂O(l)
(2) H₂WO₄(c) + 2 NaOH(16.3 H₂O) → Na₂WO₄(20,000 H₂O) + 2 H₂O(l)
Based on these data and the heats of dilution for NaOH(aq)², and Na₂WO₄(aq)³, we obtain ΔHf₂₉₈⁰ = -118.0 ± 1.6 kcal/mol for WOCl₄(c) + 4OH⁻(∞H₂O) → H₂WO₄(c) + 4Cl⁻(∞H₂O) + H₂O(l). This leads to ΔHf₂₉₈⁰(WOCl₄,c) = -160.4 ± 2 kcal/mol, using ΔHf₂₉₈⁰(H₂WO₄,c) = -270.5 ± 0.4 kcal/mol⁴.

Heat Capacity and Entropy.

Cp₃₀₀ = 35.0 gibbs/mol is estimated using Kopp's rule. Since the melting point of WOCl₄(c) is approximately 500°K, which is relatively low for oxygen to reach its maximum contribution, we estimate Cp₅₀₀ = 40.0 gibbs/mol based on the values for WO₂(c), WO₃(c) and WCl₆(c).

The entropy, S₂₉₈⁰ = 41.3 eu, is calculated from ΔS₄₅₇⁰ = 44.5 eu for WOCl₄(c) → WOCl₄(g) obtained from the second law analysis of the vapor pressure equation given by S. A. Shchukarev and A. V. Suvorov⁴. See WOCl₄(g) table (Mar. 31, 1967) for details.

It is surprising that this entropy is smaller than the corresponding value for WOF₄(c). See WOF₄(c) table (Mar. 31, 1967) for details.

Melting Data.

Tm is calculated as the temperature at which the gibbs energies of formation of crystal and liquid are equal. The difference between the heats of formation of crystal and liquid at the melting point is ΔHm⁰. This ΔHm⁰ is derived from 2nd law analyses of the vapor pressure equation determined by Shchukarev and Suvorov⁴. See WOCl₄(l,g) tables (Mar. 31, 1967) for details.

References.

1. S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. **3**, 2642 (1958).
2. "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NBSOS-NBS2, Natl. Bur. Std., Washington, D.C., Apr. 1965.
3. We have assumed ΔH⁰dil = 0 ± 0.5 kcal/mol for Na₂WO₄(20,000 H₂O) → Na₂WO₄(190,000 H₂O).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev et al., Zh. Neorg. Khim. **2**, 357 (1956), **3**, 2650 (1958), **5**, 1650 (1960), have been revised and they are not used here.
5. JANAF H₂WO₄(c) table dated Mar. 31, 1967.

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^b	ΔG ^c	Log K _p
100							
200							
298							
400	43.500	60.600	60.600	.000	-150.711	-127.370	93.365
500	43.500	60.869	60.601	.080	-150.678	-127.226	92.684
600	43.500	61.183	62.307	.410	-149.533	-119.273	89.307
700	43.500	61.500	65.559	.870	-147.255	-115.554	86.167
800	43.500	61.821	69.137	13.130	-143.432	-105.767	81.526
900	43.500	62.155	72.734	17.480	-138.048	-99.249	76.987
1000	43.500	62.500	76.247	21.830	-132.502	-92.957	72.395
	43.500	106.659	79.569	26.180	-140.981	-86.558	67.091
	43.500	113.242	82.711	30.530	-139.486	-80.921	62.665

Mar. 31, 1967

TUNGSTEN OXYTETRACHLORIDE (WOCl₄)

(LIQUID)

OPW = 341.6614

S^o_{298.15} = [60.6 ± 4] gibbs/mol

ΔH^o_{298.15} = -150.711 kcal/mol

T_m = 484°K

ΔH^o_m = 10.846 ± 3 kcal/mol

T_b = 493°K

ΔH^o_v = 10.5 kcal/mol

Heat of Formation.

The heat of formation, ΔH^o_{f298}(WOCl₄, l) = -150.711 kcal/mol, is calculated from that of the gas by subtracting the heat of vaporization ΔH^o_{v298} = 13.643 kcal/mol. The latter is obtained by the third law method from the vapor pressure equation given by S. A. Shchukarev* and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Second law analysis gives ΔH^o_{f501.9} = 10.32 kcal/mol (ΔH^o_{f298} = 13.643 kcal/mol) and the boiling point T_b = 493°K. *Earlier data reported by Shchukarev et al., Zh. Neorg. Khim. 1, 357 (1956); 2, 2630(1958); and 3, 1650 (1960), have been revised and they are not used here.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom as suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1959.

The entropy, S^o₂₉₈ = 80.8 eu, is calculated from ΔS^o_{f298} = 20.9 eu for WOCl₄(l) → WOCl₄(g) obtained from the second law analysis of the vapor pressure equation given by Shchukarev and Suvorov, loc. cit.

Melting Data.

See WOCl₄(c) table (Mar. 31, 1967) for details.

Vaporization Data.

T_b is calculated as the temperature at which the Gibbs energies of formation of liquid and gas are equal. The difference between the heats of formation of liquid and gas at the boiling point is ΔH^o_v.

Tungsten Oxytetrachloride (WOCl₄)

(Ideal Gas) GFW = 341.6614

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	kcal/mol	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	-135.776	-	INFINITE
100	15.000	47.008	100.000	-	-136.533	-	789.503
200	22.652	67.084	100.000	-	-137.283	-	789.503
250	25.367	90.097	100.000	-	-137.668	-	79.811
300	25.414	90.254	90.097	0.047	-137.069	-122.432	89.191
400	27.395	97.859	81.121	2.692	-137.024	-117.557	84.230
500	28.631	104.115	93.113	5.501	-136.891	-112.703	49.282
600	29.436	109.412	95.399	5.408	-136.711	-107.881	39.296
700	29.981	113.993	97.736	11.380	-136.505	-103.092	32.187
800	30.362	118.022	100.025	11.398	-136.291	-98.336	26.664
900	30.637	121.615	102.228	17.449	-136.069	-93.403	22.730
1000	30.842	124.854	104.331	20.323	-135.850	-88.397	19.428
1100	30.998	127.802	106.333	23.414	-135.635	-84.214	16.732
1200	31.119	130.504	108.236	26.722	-135.428	-79.547	14.486
1300	31.215	132.999	110.046	29.339	-135.230	-74.599	12.592
1400	31.282	135.315	111.769	32.964	-135.041	-70.264	10.969
1500	31.334	137.476	113.412	36.996	-134.865	-65.844	9.564
1600	31.406	139.501	114.980	39.235	-134.700	-61.038	8.337
1700	31.449	141.407	116.479	42.377	-134.547	-56.333	7.255
1800	31.466	143.205	117.914	45.524	-134.409	-51.544	6.295
1900	31.517	144.909	119.290	48.674	-134.283	-47.258	5.436
2000	31.543	146.526	120.612	51.827	-134.175	-42.681	4.664
2100	31.566	148.065	121.883	54.981	-134.079	-38.109	3.966
2200	31.586	149.534	123.107	58.141	-134.002	-33.544	3.332
2300	31.604	150.939	124.287	61.300	-133.939	-28.977	2.753
2400	31.619	152.288	125.425	64.461	-133.893	-24.412	2.223
2500	31.633	153.575	126.526	67.624	-133.866	-19.854	1.736
2600	31.645	154.816	127.590	70.784	-133.854	-15.292	1.295
2700	31.656	156.011	128.621	73.951	-133.867	-10.734	0.891
2800	31.665	157.162	129.620	77.119	-133.914	-6.164	0.541
2900	31.674	158.273	130.589	80.286	-134.002	-1.604	0.211
3000	31.682	159.347	131.529	83.454	-134.138	2.960	-
3100	31.689	160.386	132.444	86.622	-134.335	7.532	-
3200	31.695	161.392	133.333	89.791	-134.599	12.111	-
3300	31.701	162.368	134.198	92.961	-134.936	16.700	-
3400	31.707	163.314	135.040	96.132	-135.354	21.306	-
3500	31.712	164.234	135.861	99.303	-135.869	25.913	-
3600	31.716	165.127	136.662	102.474	-136.504	30.549	-
3700	31.720	165.996	137.443	105.644	-145.591	35.246	-
3800	31.724	166.842	138.206	108.818	-145.677	40.133	-
3900	31.728	167.666	138.951	111.991	-145.771	45.227	-
4000	31.731	168.469	139.678	115.164	-145.872	49.220	-
4100	31.734	169.253	140.390	118.337	-145.976	53.113	-
4200	31.737	170.018	141.087	121.510	-146.087	56.919	-
4300	31.740	170.765	141.768	124.684	-146.201	60.641	-
4400	31.742	171.494	142.436	127.854	-146.321	64.281	-
4500	31.744	172.208	143.089	131.033	-146.445	67.820	-
4600	31.746	172.905	143.730	134.207	-146.570	71.336	-
4700	31.748	173.588	144.356	137.382	-146.700	74.825	-
4800	31.750	174.256	144.974	140.557	-146.833	78.291	-
4900	31.752	174.911	145.578	143.731	-146.968	81.744	-
5000	31.754	175.553	146.171	146.907	-147.104	85.198	-
5100	31.755	176.182	146.754	150.083	-147.241	88.654	-
5200	31.757	176.798	147.325	153.259	-147.381	92.111	-
5300	31.758	177.403	147.897	156.434	-147.522	95.568	-
5400	31.760	177.997	148.459	159.610	-147.665	99.021	-
5500	31.761	178.579	149.022	162.786	-147.807	102.474	-
5600	31.762	179.152	149.516	165.962	-147.951	105.929	-
5700	31.763	179.714	150.041	169.138	-148.097	109.381	-
5800	31.764	180.266	150.537	172.315	-148.241	112.831	-
5900	31.765	180.809	151.005	175.491	-148.386	116.274	-
6000	31.766	181.343	151.505	178.664	-148.539	119.714	-

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRACHLORIDE (WOCl₄)

(IDEAL GAS)

OPW = 341.6614

Point Group [C_{2v}]

ΔH°₀ = -135.8 ± 5 kcal/mol

S°_{298.15} = [90.1] gibbs/mol

ΔH°_{298.15} = -137.0 ± 5 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

W, cm ⁻¹	W, cm ⁻¹	W, cm ⁻¹
[1000] (1)	[350] (1)	[200] (1)
[1000] (1)	[350] (1)	[200] (1)
[480] (1)	[300] (1)	[100] (1)
[480] (1)	[300] (1)	[100] (1)
[480] (1)	[300] (1)	[100] (1)

Bond Distances: W-Cl = [2.26] Å W-O = [1.81] Å

Bond Angle: Cl-W-O* = Cl-W-Cl* = [120°]

Cl-W-Cl** = Cl-W-O* = [90°]

Cl-W-Cl** = [180°]

*Equatorial **Axial

Product of the Moments of Inertia: I_AI_BI_C = [5.873 x 10⁻¹¹²] g³ cm⁶

Heat of Formation

The heat of formation, ΔH°₂₉₈(WOCl₄, g) = -137.0 kcal/mol, is calculated from ΔH°₂₉₈ = 23.4 kcal/mol for WOCl₄(c) → WOCl₄(g). The latter is obtained by the third law method from the vapor pressure equation given by S. A. Shchukarev* and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Second law analysis gives ΔH°₂₉₈ = 23.4 kcal/mol.

*Earlier data reported by Shchukarev et al., Zh. Neorg. Khim. 1, 357 (1956), 3, 2630 (1956), 5, 1650 (1960), have been revised and they are not used here.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of SOP₄(g), reported by P. L. Goggin, H. L. Roberts and L. A. Woodward¹. The bond distances W-O and W-Cl are estimated to be the same as those in WO₃(g) and WOCl₂(g), respectively. The three principal moments of inertia are I_A = 8.260 x 10⁻³⁶, I_B = 1.052 x 10⁻³⁷ and I_C = 6.757 x 10⁻³⁶ g cm².

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for SOP₄(g)², WOCl₂(g)³, CrO₂Cl₂(g)^{4,5}, WO₃(g)⁶, and WOCl₆(g)⁶. The frequencies are not listed in point group order.

References

1. P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. 57, 1877 (1961).
2. T. V. Iorns and P. E. Starford, J. Am. Chem. Soc. 88, 4819 (1966).
3. C. G. Barracough and J. Stals, Aust. J. Chem. 19, 741 (1966).
4. P. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta 1959, 709 (1959).
5. H. Stammreich, K. Kawai and Y. Tavares, Spectrochim. Acta 1959, 438 (1959).
6. JANAF WO₃(g) table (Sept. 30, 1966), WOCl₆(g) table (Dec. 31, 1966).

CIOW

Lead Tetrachloride (PbCl₄)
(Ideal Gas) Mol. Wt. = 349.04

INTERIM TABLE

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0							
100	10.070	48.470	112.093	5.4631	74.631	74.631	INFINITE
200	24.499	92.592	94.084	4.362	74.155	72.084	157.532
298	34.194	91.919	91.919	2.300	73.138	68.998	75.383
300	34.194	91.919	91.919	2.300	73.138	68.998	75.383
400	24.183	92.064	91.919	.045	74.997	65.957	68.047
500	24.675	99.121	92.476	2.494	74.456	62.966	34.401
600	25.180	104.704	94.703	5.000	74.733	60.007	26.228
700	25.374	109.313	96.795	7.329	74.632	57.071	20.787
800	25.374	113.234	100.845	9.073	74.714	53.461	16.847
900	25.374	116.459	102.765	10.186	74.568	49.763	13.258
1000	25.665	119.459	104.610	11.517	74.517	46.676	9.764
1100	25.694	124.809	106.337	20.319	75.442	41.596	6.264
1200	25.714	127.066	109.514	25.282	75.282	38.222	4.015
1300	25.714	129.129	111.843	28.343	75.282	35.282	2.493
1400	25.748	131.032	113.086	29.036	74.199	32.396	1.507
1500	25.769	132.769	112.381	30.412	74.119	29.340	4.275
1600	25.766	134.452	111.709	33.148	75.046	26.291	3.591
1700	25.762	136.088	110.166	36.343	74.914	23.202	2.893
1800	25.762	137.682	108.734	40.922	74.857	17.164	1.974
1900	25.762	139.235	107.404	43.901	74.811	14.129	1.544
2000	25.762	140.750	106.170	46.080	117.220	9.545	.993
2100	25.762	142.235	105.035	48.343	116.995	4.700	.007
2200	25.762	143.688	103.900	50.688	116.919	5.816	.530
2300	25.607	145.092	102.765	52.402	116.871	10.927	.995
2400	25.607	146.452	101.629	54.582	116.846	16.039	1.348
2500	25.607	147.766	100.494	56.922	116.846	21.149	1.712
2600	25.607	149.035	99.359	59.407	116.846	26.259	2.083
2700	25.607	150.266	98.224	61.942	116.846	31.369	2.454
2800	25.607	151.459	97.089	64.527	116.846	36.479	2.825
2900	25.607	152.613	95.954	67.162	116.846	41.589	3.196
3000	25.607	153.727	94.819	69.847	116.846	46.699	3.566
3100	25.617	154.801	93.684	72.582	117.098	41.606	2.933
3200	25.617	155.835	92.549	75.367	117.256	36.513	2.300
3300	25.617	156.829	91.414	78.202	117.420	31.420	1.667
3400	25.617	157.782	90.279	81.087	117.588	26.327	1.034
3500	25.621	158.695	89.144	84.022	117.759	21.234	.401
3600	25.621	159.568	87.009	87.009	117.932	16.141	-.233
3700	25.621	160.401	84.874	90.094	118.107	11.048	-.566
3800	25.621	161.195	82.739	93.279	118.284	6.955	-.900
3900	25.621	161.949	80.604	96.564	118.462	2.862	1.233
4000	25.621	162.663	78.469	100.000	118.642	-1.233	1.566
4100	25.624	163.337	76.334	103.587	118.824	-3.337	1.899
4200	25.624	163.970	74.199	107.322	119.009	-5.442	2.232
4300	25.624	164.563	72.064	111.107	119.197	-7.547	2.565
4400	25.624	165.116	69.929	114.946	119.388	-9.652	2.898
4500	25.624	165.639	67.794	118.839	119.581	-11.757	3.231
4600	25.624	166.132	65.659	122.788	119.776	-13.862	3.564
4700	25.624	166.595	63.524	126.793	119.973	-15.967	3.897
4800	25.624	167.028	61.389	130.854	120.172	-18.072	4.230
4900	25.624	167.431	59.254	134.969	120.373	-20.177	4.563
5000	25.624	167.804	57.119	139.139	120.576	-22.282	4.896
5100	25.624	168.147	54.984	143.364	120.781	-24.387	5.229
5200	25.624	168.460	52.849	147.644	120.987	-26.492	5.562
5300	25.624	168.743	50.714	151.979	121.194	-28.597	5.895
5400	25.624	169.006	48.579	156.369	121.402	-30.702	6.228
5500	25.624	169.249	46.444	160.814	121.611	-32.807	6.561
5600	25.624	169.472	44.309	165.314	121.821	-34.912	6.894
5700	25.624	169.675	42.174	169.869	122.032	-37.017	7.227
5800	25.624	169.858	40.039	174.479	122.243	-39.122	7.560
5900	25.624	170.021	37.904	179.144	122.454	-41.227	7.893
6000	25.624	170.164	35.769	183.864	122.665	-43.332	8.226

June 30, 1962

Lead Tetrachloride (PbCl₄) (Ideal Gas)

Mol. Wt. = 349.04
ΔH_f⁰ 298.15 = [-75] kcal. mole⁻¹
ΔG_f⁰ 298.15 = 91.9 cal. deg.⁻¹ mole⁻¹
Point group T_d

Vibrational Levels and Multiplicities

ω, cm. ⁻¹
326 (1)
85 (2)
341 (3)
99 (3)

Pb-Cl distance = 2.43 Å
I_AB₂C = 7.9660 X 10⁻¹¹² g.³ cm.⁶
σ⁻ = 12

Heat of Formation. ΔH_f⁰ 298.15 was estimated from the value of ΔH_f⁰ 298.15 for PbCl₂(s), using the relation between ΔH_f⁰ 298.15 for dihalides and that for tetrahalides of titanium and zirconium as reference.

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagarajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

Cl₄Pb

Cl₄Pb

Titanium Tetrachloride (TiCl₄)

(Crystal)

GFW = 189.712

Cl₄Ti

(CRYSTAL)

TITANIUM TETRACHLORIDE (TiCl₄)

GFW = 189.712

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	20.000	22.000	INFINITE	6.437	-195.704	-195.704	INFINITE
100	24.441	26.441	52.654	2.665	-195.536	-195.536	43.103
200	26.859	28.329	52.654	2.665	-195.536	-195.536	43.103
298	30.943	33.927	49.927	2.000	-194.607	-175.733	126.616
300	31.000	50.119	49.928	3.057	-194.791	-175.614	127.935
400	33.350	59.360	51.174	3.282	-193.644	-169.361	92.535
500	34.600	66.994	53.600	6.697	-192.781	-163.361	71.405

S°_{298.15} = 49.93 ± 0.1 gibbs/mol
Tm = 249.05°K
ΔHf°₀ = -195.7 ± 1.0 kcal/mol
ΔHf°_{298.15} = -194.807 ± 1.0 kcal/mol
ΔHm° = 2.382 kcal/mol

Heat of Formation

The heat of formation, ΔHf°₂₉₈ of TiCl₄(c) is calculated from the corresponding quantity for TiCl₄(l) and the values of H°_{298.05} - H°_{298.15} for both crystal and liquid.

Heat Capacity and Entropy

The heat capacity of TiCl₄(c) has been reported by Latimer (1) and by Furukawa (2). The data from the latter investigation are adopted. These data lead to a value of 44.5 eu for S°_{249.05}. This compares with Latimer's value (1) of 43.8 eu for the same quantity. The heat capacity of the solid is extrapolated to a value of 18R at 600°K, based on the known heat capacities of TiBr₄(c) and TiI₄(c). The hypothetical entropy at 298°K is based on the integration of the extrapolated curve and the value at the melting point.

Melting Data

The triple point is reported to be 249.05°K, with a measured heat of fusion of 2.382 kcal/mol, by Furukawa (2). Latimer (1) reported values of 248.0°K and 2.233 kcal/mol for these quantities. The former data are adopted.

References

1. W. M. Latimer, J. Am. Chem. Soc. 44, 90 (1922).
2. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1954.

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1957

Cl₄Ti

Titanium Tetrachloride (TiCl₄)

(Liquid)

GFW = 189.712

T, °K	C _p ^a	S ^b	-(C _p ^a - H ²⁹⁸)/T	H ^c - H ²⁹⁸	ΔH ^f	ΔG ^f	Log K _p
100	34.584	46.428	63.406	-3.400	-193.496	-181.719	198.573
200	34.704	60.326	60.326	.000	-192.200	-176.226	159.177
298							
300	34.709	60.581	60.327	.064	-192.177	-176.127	128.308
400	34.936	70.557	61.691	3.547	-190.972	-170.961	93.408
500	35.153	78.376	64.274	7.051	-189.820	-168.091	72.598
600	35.370	84.805	67.176	10.577	-188.698	-161.452	58.809
700	35.586	90.253	70.995	14.123	-187.505	-152.704	47.177
800	35.798	94.843	74.801	17.685	-186.243	-142.717	37.483
900	36.020	99.269	78.618	21.285	-185.030	-148.542	36.071
1000	36.237	103.075	81.177	24.898	-184.369	-144.503	31.581

TITANIUM TETRACHLORIDE (TiCl₄)

(LIQUID)

GFW = 189.712

S^{298.15} = 60.326 gibbs/molΔH^{f298.15} = -192.2 ± 0.9 kcal/molT_m = 249.05°KΔH_m^o = 2.382 kcal/molT_b = 409°KΔH_v^o = 8.55 kcal/mol

Heat of Formation

The heat of formation, ΔH^{f298.15}, of TiCl₄(l) is calculated from that of TiCl₄(g) and the value of ΔH_v^{298.15}. The value of ΔH_v²⁹⁸ is determined from second and third law analyses of fugacity as follows.

Source	Method	Range	No. Pts.	2nd Law	3rd Law	Drift, eu	ΔH ^f ₂₉₈
1. Pike and Foster (1959) (1)	Manometric	363-415	18*	9.82±0.02	9.83	0.0±0.1	-192.2
2. Seryakov et al. (1960) (2)	Manometric	358-412	8	9.79±0.03	9.84	0.1±0.1	-192.2
3. Schafer et al. (1953) (3)	Isoteniscope	313-358	17*	9.86±0.02	9.82	-0.1±0.0	-192.2
4. Schafer et al. (1953) (3)	Isoteniscope	313-357	16**	9.80±0.01	9.82	0.0±0.0	-192.2
5. Schafer et al. (1953) (3)	Isoteniscope	313-357	16	9.91±0.02	9.83	-0.2±0.1	-192.2
6. Schafer et al. (1953) (3)	Isoteniscope	312-359	17	9.90±0.02	9.83	-0.2±0.1	-192.2
7. Weed (1957) (4)	Manometric	298-319	***	9.79±0.01	9.82	0.1±0.0	-192.2
8. Weed (1957) (4)	Manometric	298-319	***	9.81±0.01	9.82	0.0±0.0	-192.2
9. Weed (1957) (4)	Spectra	250-302	***	9.69±0.01	9.80	0.4±0.0	-192.2

* two points rejected due to failure of a statistical test

** three points rejected due to failure of a statistical test

*** selected points from extensive data

Third law analyses of the several vapor pressure sets result in drifts which are proportional to the mean temperatures. Conversion of these data to fugacity eliminates this temperature dependence and the drifts are then scattered randomly about a constant value. This constant value is made to be essentially zero by methods described on the TiCl₄(g) table. The conversion to fugacity was made using Pitzer's method for normal fluids (5). The calculation was carried out using the value of 45.7 atm for the critical pressure, P_c, reported by Minzer (6) and estimated values of 643 ± 15°K for the critical temperature, T_c, and 0.23 ± 0.03 for the acentric constant, ω. Schafer et al. (2) reported a calorimetric determination of ΔH_v²⁹⁸. Their value of 9.9 ± 0.2 kcal/mol was used to check the reliability of their equipment, assuming that the vapor pressure data (3) gave a more accurate determination of ΔH_v²⁹⁸. The adopted value of ΔH_v²⁹⁸ is 9.82 ± 0.02 kcal/mol.

Heat Capacity and Entropy

The entropy and heat capacity of TiCl₄(l) has been measured by Furukawa (8). His reported values are adopted.

Melting Data

See TiCl₄(c) table for details.

Vaporization Data

The boiling temperature, T_b, is taken as the temperature at which K_p = 1 for the reaction TiCl₄(l) = TiCl₄(g). The vapor pressure data are discussed above.

References

1. F. P. Pike and C. T. Foster, Jr., *J. Chem. Eng. Data* **4**, 305 (1959).
2. G. V. Seryakov, S. A. Vaks, L. S. Sidorina, Zhur. Obshch. Khim **30**, 2130 (1960).
3. H. Schafer and F. Zeppenick, *Z. Anorg. Chem.* **272**, 274 (1953).
4. H. C. Weed, Ph.D. Thesis, The Ohio State University, 1957.
5. G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1961.
6. W. Minzer, Naturwissenschaften **45**, 126 (1958).
7. H. Schafer, G. Breil and G. Pfeiffer, *Z. Anorg. Chem.* **276**, 325 (1954).
8. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1964.

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	-0.000	-0.000	INFINITE	-5.166	-182.026	-182.026	INFINITE
100	16.117	63.412	103.421	-4.001	-182.387	-176.501	352.299
200	20.352	76.076	86.762	-2.900	-182.441	-176.501	352.299
298	22.352	84.793	95.793	-2.000	-182.400	-177.721	177.721
300	22.081	84.935	95.794	-0.042	-182.399	-173.667	126.516
400	24.008	91.690	85.707	2.393	-182.326	-170.767	23.303
500	24.610	97.118	87.464	4.827	-182.244	-167.886	73.393
600	24.942	101.639	89.461	7.307	-182.168	-165.022	40.109
700	25.183	105.504	91.481	9.815	-182.102	-162.171	50.632
800	25.330	108.677	93.451	12.341	-182.058	-159.328	43.526
900	25.433	111.467	95.334	14.879	-182.036	-156.486	38.000
1000	25.507	114.551	97.124	17.427	-182.040	-153.650	33.580
1100	25.563	116.985	98.421	19.980	-182.070	-150.943	29.943
1200	25.603	119.211	100.426	22.539	-182.063	-147.927	26.941
1300	25.639	121.262	102.193	25.101	-182.019	-144.001	24.377
1400	25.665	123.163	103.401	27.666	-182.991	-142.076	22.179
1500	25.686	124.934	104.778	30.234	-182.980	-139.156	20.275
1600	25.704	126.582	106.090	32.803	-182.990	-136.233	18.609
1700	25.719	128.151	107.343	35.375	-183.019	-133.308	17.136
1800	25.731	129.622	108.540	37.947	-183.074	-130.385	15.631
1900	25.741	131.013	109.686	40.521	-183.151	-127.453	14.660
2000	25.750	132.334	110.766	43.095	-183.245	-124.526	13.590
2100	25.756	133.590	111.842	45.671	-183.360	-121.598	12.413
2200	25.765	134.784	112.856	48.247	-183.499	-118.624	11.175
2300	25.770	135.934	113.837	50.824	-183.630	-115.642	10.912
2400	25.776	137.031	114.781	53.401	-183.745	-112.657	10.168
2500	25.780	138.083	115.697	55.979	-183.845	-109.666	9.462
2600	25.784	139.094	116.573	58.557	-183.927	-106.666	8.849
2700	25.788	140.066	117.425	61.135	-184.000	-103.666	8.262
2800	25.791	141.006	118.250	63.714	-184.058	-100.666	7.717
2900	25.794	141.911	119.051	66.294	-184.100	-97.666	7.209
3000	25.796	142.785	119.827	68.873	-184.127	-94.666	6.735
3100	25.799	143.631	120.586	71.453	-184.145	-91.666	6.291
3200	25.801	144.450	121.315	74.033	-184.155	-88.666	5.874
3300	25.803	145.244	122.026	76.613	-184.158	-85.666	5.482
3400	25.804	146.014	122.722	79.193	-184.155	-82.666	5.113
3500	25.806	146.762	123.396	81.774	-184.145	-79.666	4.765
3600	25.807	147.489	124.056	84.355	-184.125	-76.666	4.420
3700	25.809	148.197	124.700	86.935	-184.095	-73.666	4.081
3800	25.810	148.885	125.328	89.516	-184.055	-70.666	3.748
3900	25.811	149.555	125.940	92.097	-184.005	-67.666	3.421
4000	25.812	150.209	126.539	94.679	-183.945	-64.666	3.097
4100	25.813	150.846	127.124	97.260	-183.875	-61.666	2.784
4200	25.814	151.466	127.696	99.841	-183.795	-58.666	2.481
4300	25.815	152.076	128.256	102.423	-183.705	-55.666	2.188
4400	25.816	152.669	128.804	105.004	-183.605	-52.666	1.904
4500	25.817	153.249	129.341	107.586	-183.505	-49.666	1.631
4600	25.817	153.817	129.867	110.168	-183.405	-46.666	1.368
4700	25.818	154.372	130.383	112.749	-183.305	-43.666	1.115
4800	25.819	154.916	130.886	115.331	-183.205	-40.666	0.872
4900	25.819	155.448	131.384	117.913	-183.105	-37.666	0.639
5000	25.820	155.969	131.870	120.495	-183.005	-34.666	0.416
5100	25.820	156.481	132.348	123.077	-182.905	-31.666	0.203
5200	25.821	156.982	132.817	125.659	-182.805	-28.666	0.000
5300	25.821	157.474	133.278	128.241	-182.705	-25.666	-0.203
5400	25.822	157.957	133.730	130.823	-182.605	-22.666	-0.416
5500	25.822	158.431	134.175	133.405	-182.505	-19.666	-0.639
5600	25.823	158.896	134.615	135.988	-182.405	-16.666	-0.872
5700	25.823	159.353	135.042	138.570	-182.305	-13.666	-1.115
5800	25.823	159.802	135.465	141.152	-182.205	-10.666	-1.368
5900	25.824	160.243	135.882	143.735	-182.105	-7.666	-1.631
6000	25.824	160.677	136.291	146.317	-182.005	-4.666	-1.904

Sept. 30, 1961; Mar. 31, 1964; Dec. 31, 1967

TITANIUM TETRACHLORIDE (TiCl₄)

(IDEAL GAS)

GFW = 189.712

Point Group T_dS₂₉₈ = 84.8 ± 0.7 gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies
ω, cm⁻¹ ω, cm⁻¹388 (1) 498.5 (3)
111 (2) 131 (3)Bond Distance: Ti-Cl = 2.185 Å
Bond Angle: Cl-Ti-Cl = 109° 28'Product of the Moments of Inertia: I_AI_BI_C = 4.2092 × 10⁻¹¹² g cm⁶

σ = 12

The heat of formation, ΔH_{f298}^o, of TiCl₄(g) and TiCl₄(l) has been measured by several investigators. The results of these measurements are as follows.

Investigations

Johnson et al. (1959) (1)
Farber and Darnell (1955) (2)
Shinner and Ruchwein (1955) (3)
Gross et al. (1957) (4)
Krievie et al. (1956) (5)
Thomsen (1982) (6)

Method

Calorimetric
Equilibrium
Calorimetric
Calorimetric
Calorimetric

Reaction

Ti(c)+2Cl₂(g) = TiCl₄(g)
TiO₂(c)+4HCl(g) = TiCl₄(g)+2H₂O(g)
Ti(c)+xCl₂(g) = [TiCl₄(x-2)C₂] soln
Ti(c)+xCl₂(g) = [TiCl₄(x-2)C₂] soln
Ti(c)+xCl₂(g) = [TiCl₄(x-2)C₂] soln
TiCl₄(l)+2H₂O(l) = 4HCl(0.002 m)+TiO₂(c)ΔH_{f298}^o, kcal/mol(-192.2) -182.440.7
(-192.7) -182.940.5
-190.343.0 (-180.5)
-191.5±0.3 (-181.7)
-190.0±0.4 (-180.2)
-194.5 (-184.7)The chosen value of ΔH_{f298}^o is that reported by Johnson et al. (1). This investigation has the advantage of being independent of the heat of vaporization of chlorine and any heats of solution in deriving the value of the heat of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura et al. (2). The tetrahedral structure was established by the Raman work of Bhagavantam (3). The vibrational frequencies determined from the infrared and Raman spectra of TiCl₄ by Hawkins and Carpenter (3) are adjusted downward 8 cm⁻¹ for ν₂ and ν₄ so that the heats of vaporization determined by both second and third law methods are in agreement. See TiCl₄(l) table for details. The principal moments of inertia are: I_A = I_B = I_C = 74.943 × 10⁻³⁹ g cm².

References

1. W. H. Johnson, R. A. Nelson, and E. J. Prosen, J. Res. Natl. Bur. Std. 52A, 49 (1959).
2. M. Farber and M. Darnell, J. Chem. Phys. 23, 1460 (1955).
3. G. B. Skinner and R. A. Ruchwein, J. Phys. Chem. 59, 113 (1955).
4. P. Gross, C. Hayman, and D. L. Levi, Trans. Faraday Soc. 53, 1601 (1957).
5. W. F. Krievie, S. F. Vango, and D. M. Mason, J. Chem. Phys. 25, 519 (1956).
6. J. Thomsen, Thermochemische Untersuchungen, I. (Verlag, J. A. Barth, Leipzig, 1882).
7. H. Kimura, K. Kimura, M. Aoki, and S. Shibata, Bull. Chem. Soc. Japan 29, 95 (1956).
8. S. Bhagavantam, Indian J. Phys. 7, 79 (1932).
9. N. J. Hawkins and D. R. Carpenter, J. Chem. Phys. 23, 1700 (1955).

Cl₄WTungsten Tetrachloride (WCl₄)

GFW = 325.662

(Crystal)

QFW = 325.662

(CRYSTAL)

TUNGSTEN TETRACHLORIDE (WCl₄)

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
100						
200						
298	31.000	47.400	.000	105.900	85.939	62.987
300	31.030	47.592	.057	105.884	85.805	62.509
350	32.335	48.568	3.150	104.948	83.550	61.500
500	33.640	51.004	6.554	103.973	72.554	51.071
600	34.945	53.712	9.954	102.892	66.826	44.341
700	36.250	56.482	13.213	101.710	60.926	37.116
800	37.555	59.208	17.204	100.428	55.166	30.071
900	38.840	61.912	21.025	99.052	49.590	23.042
1000	39.720	64.397	24.165	97.527	44.117	16.035
1100	40.840	66.843	29.004	95.946	38.920	9.733
1200	41.570	69.192	33.126	94.299	33.807	6.157
1300	42.170	71.448	37.313	92.602	28.834	4.847
1400	42.700	73.609	41.557	90.863	23.994	3.746
1500	43.170	75.688	45.851	89.109	19.274	2.809
1600	43.600	77.697	50.190	87.285	14.683	2.006
1700	44.000	79.611	54.570	85.454	10.168	1.311
1800	44.400	81.465	58.990	83.598	5.859	.708
1900	44.760	83.263	63.449	81.717	1.856	.179
2000	45.100	85.052	67.942	79.816	-2.614	-.426

ΔHf° = Unknown

ΔHf°_{298.15} = -105.9 ± 15 kcal/molS°_{298.15} = [47.4] gibbs/mol

Td = [771]°K

Heat of Formation.

The heat of formation, ΔHf°₂₉₈(WCl₄, c) = -105.9 kcal/mol, is calculated from ΔHf°₂₉₈ = 58.9 kcal/mol for 3WCl₄(c) = WCl₂(c) + 2WCl₅(g). The value of ΔHf°₂₉₈ is calculated by the third law method from decomposition pressure data in the temperature range from 354°C to 436°C reported by S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The second law ΔHf°₂₉₈ = 73.6 ± 7.9 kcal/mol and the third law drift is -24 ± 12 eu, which would correspond to a total entropy discrepancy of -8 ± 4 eu per mole of WCl₄. This entropy discrepancy is probably within the combined uncertainty of the data and the estimated entropies for the three species. S. A. Shchukarev et al., Vestnik Leningrad. Univ. 14, No. 10, Ser. Fiz. i Khim., No. 2, 78 (1959), have shown that decomposition pressures are essentially independent of the composition in the solid phase until WCl₄(c) is almost completely decomposed to WCl₂(c). This is consistent with the assumption of solid phase activities of unity which we have used in the equilibrium analysis.

Heat Capacity and Entropy.

Cp₂₉₈ = 8.2 gibbs/g-atom and Cp₇₀₀ = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 700°, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy of WCl₄(c), S°₂₉₈ = 47.4 eu, is estimated by the method of W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, 1952.

Temperature of Decomposition.

Td is calculated as the temperature at which the Gibbs energy change of the reaction 3 WCl₄(c) = WCl₂(c) + 2 WCl₅(g) approaches zero. We have also derived an approximate value of decomposition temperature, Td = 744°K, by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by S. A. Shchukarev et al., Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The difference between the two decomposition temperatures is related to the second law entropy and the adopted entropy.

Cl₄W

(CRYSTAL)

ZIRCONIUM TETRACHLORIDE (ZrCl₄)

GFV = 233.032

Zirconium Tetrachloride (ZrCl₄)

GFV = 233.032

S_{298.15} = 43.36 ± 0.7 gibbs/mol $\Delta H_f^\circ = -234.42 \pm 0.28$ kcal/mol $\Delta H_f^\circ = -234.17 \pm 0.28$ kcal/mol $\Delta H_m = 12 \pm 3$ kcal/mol $\Delta H_{s,298.15}^\circ = 26.4 \pm 0.3$ kcal/molT₀ = 606.8°KT_m = 710°K

Heat of Formation

Gal'chenko et al. (1) determined the heat of formation of ZrCl₄(c) by the direct chlorination of the highly pure Zr metal in a bomb calorimeter. Complete chlorination of the metal was accomplished as indicated by the absence of unreacted metal and of lower chlorides. Their value, $\Delta H_f^\circ(\text{ZrCl}_4, c) = -234.17 \pm 0.28$ kcal/mol, is adopted in the tabulation.

Gross et al. (2) measured calorimetrically $\Delta H_{298}^\circ = -225.89$ kcal/mol for Zr(c) + 2Cl₂(g) + ZrCl₄(c). Corrections for the difference in heat content between liquid and gaseous chlorine at 25°C and 1 atm led to the value of standard heat of formation, $\Delta H_f^\circ(\text{ZrCl}_4, c) = -234.7 \pm 0.4$ kcal/mol, which is in good agreement with the value adopted. Siemonsen and Siemonsen (3) also measured the heat of formation by direct chlorination of the metal in an enameled bomb calorimeter. However, they did not report their detailed experimental procedure, neither the purity of their sample, nor the corrections. The value was given as $\Delta H_{298}^\circ = -231.9 \pm 0.5$ kcal/mol.

Heat Capacity and Entropy

Todd (4) measured the low temperature heat capacities from 52.6 to 296.7°K, and made an extrapolation to 0°K which yielded an entropy of 8.12 eu at 51°K. We have adopted the measured heat capacities, but have made our own extrapolation to 0°K, based on the ratio of the measured heat capacities of ZrF₄ (5), TiF₄ (6), and TiCl₄ (7) from 6° to 50°K. This extrapolation gives S₅₀ = 6.758 ± 0.7 eu which is used in the table. Coughlin and King (8) measured high temperature enthalpy data from 335.9° to 566.8°K by drop calorimetry. Their data are smoothly joined with Todd's low temperature heat capacities and adopted in the table.

Melting Data

The melting point, 710°K, has been observed by Rahlfs and Fischer (9), Palko et al. (10), Denisova et al. (11, 12).

Palko et al. derived the heat of melting as 9 ± 2.5 kcal/mol from their vapor pressure data. Denisova et al. (11, 12) determined thermographically the heat of melting as 14 ± 3 kcal/mol and also determined the heat of vaporization at 710°K as 10.4 kcal/mol combined with the heat of sublimation at 710°K (23.8 kcal/mol) gives the heat of melting as 13.4 kcal/mol. A weighted average 12 ± 3 kcal/mol is adopted for the heat of melting.

Heat of Sublimation

Several investigators have measured the vapor pressure of ZrCl₄(c) by the static method. Second and third law analyses for the vapor pressure data are summarized below:

Source	No. of Points	Temperature Range (°K)	$\Delta H_{s,298}^\circ$ (kcal/mol)	Drift (eu)
Rahlfs and Fischer (9)	11	535-607	27.516	26.379
Palko et al. (10)	86*	500-689	26.255	26.435
Denisova et al. (11)	17**	628-708	26.515	26.376
				44.81
				-0.29±0.51

* 4 points rejected due to failure of a statistical test.

** 1 point rejected due to failure of a statistical test.

The third law value, $\Delta H_{s,298}^\circ = 26.4$ kcal/mol, is adopted in the tabulation.

The sublimation temperature is obtained from the Gibbs free energy crossover between solid and gas. Rahlfs and Fischer (9) reported the sublimation temperature as 604°K.

Since the sublimation temperature is lower than the melting point, the liquid phase is thermodynamically unstable at normal conditions.

References

1. G. L. Gal'chenko, D. A. Gedakyan and B. T. Timofeev, Russ. J. Inorg. Chem. (Eng. transl.) **13**, 159 (1968).
2. P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. **53**, 1285 (1957).
3. H. Siemonsen and U. Siemonsen, Z. Elektrochem. **56**, 643 (1952).
4. S. S. Todd, J. Am. Chem. Soc. **72**, 2914 (1950).
5. E. F. Westrum, Jr., J. Chem. Eng. Data **10**, 140 (1965).
6. R. D. Eller and E. F. Westrum, Jr., J. Phys. Chem. **65**, 132 (1961).
7. G. T. Furukawa, private communication, U. S. Natl. Bur. Std., 1964.
8. J. P. Coughlin and E. G. King, J. Am. Chem. Soc. **72**, 2262 (1950).
9. O. Rahlfs and W. Fischer, Zeit. Anorg. Chem. **211**, 349 (1933).
10. A. A. Palko, A. D. Ryon and D. W. Kuhn, J. Phys. Chem. **62**, 319 (1958).
11. N. D. Denisova, E. K. Safronov and O. N. Bystrova, Russ. J. Inorg. Chem. (Eng. transl.) **11**, 1271 (1966).
12. N. D. Denisova, E. K. Safronov, A. I. Pustil'nik and O. N. Bystrova, Russ. J. Phys. Chem. (Eng. transl.) **51**, 30 (1967).

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Dec. 31, 1969

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	.000	INFINITE		5.957	-234.418	-234.418	INFINITE
100	18.640	16.652	66.682	4.983	-235.044	-227.368	466.912
200	25.680	32.445	55.905	2.692	-234.735	-219.772	240.156
298	28.630	43.360	43.360	.000	-234.170	-212.545	155.769
300	28.660	43.537	43.341	.053	-234.158	-212.610	154.741
400	29.970	51.982	44.503	2.991	-233.403	-205.259	112.148
500	30.760	58.759	46.699	6.030	-232.421	-194.276	66.666
600	31.380	64.420	49.193	9.136	-232.131	-191.432	69.799
700	31.820	69.268	51.724	12.598	-231.334	-184.704	57.667
800	32.120	73.266	54.284	16.442	-230.536	-174.536	41.655
900	32.600	77.389	56.561	19.745	-230.031	-171.536	36.077
1000	33.040	80.650	58.620	22.030	-229.323	-165.076	31.677

$\Delta H_f^\circ = -207.46 \pm 0.2 \text{ kcal/mol}$

$\Delta H_f^\circ = -207.77 \pm 0.2 \text{ kcal/mol}$

Point Group = T_d

$S_{298.15}^\circ = 88.0 \pm 0.2 \text{ gibbs/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	∞	∞	∞	∞	∞	∞
100	16.965	45.649	107.339	5.401	-207.462	INFINITE
200	21.485	76.974	90.076	4.169	-207.434	448.101
300	23.606	87.960	81.960	3.220	-207.463	220.961
400	24.430	95.031	86.915	2.446	-207.440	146.159
500	24.904	100.538	90.708	1.915	-207.436	105.260
600	25.176	105.105	92.738	1.627	-207.468	84.745
700	25.365	108.999	94.200	1.450	-207.467	69.629
800	25.456	112.391	96.782	1.287	-207.467	58.837
900	25.538	115.395	98.687	1.153	-207.447	50.744
1000	25.590	118.068	100.494	1.049	-207.339	44.450
1100	25.631	120.529	102.207	0.973	-207.360	39.416
1200	25.663	122.716	103.628	0.910	-207.410	35.295
1300	25.688	124.610	105.364	0.857	-208.341	31.851
1400	25.708	126.270	106.822	0.812	-208.271	28.933
1500	25.724	127.694	108.209	0.774	-208.214	26.432
1600	25.737	129.015	109.529	0.742	-208.171	24.266
1700	25.748	130.176	110.789	0.716	-208.142	22.370
1800	25.757	131.188	111.993	0.694	-208.123	20.697
1900	25.765	132.080	113.145	0.676	-208.120	19.211
2000	25.772	132.902	114.250	0.661	-208.129	17.881
2100	25.777	133.640	115.311	0.648	-208.154	16.684
2200	25.782	134.359	116.332	0.637	-208.190	15.601
2300	25.787	135.055	117.315	0.628	-208.245	14.598
2400	25.790	135.720	118.262	0.621	-213.304	13.677
2500	25.794	136.359	119.177	0.616	-213.367	12.832
2600	25.797	136.967	120.061	0.612	-213.436	12.055
2700	25.799	137.541	120.917	0.609	-213.507	11.337
2800	25.802	138.079	121.745	0.607	-213.583	10.673
2900	25.804	138.578	122.545	0.606	-213.665	10.055
3000	25.806	139.039	123.327	0.606	-213.750	9.480
3100	25.807	139.466	124.094	0.606	-213.842	8.943
3200	25.809	139.859	124.820	0.606	-213.939	8.440
3300	25.810	140.219	125.535	0.606	-214.043	7.969
3400	25.812	140.549	126.231	0.606	-214.152	7.524
3500	25.813	140.848	126.909	0.606	-214.264	7.108
3600	25.814	141.115	127.570	0.606	-214.385	6.715
3700	25.815	141.353	128.219	0.606	-214.510	6.343
3800	25.816	141.562	128.844	0.606	-214.640	5.991
3900	25.817	141.738	129.446	0.606	-214.775	5.657
4000	25.818	141.885	130.026	0.606	-214.915	5.340
4100	25.818	142.005	130.585	0.606	-215.061	5.039
4200	25.819	142.095	131.126	0.606	-215.210	4.752
4300	25.820	142.158	131.649	0.606	-215.364	4.479
4400	25.821	142.196	132.156	0.606	-215.520	4.219
4500	25.821	142.206	132.647	0.606	-215.680	3.969
4600	25.821	142.196	133.119	0.606	-215.844	3.731
4700	25.822	142.169	133.574	0.606	-216.008	3.503
4800	25.822	142.125	134.011	0.606	-216.175	3.285
4900	25.822	142.062	134.417	0.606	-216.342	3.078
5000	25.823	141.979	134.791	0.606	-216.509	2.882
5100	25.823	141.879	135.131	0.606	-216.676	2.696
5200	25.824	141.762	135.434	0.606	-216.842	2.520
5300	25.824	141.629	135.701	0.606	-217.008	2.354
5400	25.825	141.476	135.934	0.606	-217.174	2.200
5500	25.825	141.306	136.134	0.606	-217.339	2.057
5600	25.825	141.119	136.301	0.606	-217.504	1.924
5700	25.826	140.916	136.436	0.606	-217.668	1.801
5800	25.826	140.697	136.541	0.606	-217.831	1.688
5900	25.826	140.462	136.616	0.606	-217.994	1.584
6000	25.826	140.212	136.662	0.606	-218.156	1.489

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; Dec. 31, 1969

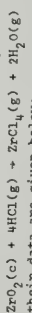
Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
376 (1)	418 (3)
99 (2)	110 (3)

Bond Distance: Zr-Cl = $2.32 \pm 0.02 \text{ \AA}$
Bond Angle: Cl-Zr-Cl = 109.2°
Product of the Moments of Inertia: $I_A I_B I_C = 6.03177 \times 10^{-112} \text{ g cm}^6$ $\sigma = 12$

Heat of Formation

The heat of formation of gaseous ZrCl_4 , $\Delta H_f^\circ = -207.77 \pm 0.2 \text{ kcal/mol}$, is calculated from the heat of formation of the crystal and the formation derived from vapor pressure data. (See JANAF ZrCl_4 (c) table dated Dec. 31, 1969). Hildenbrand et al. (1) determined the equilibrium constants by the transpiration method for the reaction:



Second and third law analyses for their data are given below:

Series	No. of Points	Temp. Range (°K)	ΔH_{298}° (kcal/mol)	Drift (eu)	ΔH_{298}° (g) (kcal/mol)
I	10	1171-1375	28.853	29.321	-205.6
II	9	1189-1374	31.397	30.007	-205.0

*Derived from third law ΔH_{298}° and ΔH_{298}° (ZrO_2 , c) = -262.3 kcal/mol , ΔH_{298}° (HCl , g) = -22.063 kcal/mol and ΔH_{298}° (H_2O , g) = -57.798 kcal/mol .

The derived heat of formation is in fair agreement with the value adopted.

Heat Capacity and Entropy

Spiridonov et al. (2) measured the bond distance $\text{Zr-Cl} = 2.32 \pm 0.02 \text{ \AA}$ in the vapor phase by electron diffraction. The molecule was also found to be a regular tetrahedron. The same bond distance was also reported by Lister and Sutton (3) and Kimura et al. (4). The three principal moments of inertia are $I_A = I_B = I_C = 84.4942 \times 10^{-39} \text{ g cm}^2$.

Wilmschurst (5) observed one fundamental vibrational frequency ($\nu_3 = 421 \text{ cm}^{-1}$) in the infrared spectrum of ZrCl_4 vapor, and made reasonable estimates ($\nu_1 = 388$, $\nu_2 = 102$ and $\nu_4 = 112 \text{ cm}^{-1}$) for the three remaining unobserved fundamentals, based on observed overtone and combination bands. Godnev et al. (6) calculated the four fundamental vibrational frequencies (382, 108, 423 and 114 cm^{-1}) from data for related group IV halides through the use of a 5-parameter potential function. Büchler et al. (7) also found in the infrared spectrum the vibrational frequency, $\nu_3 = 423 \text{ cm}^{-1}$. Delvaule and Francois (8) observed the symmetric stretching vibration ν_1 at 383 cm^{-1} from the Raman spectrum of ZrCl_4 in PCl_3 and POCl_3 , both of which form complexes with ZrCl_4 . Bobovich (9) reported the symmetric stretching vibration ν_1 at 315 cm^{-1} from a partially polarized band in his Raman spectrometric studies.

Pontrelli (10) observed in the Raman spectrum all four fundamental vibrational frequencies (376, 99, 418 and 110 cm^{-1}) which are adopted in the tabulation.

References

1. D. L. Hildenbrand, L. P. Theard, W. F. Hall, F. Ju, F. S. La Viola and M. D. Potter, Aeronutronic Div., Philco-Ford Corp., Newport, Calif., Pub. No. U-1734, N0661-0905-C, June, 1962.
2. V. P. Spiridonov, P. A. Akshinin and V. I. Tsirel'nikov, Zh. Strukt. Khim. **3**, 393 (1962).
3. M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941).
4. M. Kimura, R. Kimura, M. Aoki and S. Shibata, Bull. Chem. Soc. Japan **29**, 95 (1956).
5. J. K. Wilmschurst, J. Mol. Spectrosc. **5**, 343 (1960).
6. I. N. Godnev, A. M. Aleksandrovskaya, I. V. Nigina, Optics and Spectroscopy (Eng. transl.) **2**, 172 (1959).
7. A. Büchler, J. B. Berkowitz-Mattuck and D. H. Dugre, J. Chem. Phys. **34**, 2202 (1961).
8. M. L. Dewaulle and F. Francois, Bull. Soc. Chim. **13**, 205 (1946); J. Phys. Radium **7**, 15 (1946).
9. Ya. S. Bobovich, Optics and Spectroscopy (Eng. transl.) **11**, 85 (1961).
10. G. N. Pontrelli, Dissertation Abstract **23**, 4130 (1963).

Cl₅Mo

MOLYBDENUM PENTACHLORIDE (MoCl₅) (CRYSTAL)

GTW = 273.205

$\Delta H_f^\circ =$ unknown

$\Delta H_{298.15}^\circ = -126 \pm 2$ kcal/mol

$\Delta H_m^\circ = [4.5 \pm 1.5]$ kcal/mol

$S_{298.15}^\circ = [57 \pm 3]$ gibbs/mol

$T_m = 467^\circ K$

Heat of Formation

The heat of formation is obtained from S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. 5, 1650 (1960). The authors derived the ΔH_f° (MoCl₅, c) = -126 kcal/mol by measuring the heat of solution of MoCl₅ in NaOH(aq), which was compared with the heats of solution of MoO₃ and NaCl measured in the same solvent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of HCl₅(c). S_{298}° is estimated as 57 eu from the vapor pressure data for MoCl₅(c) + MoCl₅(g) measured by S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Transl.) 26, 2335 (1956).

Melting Data

See liquid table.

Molybdenum Pentachloride (MoCl₅)
(Crystal) GFW = 273.205

T, °K	Cp°	gibbs/mol $S^\circ - (G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0						
100						
200						
298	37.200	57.000	.000	-126.000	-101.236	74.208
300	37.220	57.210	.069	-125.980	-101.083	73.699
400	40.000	68.320	3.931	-124.783	-92.960	50.791
500	42.700	77.536	8.066	-123.396	-85.159	37.283
600	45.400	85.569	64.777	-121.790	-77.658	28.287
700	46.500	92.733	162.266	-118.709	-69.453	21.348
800	47.000	98.712	271.556	-114.011	-60.302	16.000
900	50.100	105.016	384.811	-107.942	-54.508	13.795
1000	50.900	110.337	498.374	-103.962	-50.355	11.005
1100	51.560	115.221	611.505	-101.583	-48.117	8.765
1200	52.080	119.735	724.375	-100.335	-46.399	6.820
1300	52.400	123.925	837.028	-100.000	-45.000	5.120
1400	52.650	127.809	949.422	-100.000	-44.000	3.680
1500	52.800	131.447	1061.603	-100.000	-43.000	2.380

Cl₅Mo

GFW = 273.205

(LIQUID)

MOLYBDENUM PENTACHLORIDE (MoCl₅)S_{298.15}^o = [65.441] gibbs/mol ΔH_f° _{298.15} = [-121.9205] kcal/mol ΔH_m° = [4.5 ± 1.5] kcal/molT_m = 467°K ΔH_v° = [12.0] kcal/molT_b = 537°K

Heat of Formation

The heat of formation is obtained from ΔH_f° (c) by adding ΔH_m° and the difference between H_{lm}° - H_{298}° for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed constant and estimated as 42 gibbs/mol or 7 gibbs/g-atm. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and V. K. Moksimov, Russ. J. Inorg. Chem. (English Transl.) 4, 935 (1959). ΔH_m° is estimated by comparison with that of WCl₅(c).

Vaporization Data

T_b is the temperature at which the difference between the Gibbs energy of formation for MoCl₅(l) and MoCl₅(g) approaches zero. The difference between ΔH_f° (MoCl₅, l) and ΔH_f° (MoCl₅, g) is ΔH_v° .

Molybdenum Pentachloride (MoCl₅)

GFW = 273.205

(Liquid)

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG°	Log K _p
0							
100							
200							
298	42.000	65.441		.000	-121.921	-99.673	73.062
300	42.000	65.701		.078	-121.691	-99.535	72.511
400	42.000	77.783	67.000	8.278	-130.356	-92.319	50.440
500	42.000	87.158	76.200	8.478	-118.495	-83.489	30.722
600	42.000	94.613	73.693	12.678	-117.508	-78.922	28.747
700	42.000	101.287	77.176	16.878	-116.146	-72.600	22.667
800	42.000	106.896	80.349	21.078	-114.613	-66.473	18.159
900	42.000	111.643	83.756	25.278	-113.486	-60.507	14.693
1000	42.000	116.268	86.790	29.478	-112.197	-54.691	11.953
1100	42.000	120.271	89.655	33.678	-110.914	-49.002	9.736
1200	42.000	123.925	92.360	37.878	-109.650	-43.431	7.910
1300	42.000	127.287	94.919	42.078	-108.406	-37.983	6.382
1400	42.000	130.400	97.344	46.278	-107.184	-32.580	5.066
1500	42.000	133.297	99.645	50.478	-105.986	-27.304	3.976

MOLYBDENUM PENTACHLORIDE (MoCl_5)

(IDEAL GAS)

 $GFW = 273,205$ Point Group D_{3h}
$$\Delta H_{\text{f}}^{\circ} = -106.6 \pm 1 \text{ kcal/mol}$$
$$\Delta H_{298.15}^{\circ} = -207.0 \pm 1 \text{ kcal/mol}$$
$$\Delta S_{298.15}^\circ = [95 \pm 3] \text{ gibbs/mol}$$

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

Electronic Levels and Quantum Weights

Bond Distance: Mo-Cl = 2.27 + 0.02 Å

Bond Angles: $\text{Cl}^*-\text{Mo}-\text{Cl}^\dagger = 120^\circ$ $\text{Cl}^\dagger-\text{Mo}-\text{Cl}^{**} = 90^\circ$ $\text{Cl}^{**}-\text{Mo}-\text{Cl}^{**} = 180^\circ$

Equatorial ** Axial

Product of the Moments of Inertia: $I_{I.I.} = 1.02576 \times 10^{-11} \text{ g cm}^6$

Heat of Formation

The adopted $\Delta H_{298}^\circ = -107.0$ kcal/mol is obtained from the vapor pressure data for $\text{HocCl}_5(\text{c}) = \text{HocCl}_5(\text{g})$ measured by Shchukarev et al. (1) and Saeki and Matsuzaki (2).

Source	Method	Reaction	Temperature Range, °K	ΔH_{298}° , kcal/mol	Drift e.u.	ΔH_{298}° kcal/mol
Shchukarev	Transpiration	$\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{g})$	343 - 435	19.04 ± 0.45	0.3	-106.82
Saeki	Manometric	$\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{g})$	298 - 474	16.79 ± 0.06	5.6	-107.06

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of NBCl_2 obtained from infrared and Raman spectra by Carlson (3). Structure, bond distance and bond angle are taken from Evans et al. (4). The three principal moments of inertia are $I_A = I_B = 106.1682 \times 10^{-39}$ and $I_C = 91.0074 \times 10^{-39}$ g cm². The electronic levels are estimated to be 0, 7000 and 4000 cm⁻¹, all doublets, by comparison with those of WCl_2 (g).

Sources

1. S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Transl.) **26**, 2435-9 (1956).
2. Y. Saeki and R. Matsuzaki, *Denki Kagaku* **33**, 155-8 (1965).
3. G. L. Carlson, *Spectrochim. Acta* **19**, 1291 (1963).
4. R. V. G. Evans and M. W. Lister, *Trans. Faraday Soc.* **34**, 1358-62 (1938).

2. Y. Saeki and R. Matsuzaki. Denki Kagaku 33, 155-8 (1955)

3. G. L. Carlson, Spectrochim. Acta 19, 1293 (1963).

4. R. V. G. Ewens and M. W. Liester, Trans. Faraday Soc. **34**, 1358-62 (1938); *ibid.*, **35**, 1234 (1939); *ibid.*, **36**, 1234 (1940).

T, K	Cp	S	$-(G-H^{\circ}_{298})/T$	H-H [°] ₂₉₈	ΔH [°]	ΔG [°]	Log Kp
0	18.000	0.000	INFINITE	-6.165	-106.584	-106.584	INFINITE
100	26.708	48.166	97.581	2.843	-107.513	-107.512	97.152
200	28.556	95.043	95.043	+0.000	-107.000	-93.579	66.595
300	28.580	95.220	95.043	+0.531	-106.996	-93.495	68.111
400	29.688	103.642	96.193	2.884	-106.730	-89.035	68.666
500	30.552	110.384	98.372	6.006	-106.556	-85.842	68.957
600	30.895	115.965	100.684	9.079	-106.187	-80.304	29.251
700	31.126	120.766	103.365	12.181	-105.923	-76.012	23.732
800	31.280	124.933	105.606	15.301	-105.660	-71.758	19.603
900	31.389	128.624	108.140	18.435	-105.418	-67.532	16.309
1000	31.470	131.895	110.357	21.578	-105.176	-63.338	13.684
1100	31.536	134.938	112.457	24.729	-104.942	-59.165	11.755
1200	31.594	137.685	114.447	27.885	-104.722	-55.014	10.019
1300	31.648	140.216	116.333	31.047	-104.516	-50.880	8.554
1400	31.701	142.563	118.124	34.215	-104.326	-46.761	7.300
1500	31.754	144.752	119.827	37.386	-104.155	-42.655	6.215
1600	31.809	146.603	121.449	40.566	-104.005	-38.560	5.267
1700	31.866	148.233	122.998	43.750	-103.873	-34.471	4.431
1800	31.924	150.556	124.479	46.939	-103.764	-30.394	3.690
1900	31.983	152.284	125.897	50.134	-103.674	-26.317	3.027
2000	32.042	153.896	127.258	53.336	-103.611	-22.249	2.431
2100	32.102	155.491	128.565	56.543	-103.567	-18.186	1.903
2200	32.162	156.995	129.834	59.756	-103.553	-14.119	1.403
2300	32.220	158.416	131.036	62.975	-103.566	-10.052	0.955
2400	32.278	159.769	132.205	66.200	-103.614	-5.983	0.548
2500	32.336	161.108	133.335	69.431	-103.712	-1.916	0.168
2600	32.391	162.337	134.428	72.667	-103.866	2.162	-0.182
2700	32.441	163.600	135.486	75.908	-104.068	6.240	-0.505
2800	32.486	164.761	136.511	79.155	-104.390	10.335	-0.829
2900	32.540	165.852	137.506	82.407	-111.401	15.555	-1.089
3000	32.596	167.026	138.472	85.663	-111.483	19.794	-1.319
3100	32.630	168.095	139.410	88.924	-111.571	23.139	-1.631
3200	32.671	169.132	140.323	92.189	-111.661	27.484	-1.976
3300	32.710	170.138	141.211	95.458	-111.755	31.836	-2.108
3400	32.746	171.115	142.076	98.731	-111.849	36.193	-2.266
3500	32.780	172.064	142.919	102.007	-111.951	40.540	-2.531
3600	32.812	172.988	143.742	105.287	-112.053	44.894	-2.726
3700	32.841	173.868	144.545	108.569	-112.161	49.266	-2.910
3800	32.868	174.746	145.328	111.855	-112.270	53.627	-3.084
3900	32.893	175.616	146.094	115.143	-112.385	57.999	-3.250
4000	32.916	176.451	146.843	118.433	-112.504	62.368	-3.406
4100	32.936	177.264	147.575	121.726	-112.624	66.736	-3.557
4200	32.955	178.058	148.291	125.021	-112.749	71.112	-3.700

Dec. 31, 1968

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	Log K _p
0	∞	∞	∞	∞	∞
100	15.058	64.014	107.923	- 4.391	- 81.027
200	22.874	77.094	89.165	- 4.391	- 81.027
298	26.743	87.043	78.242	- 4.391	- 81.027
300	26.792	87.209	78.242	- 4.391	- 81.027
400	28.698	95.208	88.121	- 4.391	- 81.027
500	29.717	101.732	92.600	- 4.391	- 81.027
600	30.313	107.207	97.400	- 4.391	- 81.027
700	30.939	111.025	101.272	- 4.391	- 81.027
800	31.464	114.181	104.699	- 4.391	- 81.027
900	31.914	116.680	107.679	- 4.391	- 81.027
1000	32.240	118.565	110.386	- 4.391	- 81.027
1100	32.495	120.047	112.747	- 4.391	- 81.027
1200	32.688	121.271	114.785	- 4.391	- 81.027
1300	32.822	122.285	116.540	- 4.391	- 81.027
1400	32.914	123.127	118.041	- 4.391	- 81.027
1500	32.966	123.732	119.330	- 4.391	- 81.027
1600	32.987	124.127	120.459	- 4.391	- 81.027
1700	32.987	124.359	121.467	- 4.391	- 81.027
1800	32.966	124.467	122.385	- 4.391	- 81.027
1900	32.922	124.467	123.235	- 4.391	- 81.027
2000	32.855	124.359	124.047	- 4.391	- 81.027
2100	32.768	124.047	124.732	- 4.391	- 81.027
2200	32.658	123.551	125.317	- 4.391	- 81.027
2300	32.522	122.885	125.813	- 4.391	- 81.027
2400	32.368	121.987	126.220	- 4.391	- 81.027
2500	32.196	120.885	126.540	- 4.391	- 81.027
2600	31.999	119.587	126.785	- 4.391	- 81.027
2700	31.774	118.094	126.959	- 4.391	- 81.027
2800	31.522	116.427	127.067	- 4.391	- 81.027
2900	31.247	114.594	127.113	- 4.391	- 81.027
3000	30.952	112.600	127.107	- 4.391	- 81.027
3100	30.638	110.467	127.051	- 4.391	- 81.027
3200	30.307	108.194	126.959	- 4.391	- 81.027
3300	29.962	105.785	126.830	- 4.391	- 81.027
3400	29.607	103.251	126.673	- 4.391	- 81.027
3500	29.246	100.600	126.494	- 4.391	- 81.027
3600	28.881	97.847	126.299	- 4.391	- 81.027
3700	28.514	95.000	126.087	- 4.391	- 81.027
3800	28.146	92.067	125.859	- 4.391	- 81.027
3900	27.778	89.051	125.613	- 4.391	- 81.027
4000	27.411	86.000	125.359	- 4.391	- 81.027
4100	27.046	82.914	125.094	- 4.391	- 81.027
4200	26.683	79.794	124.819	- 4.391	- 81.027
4300	26.322	76.647	124.535	- 4.391	- 81.027
4400	25.962	73.473	124.244	- 4.391	- 81.027
4500	25.603	70.273	123.947	- 4.391	- 81.027
4600	25.246	67.047	123.644	- 4.391	- 81.027
4700	24.891	63.794	123.335	- 4.391	- 81.027
4800	24.538	60.513	123.020	- 4.391	- 81.027
4900	24.187	57.204	122.700	- 4.391	- 81.027
5000	23.838	53.877	122.375	- 4.391	- 81.027
5100	23.491	50.531	122.047	- 4.391	- 81.027
5200	23.146	47.167	121.713	- 4.391	- 81.027
5300	22.803	43.785	121.375	- 4.391	- 81.027
5400	22.462	40.385	121.033	- 4.391	- 81.027
5500	22.123	36.967	120.687	- 4.391	- 81.027
5600	21.786	33.531	120.337	- 4.391	- 81.027
5700	21.451	30.077	120.000	- 4.391	- 81.027
5800	21.118	26.604	119.656	- 4.391	- 81.027
5900	20.787	23.113	119.306	- 4.391	- 81.027
6000	20.458	19.604	118.951	- 4.391	- 81.027

Dec. 31, 1960; Sept. 30, 1962

PHOSPHORUS PENTACHLORIDE (PCl₅)

Point group D_{3h}

ΔH_f° 0 = -81.0 ± 1.0 kcal. mole⁻¹

ΔH_f° 298.15 = -81.9 ± 1.0 kcal. mole⁻¹

S° 298.15 = 87.0 cal. deg.⁻¹ mole⁻¹

MOL. WT. = 208.260

(IDEAL GAS)

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

ω, cm.⁻¹

Tungsten Pentachloride (WCl₅)
(Crystal) GFW = 361.115

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	kcal/mol ΔH°	ΔG°	Log Kp
0						
100						
200						
298	37.200	52.000	0.000	-122.600	-96.056	70.411
300	37.255	52.030	-0.060	-122.580	-95.892	69.857
400	40.615	61.326	5.995	-121.380	-87.172	67.629
500	42.781	72.553	56.408	-119.973	-78.777	34.534
600	45.400	80.591	59.782	-118.344	-70.687	25.748
700	47.450	87.751	63.276	-116.513	-62.987	19.634
800	49.000	94.134	66.735	-114.534	-55.363	15.124
900	50.200	99.737	70.163	-112.414	-47.824	11.154
1000	50.900	105.355	73.485	-110.279	-41.055	8.973
1100	51.580	110.239	76.516	-108.061	-34.240	6.803
1200	52.080	114.750	79.517	-105.802	-27.688	5.032
1300	52.420	118.823	82.380	-103.505	-21.267	3.395
1400	52.640	122.426	85.116	-101.170	-15.001	2.004
1500	52.800	126.468	87.776	-98.920	-8.879	1.294

TUNGSTEN PENTACHLORIDE (WCl₅) (CRYSTAL)

GFW = 361.115

ΔH_f⁰ = UnknownΔH_f⁰_{298.15} = -122.6 ± 10 kcal/molΔH_m⁰ = 4.917 ± 1 kcal/molΔH_s⁰_{298.15} = 24.0 kcal/molS°_{298.15} = [52.0] gibbs/molT_m = 526°K

Heat of Formation.

The heat of formation, ΔH_f⁰ (WCl₅, c) = -122.6 kcal/mol, is calculated from that of the gas less the heat of sublimation, ΔH_s⁰₂₉₈ = 24.0 kcal/mol. The latter is calculated by the third law method from partial pressures of WCl₅(g) derived from the total pressure data* of S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4 Ser. Fiz. i Khim., No. 1, 120 (1959). Dimer pressures, calculated from the same authors' dimer-monomer dissociation data, are subtracted from the total pressures in order to obtain the monomer pressures. Analyses of the monomer pressures over both crystal and liquid give similar results and the average values for ΔH_s⁰₂₉₈ are 20.6 (second law) and 24.0 kcal/mol (third law) with a drift of about 7 eu.

*Earlier data reported by Shchukarev et al., Zhur. Neorg. Khim. 1, 357 (1956); 2, 2630 (1958), have been revised and are not used here.

Heat Capacity and Entropy.

Cp₂₉₈ = 6.2 gibbs/g-atom and Cp₅₂₆ = 7.25 gibbs/g-atom are estimated using the method described by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958. Between 298° and 526°, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, S°₂₉₈ = 52 eu, is estimated by comparison with those of WCl₂ (c), WCl₄ (c) and WCl₆ (c).

Melting Data.

The melting point was determined from vapor pressure data by Shchukarev et al., loc. cit. The heat of melting is the difference at the melting point between the second law heats of vaporization and sublimation derived from total vapor pressure data of Shchukarev et al., loc. cit.

Heat of Sublimation.

See the heat of formation of WCl₅(g) for details.

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	43.500	59.393	59.393	0.000	94.060	66.946
300	43.500	59.462	59.324			
400	43.500	75.077	41.100	0.080	93.910	66.613
500	43.500	81.883	64.322	8.780	89.582	66.111
					79.535	34.327
600	43.500	89.614	67.930	13.130	81.376	25.999
700	43.500	96.520	71.547	17.480	64.477	20.131
800	43.500	102.325	74.360	21.630	51.799	15.790
900	43.500	107.055	76.395	25.680	38.471	11.476
1000	43.500	112.035	81.504	30.530	24.975	9.829
1100	43.500	116.181	84.671	34.860	106.076	7.707
1200	43.500	119.966	87.274	39.230	104.651	5.962
1300	43.500	123.476	89.224	43.560	103.242	4.506
1400	43.500	126.743	90.680	47.860	101.846	3.244
1500	43.500	129.673	91.619	52.280	100.472	2.121

Dec. 31, 1962; Dec. 31, 1966

ΔH_f^o_{298.15} = -118.4 kcal/mol

ΔH_m^o = 4.917 ± 1 kcal/mol

ΔH_v^o = 16.266 kcal/mol

Heat of Formation.

The heat of formation, ΔH_f^o₂₉₈ (WCl₅(l)) = -118.4 kcal/mol, is calculated from that of WCl₅(c) by adding the heat of melting and the difference between H₅₂₆^o - H₂₉₈^o for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom.

The entropy of WCl₅(l), S_{298.15}^o = 59.393 eu, is calculated in a manner analogous to that of the heat of formation.

Melting Data.

See WCl₅(c) table for details.

Vaporization Data.

The boiling point, 561.4°K is calculated as the temperature at which the gibbs energy of formation for both WCl₅(l) and WCl₅(g) are equal. The difference in the heats of formation of WCl₅(l) and WCl₅(g) at the boiling point is the heat of vaporization. S. A. Shchukarev, G. I. Novikov and N. V. Andreeva¹ revised their previous data² and derived the boiling point as 561.2°K from their vapor pressure measurements.

References:

1. S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959).
2. S. A. Shchukarev and G. I. Novikov, Zhur. Neorg. Khim. 1, 357 (1956).

Tungsten Pentachloride (WCl₅)

(Ideal Gas) GFW = 361.115

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	hcal/mol H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	98.199	98.199	INFINITE
100	19.029	70.239	170.387	5.073	98.437	206.187
200	26.024	85.961	99.494	2.707	98.924	98.156
298	28.736	96.935	96.935	0.000	98.600	62.639
300	28.769	97.113	96.936	0.053	98.595	62.194
400	30.596	105.102	105.102	2.000	98.116	33.531
500	30.596	112.349	100.240	6.030	98.016	26.401
600	30.947	117.951	102.771	9.109	97.721	21.323
700	31.166	122.740	105.290	12.215	97.431	17.527
800	31.311	126.911	107.737	15.339	97.154	14.581
900	31.483	130.515	110.077	18.486	96.889	12.232
1000	31.690	133.919	112.298	21.621	96.629	10.315
1100	31.953	136.924	114.402	24.773	96.383	8.720
1200	31.608	139.071	116.395	27.931	96.150	7.375
1300	31.660	142.204	118.294	31.095	95.927	6.263
1400	31.711	145.327	120.104	34.269	95.714	5.329
1500	31.763	148.441	121.833	37.437	95.515	4.529
1600	31.817	151.555	123.498	40.616	95.325	3.829
1700	31.873	154.673	125.108	43.800	95.144	3.216
1800	31.930	157.797	126.661	46.991	94.973	2.681
1900	31.987	160.921	128.166	50.186	94.811	2.216
2000	32.047	164.045	129.623	53.384	94.661	1.804
2100	32.107	167.169	131.032	56.596	94.518	1.427
2200	32.166	170.293	132.397	59.810	94.384	1.082
2300	32.224	173.417	133.724	63.029	94.266	0.766
2400	32.283	176.541	135.012	66.253	94.161	0.486
2500	32.337	179.665	136.266	69.485	94.069	0.248
2600	32.392	182.789	137.499	72.722	93.971	0.044
2700	32.444	185.913	138.713	75.964	93.880	0.000
2800	32.494	189.037	140.000	79.211	93.792	0.000
2900	32.543	192.161	141.266	82.462	93.707	0.000
3000	32.588	195.285	142.512	85.719	93.627	0.000
3100	32.632	198.409	143.748	88.980	93.552	0.000
3200	32.673	201.533	144.974	92.245	93.481	0.000
3300	32.712	204.657	146.198	95.512	93.414	0.000
3400	32.748	207.781	147.422	98.786	93.351	0.000
3500	32.782	210.905	148.646	102.064	93.292	0.000
3600	32.814	214.029	149.870	105.344	93.239	0.000
3700	32.843	217.153	151.094	108.627	93.192	0.000
3800	32.869	220.277	152.318	111.910	93.150	0.000
3900	32.892	223.401	153.542	115.192	93.112	0.000
4000	32.917	226.525	154.766	118.474	93.078	0.000
4100	32.938	229.649	155.990	121.756	93.048	0.000
4200	32.956	232.773	157.214	125.038	93.021	0.000
4300	32.971	235.897	158.438	128.320	93.000	0.000
4400	32.984	239.021	159.662	131.602	92.982	0.000
4500	32.997	242.145	160.886	134.884	92.967	0.000
4600	33.012	245.269	162.110	138.166	92.955	0.000
4700	33.021	248.393	163.334	141.448	92.946	0.000
4800	33.028	251.517	164.558	144.730	92.940	0.000
4900	33.036	254.641	165.782	148.012	92.936	0.000
5000	33.041	257.765	167.006	151.294	92.934	0.000
5100	33.045	260.889	168.230	154.576	92.933	0.000
5200	33.048	264.013	169.454	157.858	92.933	0.000
5300	33.050	267.137	170.678	161.140	92.933	0.000
5400	33.051	270.261	171.902	164.422	92.933	0.000
5500	33.051	273.385	173.126	167.704	92.933	0.000
5600	33.048	276.509	174.350	171.000	92.933	0.000
5700	33.045	279.633	175.574	174.300	92.933	0.000
5800	33.042	282.757	176.798	177.600	92.933	0.000
5900	33.038	285.881	178.022	180.900	92.933	0.000
6000	33.034	289.005	179.246	184.200	92.933	0.000

Dec. 31, 1982 Dec. 31, 1986

TUNGSTEN PENTACHLORIDE (WCl₅)

(IDEAL GAS)

OPW = 361.116

Point Group [D_{3h}]

S°_{298.15} = [96.9] gibbs/mol

Ground State Quantum Weight = [2]

ΔH°₀ = -98.2 ± 8 kcal/mol

ΔH°_{298.15} = -98.6 ± 8 kcal/mol

Electronic Levels and Quantum Weights

E ₁ , cm ⁻¹	E ₂
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[480] (1)	[350] (2)
[400] (1)	[150] (2)
[380] (1)	[100] (2)
[130] (1)	[180] (2)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl* = [120]° Cl*-W-Cl** = [180]°

* Equatorial ** Axial

Product of the Moments of Inertia: I_AI_BI_C = [9.98 x 10⁻¹¹²] g³ cm⁶

σ° = [6]

Heat of Formation

The heat of formation, ΔH°_{f,298} (WCl₅, g) = -98.6 kcal/mol, is calculated from ΔH°_{f,298} = 19.4 kcal/mol for WCl₆(g) → WCl₅(g) + 1/2 Cl₂(g). The value of ΔH°_{f,298} is calculated by the third law method from the equation for log Kp given by S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). The second law ΔH°_{f,298} is 24.6 kcal/mol and the third law drift is -8.5 eu.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of MoCl₅ determined by electron diffraction by R. V. G. Evans and M. W. Lister, Trans. Faraday Soc. 34, 1358 (1938). The bond distance is estimated to be the same as that in WCl₆(g). The three principal moments of inertia are: I_A = I_B = 105.23 x 10⁻³⁹ and I_C = 90.20 x 10⁻³⁹ g cm².

All vibrational frequencies are estimated from those of SbCl₅, PCl₅, NbCl₅ and TaCl₅ obtained from infrared and Raman spectra by G. L. Carlson, Spectrochim. Acta 19, 1291 (1963).

If it is considered that the metal atoms are effectively ionized, then the W⁵⁺ will have a single d electron in a field of chloride ions. The electronic splitting would be roughly the inverse of that in CuCl₂(g) as given by C. W. DeKock and D. M. Gruen, J. Chem. Phys. 45, 4387 (1966), where Cu has a d⁹ configuration. By analogy with the splitting in CuCl₂, the low lying electronic levels are estimated to be 7000 cm⁻¹ and 14000 cm⁻¹, both doublets.

Cl₅W

Cl₅W

Point Group D_{2h}

$$\Delta H_f^\circ 0 = -157.34 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ 298.15 = -156.40 \pm 2.0 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = [128.35] \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 1

Iron Trichloride, Dimeric ((FeCl₃)₂)

(Ideal Gas)

Mol. Wt. = 324.412

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	31.400	97.71	157.335	9.467	-157.335	-157.335	INFINITE
200	31.260	122.184	156.963	3.981	-156.963	-156.963	101.208
298	31.508	128.350	156.400	0.000	-156.400	-156.400	104.697
300	31.533	128.607	156.390	0.077	-156.390	-156.390	104.191
400	32.466	140.698	155.927	4.282	-155.927	-155.927	75.750
500	32.891	150.222	155.361	8.251	-155.361	-155.361	56.779
600	33.139	158.066	155.222	12.453	-155.222	-155.222	47.406
700	33.290	164.728	155.102	17.171	-155.102	-155.102	39.327
800	33.390	170.516	154.999	21.510	-154.999	-154.999	32.270
900	33.458	175.631	154.906	25.952	-154.906	-154.906	26.553
1000	33.508	180.212	154.831	30.601	-154.831	-154.831	21.768
1100	33.544	184.361	154.766	34.554	-154.766	-154.766	17.654
1200	33.572	188.151	154.726	38.700	-154.726	-154.726	13.863
1300	33.594	191.639	154.700	43.068	-154.700	-154.700	10.466
1400	33.611	194.871	154.685	47.628	-154.685	-154.685	7.496
1500	33.625	197.880	154.680	51.960	-154.680	-154.680	4.936
1600	33.637	200.696	154.675	56.353	-154.675	-154.675	2.779
1700	33.646	203.342	154.676	60.717	-154.676	-154.676	1.057
1800	33.654	205.836	154.680	65.082	-154.680	-154.680	0.444
1900	33.661	208.197	154.685	69.448	-154.685	-154.685	0.302
2000	33.666	210.457	154.692	73.814	-154.692	-154.692	0.217
2100	33.671	212.567	154.698	78.181	-154.698	-154.698	0.156
2200	33.676	214.559	154.707	82.546	-154.707	-154.707	0.110
2300	33.679	216.540	154.716	86.910	-154.716	-154.716	0.075
2400	33.683	218.509	154.724	91.274	-154.724	-154.724	0.048
2500	33.686	220.459	154.732	95.638	-154.732	-154.732	0.027
2600	33.688	222.396	154.740	100.002	-154.740	-154.740	0.010
2700	33.690	224.324	154.748	104.366	-154.748	-154.748	0.003
2800	33.692	226.245	154.755	108.730	-154.755	-154.755	0.000
2900	33.694	228.159	154.762	113.094	-154.762	-154.762	0.000
3000	33.696	230.068	154.769	117.458	-154.769	-154.769	0.000
3100	33.698	231.969	154.776	121.822	-154.776	-154.776	0.000
3200	33.699	233.862	154.783	126.186	-154.783	-154.783	0.000
3300	33.700	235.748	154.790	130.550	-154.790	-154.790	0.000
3400	33.701	237.626	154.797	134.914	-154.797	-154.797	0.000
3500	33.702	239.500	154.804	139.278	-154.804	-154.804	0.000
3600	33.703	241.371	154.811	143.642	-154.811	-154.811	0.000
3700	33.704	243.238	154.818	147.999	-154.818	-154.818	0.000
3800	33.705	245.101	154.825	152.356	-154.825	-154.825	0.000
3900	33.706	246.959	154.832	156.713	-154.832	-154.832	0.000
4000	33.707	248.812	154.839	161.070	-154.839	-154.839	0.000
4100	33.708	250.661	154.846	165.427	-154.846	-154.846	0.000
4200	33.709	252.506	154.853	169.784	-154.853	-154.853	0.000
4300	33.710	254.347	154.860	174.141	-154.860	-154.860	0.000
4400	33.711	256.184	154.867	178.498	-154.867	-154.867	0.000
4500	33.712	258.017	154.874	182.855	-154.874	-154.874	0.000
4600	33.713	259.846	154.881	187.212	-154.881	-154.881	0.000
4700	33.714	261.671	154.888	191.569	-154.888	-154.888	0.000
4800	33.715	263.492	154.895	195.926	-154.895	-154.895	0.000
4900	33.716	265.310	154.902	200.283	-154.902	-154.902	0.000
5000	33.717	267.125	154.909	204.640	-154.909	-154.909	0.000
5100	33.718	268.938	154.916	208.997	-154.916	-154.916	0.000
5200	33.719	270.749	154.923	213.354	-154.923	-154.923	0.000
5300	33.720	272.558	154.930	217.711	-154.930	-154.930	0.000
5400	33.721	274.364	154.937	222.068	-154.937	-154.937	0.000
5500	33.722	276.168	154.944	226.425	-154.944	-154.944	0.000
5600	33.723	277.970	154.951	230.782	-154.951	-154.951	0.000
5700	33.724	279.771	154.958	235.139	-154.958	-154.958	0.000
5800	33.725	281.571	154.965	239.496	-154.965	-154.965	0.000
5900	33.726	283.371	154.972	243.853	-154.972	-154.972	0.000
6000	33.727	285.171	154.979	248.210	-154.979	-154.979	0.000

June 30, 1985

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[300] (1)	[110] (1)	[230] (1)	[85] (1)
[200] (1)	[350] (1)	[85] (1)	[70] (1)
[120] (1)	[100] (1)	[70] (1)	[260] (1)
[95] (1)	[18] (1)	[260] (1)	[110] (1)
[35] (1)	[310] (1)	[110] (1)	[90] (1)
[250] (1)	[110] (1)	[90] (1)	

Bond Distances: Fe-Cl = 2.11 ± 0.03 Å Fe-Cl_{bridge} = 2.28 ± 0.03 ÅBond Angle: Cl-Fe-Cl = 128 ± 3° Cl_{bridge}-Fe-Cl_{bridge} = 92 ± 3°Product of the Moments of Inertia: I_AI_BI_C = 7.35910 × 10⁻¹¹¹ g. cm.⁶

Heat of Formation.

The vaporization of FeCl₃(c) is complex. It involves three possible chemical reactions, i.e. (1) 2FeCl₃(c) = Fe₂Cl₆(g); (2) FeCl₃(c) = FeCl₂(g) + Cl₂(g); and (3) 2FeCl₃(c) = 2FeCl₂(g) + Cl₂(g). Although these equilibria have been studied previously by many investigators, a review of their reported data reveals inconsistencies and errors. At room temperature the main vapor species present above FeCl₃(c) is Fe₂Cl₆(g), a dimer of FeCl₃(g). As temperature increases, the dimer gradually decomposes into monomers (FeCl₃·g). Simultaneously, part of FeCl₃(c) also decomposes into FeCl₂(g) and Cl₂(g). Therefore in order to obtain the partial pressure of Fe₂Cl₆(g), the partial pressures of other vapor species, e.g. Cl₂(g) and FeCl₃(g), must be known and deducted from the observed total pressures. However, only few investigators made such corrections. The total pressures above FeCl₃(c), at 500-600°K., have been determined by Maier¹ and Johnston², respectively. The partial pressures of Fe₂Cl₆(g) were evaluated by the subtraction of the calculated equilibrium pressures of Cl₂(g) obtained from reaction (3), from the reported total pressures. The partial pressures of FeCl₃(g) were found to be insignificant at these temperatures. Using the partial pressures obtained for Fe₂Cl₆(g), the enthalpy change (ΔH°_f 298.15°) of reaction (1) was derived by both the second and third law methods. Then the value of ΔH°_f 298.15° (Fe₂Cl₆·g) was calculated. The results are given in the table.

Wilson and Gregory³ have investigated the vaporization and thermal decomposition equilibria of FeCl₃(c) by gas saturation flow and diaphragm gage techniques. Using the partial pressures for Fe₂Cl₆(g), calculated from an equation, the values of ΔH°_f 298.15° and ΔH°_f 298.15° were also evaluated and listed in the table. Based on the total pressures measured by Stirrman⁴ and Sano⁵, the equations for the pressures of Fe₂Cl₆(g) and Cl₂(g) in equilibrium with FeCl₃(c) and FeCl₂(c) as a function of temperature were reported by Wilson and Gregory³. The corresponding values of ΔH°_f 298.15° and ΔH°_f 298.15° were hence calculated. A brief summary and discussion of results of some other previous investigators were also given in the same report.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	ΔH° _f 298.15° kcal. mole ⁻¹
Maier ¹	489.6-591.5	32.18 ± 0.40	34.67	-156.25 ± 0.50
Johnston, et al. ²	505.2-562.2	34.61 ± 0.49	34.50	-156.42 ± 0.50
Wilson and Gregory ³	463.4-577.2	34.46	34.45	-156.47 ± 0.40
Stirrman ⁴	526.2-574.2	35.04	34.49	-156.43 ± 0.50
Sano ⁵	513.2-569.2	30.67	34.76	-156.16 ± 0.50

*Based on the third law values for ΔH°_f 298.15°.

1 C. O. Maier, U. S. Bur. Mines Tech. Paper 380 (1925).

2 H. P. Johnston, H. C. Weingartner and W. E. Mirache, J. Am. Chem. Soc. **64**, 241 (1942).3 L. E. Wilson and N. W. Gregory, J. Phys. Chem. **52**, 435 (1958).4 E. Stirrman, Neues Jahrb. Mineral., Geol., Palsont., **52A**, 334 (1925).5 K. Sano, J. Chem. Soc. Japan, **59**, 1073 (1958).The value of ΔH°_f 298.15° for Fe₂Cl₆(g) is selected as -156.4 ± 2.0 kcal. mole⁻¹.

Heat Capacity and Entropy.

The molecular structure, bond distances and angles were obtained from E. Z. Zasorin, N. O. Rembid and P. A. Alkhin, Zh. Strukt. Khim., **4**, 910 (1963). The vibrational frequencies were estimated by comparison with those for Al₂Cl₆(g) such that the values of ΔH°_f derived from the equilibrium data by the second and third law methods are in reasonable agreement. The three principal moments of inertia are: I_A = 2.79395 × 10⁻³⁷, I_B = 1.16349 × 10⁻³⁷ and I_C = 2.26383 × 10⁻³⁷ g. cm.²

Molybdenum Hexachloride (MoCl₆)
(Crystal)

GFW = 308.658

MOLYBDENUM HEXACHLORIDE (MoCl₆)

(CRYSTAL)

GFW = 308.658

 $\Delta H_f^\circ = \text{unknown}$ $\Delta H_{298.15}^\circ = [-125 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = [61.0 \pm 4.0] \text{ gibbs/mol}$ $T_s = [527]^\circ\text{K}$

Heat of Formation

G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. 10, 576-8 (1965), assumed that the equilibrium $\text{MoCl}_5(\text{c}) = \text{MoCl}_3(\text{g}) + 1/2 \text{Cl}_2(\text{g})$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics. $\Delta H_f^\circ = 4 \text{ kcal/mol}$ and $\Delta S_{298}^\circ = 8 \text{ eu}$, of the equilibrium $\text{MoCl}_5(\text{c}) = \text{MoCl}_3(\text{c}) + 1/2 \text{Cl}_2(\text{g})$, from which they obtained the $\Delta H_{298}^\circ(\text{MoCl}_5, \text{c}) = -125 \text{ kcal/mol}$.

Heat Capacity and Entropy

The adopted heat capacity is the same as that of $\text{WCl}_5(\text{g}, \text{c})$, since the heat capacities of W and Mo are almost the same. The entropy is estimated from that of $\text{MoCl}_5(\text{c})$ by the addition of 4 eu due to one extra chlorine atom in the molecule.

Vaporization Data

The sublimation point is calculated from the free energy crossover between crystal and gas. However, it should be noted that $\text{MoCl}_5(\text{c})$ is unstable with respect to $\text{MoCl}_3(\text{c})$ at all temperatures and thus sublimation could occur only under an atmosphere of Cl_2 .

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	$\frac{\text{kcal/mol}}{\Delta H_f^\circ}$	ΔG_f°	Log Kp
0							
100							
200							
298							
300	41.900	61.000	61.000	.000	-125.000	-93.484	60.526
400	42.000	61.260	61.001	.078	-124.978	-93.289	67.961
500	46.000	73.860	62.666	4.478	-123.658	-82.918	45.304
600	50.000	84.597	66.030	9.283	-122.028	-72.913	31.670
700	53.300	94.031	69.924	14.463	-120.086	-63.267	23.045
800	54.900	102.378	73.979	19.679	-117.947	-53.966	16.849
900	55.700	109.767	77.999	25.414	-115.722	-44.980	12.288
1000	55.900	116.340	81.901	30.995	-113.469	-36.269	8.807
1100	56.000	122.235	85.645	36.590	-111.222	-27.815	6.079
1200	56.100	127.577	89.218	42.195	-108.982	-19.582	3.891
1300	56.200	132.443	92.621	47.810	-106.753	-11.554	2.104
1400	56.300	136.965	95.861	53.435	-104.535	-3.711	.624
1500	56.387	141.140	98.988	59.069	-102.331	3.962	.619
	56.400	145.031	101.892	64.708	-100.147	11.479	1.672

Molybdenum Hexachloride (MoCl₆)

(Ideal Gas) GFW = 308.658

Point Group O_h $\Delta H_f^\circ = [-104.7 \pm 30] \text{ kcal/mol}$ $S_{298.15}^\circ = [100.3 \pm 4] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-105.0 \pm 20] \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
[347] (1)	[144] (3)
[326] (2)	[171] (3)
[390] (3)	[106] (3)

Bond Distance: Mo-Cl = [2.26] Å

Bond Angle: Cl-Mo-Cl = [90°]

 $\sigma = 24$ Product of the Moments of Inertia: $I_A I_B I_C = [1.7398 \times 10^{-111}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. **10**, 576-82 (1965), assumed that the equilibrium $\text{MoCl}_5(\text{c}) = \text{MoCl}_5(\text{g}) + 1/2 \text{Cl}_2(\text{g})$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta H_f^\circ = 2.5 \text{ kcal/mol}$ and $\Delta S_f^\circ = 10 \text{ eu}$ of the equilibrium $\text{MoCl}_5(\text{g}) = \text{MoCl}_5(\text{g}) + 1/2 \text{Cl}_2(\text{g})$, from which they obtained the $\Delta H_{298}^\circ(\text{MoCl}_5 \text{ g}) = -105 \text{ kcal/mol}$.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of MoF_6 and WF_6 , given by K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York - London, 1963, and WCl_6 given by J. C. Evans and G. Y. S. Lo, J. Mol. Spectrosc. **28**, 147 (1968).

Structure, bond distance and bond angle are estimated to be the same as those of WCl_6 . The three principal moments of inertia are $I_A = I_B = I_C = 120.2684 \times 10^{-39} \text{ g cm}^2$.

Dec. 31, 1968

Tungsten Hexachloride, Alpha (α -WCl₆)
(Crystal) GFW = 396.568

T, K	Cp	$\frac{g\text{ cal}}{\text{mole}^\circ\text{K}}$ S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal}}{\text{mole}}$ ΔH°	ΔG°	Log Kp
100							
200							
298	41.926	57.000	57.000	.000	-141.900	-104.903	79.828
300	42.000	57.200	57.001	.076	-141.876	-104.899	79.167
400	46.000	69.450	58.656	8.478	-140.557	-97.831	53.452
500	50.000	82.407	42.231	10.274	-137.917	-87.841	36.221
600	53.100	92.224	36.476	15.444	-135.965	-77.525	26.218
700	54.820	100.551	30.657	20.652	-133.676	-66.593	16.016
800	55.950	107.510	25.000	25.510	-131.577	-55.493	6.016
900	56.900	114.510	19.510	31.265	-129.306	-43.723	12.074
1000	56.000	120.408	14.265	37.563	-127.044	-31.904	8.962
1100	56.000	125.745	9.506	43.163	-124.799	-19.509	6.459
1200	56.000	130.606	5.992	48.163	-122.564	-7.110	3.708
1300	56.000	135.000	2.700	52.400	-120.340	5.110	1.276
1400	56.000	139.250	0.420	55.983	-118.175	13.173	1.276
1500	56.000	143.114	0.000	59.405	-116.001	21.173	1.057

TUNGSTEN HEXACHLORIDE, ALPHA (α -WCl₆) (CRYSTAL)

OPW = 396.568

Cl₆W

ΔH°_0 = Unknown
 $\Delta H^\circ_{298.15} = -141.9 \pm 6 \text{ kcal/mol}$
 $\Delta H^\circ (a_1 \rightarrow a_2) = [1.0] \text{ kcal/mol}$
 $\Delta H^\circ (a_2 \rightarrow \beta) = 3.77 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = 23.9 \text{ kcal/mol}$

$S^\circ_{298.15} = [57.0] \text{ gibbs/mol}$
 $Tt (a_1 \rightarrow a_2) = 450 \pm 10^\circ\text{K}$
 $Tt (a_2 \rightarrow \beta) = 503 \pm 3^\circ\text{K}$

Heat of Formation.

S. A. Shchukarev, I. V. Vasilkova and G. I. Novikov, Zh. Neorg. Khim., 3, 2642 (1958), have measured calorimetrically the heat of solution of WCl₆(c) and also of H₂WO₄(c) in a 12% solution of NaOH as -188.0 ± 0.3 and -13.6 ± 0.11 kcal/mol, respectively. Based on these data and a heat of dilution value for Na₂WO₄ which is essentially zero, we obtain $\Delta H^\circ_{298} = -174.4 \pm 0.3 \text{ kcal/mol}$ for WCl₆(c) + 6NaOH(18.3H₂O) → H₂WO₄(c) + 6NaCl(22.00H₂O) + 2H₂O(l). This reaction gives from JANAP Tables and from V. B. Parker, "Thermal Properties of Aqueous Unit-univalent Electrolytes," NSRDS-NBS2, Natl. Bur. Std., Washington, D.C., April, 1965. The authors have suggested a possible uncertainty of the order of 5 kcal/mol due to the slowness of the dissolution of WCl₆(c).

Heat Capacity and Entropy.

J. R. Welty¹ has measured the enthalpy changes for WCl₆(a,c) in the temperature range from 405° to 502.4°K by drop calorimetry. Few points were measured in the region of the $a_1 \rightarrow a_2$ transition and no attempt was made to investigate the phase present at the conclusion of the drop. Thus, these data appear to be inadequate to define the heat capacities of the a_1 and a_2 phases. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy $S^\circ_{298} = 57.0 \text{ eu}$, is calculated from that of the gas using $\Delta S^\circ_{298} = 43.155 \text{ eu}$ from the vaporization and sublimation data given in the WCl₆(g) table (December 31, 1966).

Transition Data.

Transition temperatures and heats of transition have been reported by the following investigators, and their results are summarized as follows:

Investigator	Method	$a_1 \rightarrow a_2$ transition		$a_2 \rightarrow \beta$ transition	
		Temperature (°K)	ΔH° (kcal/mol)	Temperature (°K)	ΔH° (kcal/mol)
Ketelaar ² et al.	Vapor pressure	441	-	500	3.4
Stevenson ³	Cooling curve	458	-	503	-
Welty ¹	Vapor pressure	-	-	503	1.9
Shchukarev ⁴ et al.	Drop calorimetric	-	-	504	3.4
Dobrotin ⁵	Vapor pressure	-	-	504	3.4
	Approximate calorimetric	-	-	493 ± 10	5.5

The adopted $\Delta H^\circ_{450} (a_1 \rightarrow a_2)$ and $\Delta H^\circ_{503} (a_2 \rightarrow \beta)$ are calculated as 1.0 and 3.77 kcal/mol, respectively, based on the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to a_1 phase as the final state, although no experimental evidence for this is given.

Melting Data.

See WCl₆ (p.c) table (December 31, 1966).

Heat of Sublimation.

See WCl₆(g) table (December 31, 1966) for detailed information about sublimation data.

References:

1. J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
2. J. A. A. Ketelaar, O. W. Oosterhout and P. B. Braun, Rec. Trav. Chim., 62, 597 (1943).
3. F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines Rept. Invest. 6367 (1964).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, Ser. Fiz. i Khim., No. 1, 87 (1961).
5. R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. 19, No. 4, Fiz. i Khim. No. 1, 95 (1964).

Cl₆W

T, °K	C_p	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	Log K _p
100							
200							
298	45,000	67,066	67,066	.000	-136,921	-106,925	78.378
300	45,000	67,344	67,067	.083	-136,894	-106,739	77.759
400	45,000	80,790	68,432	4,583	-135,473	-95,906	52.947
500	45,000	94,136	75,157	13,583	-132,851	-78,197	28.483
600	45,000	98,436	75,497	13,583	-132,851	-78,197	28.483
700	45,000	105,473	79,640	18,083	-131,606	-69,187	21.601
800	45,000	111,482	83,253	22,583	-130,387	-60,357	16.489
900	45,000	116,792	86,689	27,083	-129,209	-51,650	12.524
1000	45,000	121,323	89,740	31,583	-128,095	-43,120	9.724
1100	45,000	125,612	93,009	36,083	-126,900	-34,683	6.891
1200	45,000	129,728	95,908	40,583	-125,775	-26,350	4.799
1300	45,000	133,130	98,650	45,083	-124,697	-18,110	3.045
1400	45,000	136,684	101,248	49,583	-123,576	-9,953	1.558
1500	45,000	139,769	103,714	54,083	-122,502	-1,875	.273

The entropy of $WCl_6(\beta, c)$, $S^\circ_{298.15} = 67.066$ eu, is calculated in a manner analogous to that of the heat of formation.

Transition Data.

See $WCl_6(g, c)$ table (Dec. 31, 1966).

Melting Data.

Melting point and heat of melting have been reported by the following investigators, and their results are summarized as follows:

Investigator	Method	Melting Point (°K)	ΔH_m° (kcal/mol)
Ketelaar ² et al.	Vapor pressure	557	2.3
Stevenson ³	Cooling curve	555	-
Welty ¹	Vapor pressure	555	1.5
Shchukarev ⁴ et al.	Drop calorimetric	556	1.6
Dobrotin ⁵ et al.	Vapor pressure	564	2.0
	Approximate calorimetric	545 ± 12	4.2

The adopted heat of melting, $\Delta H_{555}^\circ = 1.6$ kcal/mol, is calculated from the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is available.

Heat of Sublimation.

$\Delta H_{298.15}^\circ$ is calculated as the difference between $\Delta H_{298.15}^\circ$ for $WCl_6(\beta, c)$ and $WCl_6(g)$.

References.

1. J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
2. J. A. A. Ketelaar, G. W. Oosternhout and P. B. Braun, Rec. Trav. Chim. **62**, 597 (1943).
3. T. D. Stevenson, Ph.D. Thesis, Oregon State University, (1962); U.S. Bur. Mines Rept. Invest. 6567 (1964).
4. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
5. R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev, Vestnik Leningrad. Univ. **19**, No. 4, Ser. Fiz. i Khim., No. 1, 95 (1964).

Dec. 31, 1966

Tungsten Hexachloride (WCl₆)

(Liquid)

GF_W = 396.568

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H^\circ_{298})/T}$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log K _p
100						
200						
298	48.000	68.095	68.085	.000	-136.091	106.399
300	48.000	68.382	68.086	.089	-136.058	106.215
400	48.000	82.191	69.469	9.689	-134.357	87.531
500	48.000	97.992	73.284	24.708	-132.657	87.231
600	48.000	101.653	77.505	34.489	-131.115	86.332
700	48.000	108.052	81.997	49.289	-129.576	85.657
800	48.000	115.462	85.351	64.089	-128.061	85.205
900	48.000	121.115	89.017	78.889	-126.573	84.934
1000	48.000	126.173	92.484	93.689	-125.109	84.634
1100	48.000	130.747	95.758	108.489	-123.664	84.376
1200	48.000	134.924	98.850	123.289	-122.239	84.140
1300	48.000	138.766	101.775	138.089	-120.831	83.918
1400	48.000	142.323	104.546	152.889	-119.440	83.708
1500	48.000	145.635	107.176	167.689	-118.066	83.509

TUNGSTEN HEXACHLORIDE (WCl₆) (LIQUID)

GF_W = 396.568

$\Delta H^\circ_{298.15} = -136.091 \text{ kcal/mol}$

$\Delta H_m^\circ = 1.60 \text{ kcal/mol}$

$\Delta H_v^\circ = 14.319 \text{ kcal/mol}$

$S^\circ_{298.15} = [68.085] \text{ gibbs/mol}$

$T_m = 555 \pm 2^\circ \text{K}$

$T_b = 613.6^\circ \text{K}$

Heat of Formation.

The heat of formation, $\Delta H^\circ_{298.15}(\text{WCl}_6(l)) = -136.091 \text{ kcal/mol}$, is calculated from that of $\text{WCl}_6(\beta, c)$ by adding the heat of melting and the difference between $H^\circ_{555} - H^\circ_{298.15}$ for $\text{WCl}_6(\beta, c)$ and $\text{WCl}_6(l)$.

Heat Capacity and Entropy.

J. R. Welty, Ph.D. Thesis, Oregon State University (1962), has measured the enthalpy changes for $\text{WCl}_6(l)$ in the temperature range from 560° to 603°K by drop calorimetry. Since the temperature range was very short and no attempt was made to investigate the phase present at the conclusion of the drop, we feel that the enthalpy data are insufficient to define the heat capacity accurately. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy of $\text{WCl}_6(l)$, $S^\circ_{298.15} = 68.085 \text{ eu}$, is calculated in a manner analogous to that of the heat of formation.

Melting Data.

See $\text{WCl}_6(\beta, c)$ table dated Dec. 31, 1966.

Vaporization Data.

The boiling point, 613.6°K, is calculated as the temperature at which the Gibbs energies of formation for both $\text{WCl}_6(l)$ and $\text{WCl}_6(g)$ are equal. The difference in the heats of formation of $\text{WCl}_6(l)$ and $\text{WCl}_6(g)$ at the boiling point is the heat of vaporization.

J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 82, 597 (1943), have determined the boiling point and the heat of vaporization as 609.7°K and 15.24 kcal/mol, respectively, from vapor pressure measurements. S. A. Shchukarev and A. V. Suvorov revised their previous data^{2,3} and gave the boiling point and the heat of vaporization as 616.2°K and 14.7 kcal/mol, respectively, from their vapor pressure measurements.

See $\text{WCl}_6(g)$ table, dated Dec. 31, 1966, for detailed information about vaporization data.

References:

1. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 15, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
2. S. A. Shchukarev and G. I. Novikov, Zh. Neorg. Khim. 1, 357 (1956).
3. S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and A. K. Baev, Zh. Neorg. Khim. 3, 2630 (1958).

Point Group O_h
ΔH_f⁰_{298.15} = -117.6 ± 6 kcal/mol
ΔH_f⁰_{298.15} = -118.0 ± 6 kcal/mol
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	ω _i , cm ⁻¹
(360) (1)	(140) (3)
(340) (2)	(180) (3)
375 (3)	(120) (3)

Bond Distance: W-Cl = 2.26 Å

Bond Angle: Cl-W-Cl = 90°

Product of the Moments of Inertia: I_AI_BI_C = 1.7596 x 10⁻¹¹¹ g³ cm⁶

σ = 24

Heat of Formation

The heat of formation of WCl₆(g), ΔH_f⁰₂₉₈ = -118.0 kcal/mol, is calculated from that of the crystal plus the adopted heat of sublimation, ΔH_{sub}⁰₂₉₈ = 23.9 kcal/mol for WCl₆(s) → WCl₆(g). The latter was obtained from third law analysis of the vapor pressure data 1,2,3,4, using all JANAP functions (Dec. 31, 1966).

Investigator	Phase Studied	Temp. range, °K	No. of Points	ΔH _f ⁰ ₂₉₈ (kcal/mol)	Drift (eu)	ΔH _f ⁰ ₂₉₈ (WCl ₆ /g)***
Stevenson ¹	α, c	462 - 502	38	20.9 ± 0.5	23.74	6.2 ± 1.0
	β*, c	503 - 551	15	23.1 ± 0.2	23.89	1.5 ± 0.3
	1*	557 - 598	13	24.2 ± 0.1	23.89	-0.6 ± 0.1
Shchukarev ²	α, c	**	-	22.0	23.80	4.0
et al.	β*, c	-	-	25.8	23.98	0.4
	1*	-	-	24.1	23.98	-0.2
Ketelaar ³	α, c	425 - 500	21	23.1 ± 0.1	23.94	1.7 ± 0.4
et al.	β*, c	504 - 554	21	24.4 ± 0.1	23.91	-0.8 ± 0.1
	1*	523 - 635	21	24.4 ± 0.1	23.85	-1.0 ± 0.1
Vernon ⁴	α, c	298 - 423	4	16.1 ± 4.1	21.02	10.8 ± 12.8

A. A. Vernon⁴ has also determined the equilibrium constants in the temperature range from 1360° to 1600°K for the decomposition of WCl₆(g) to W(c) and Cl₂(g) by reaction of the sample with a hot tungsten filament in a vacuum bulb. Using the reported equilibrium constants, the heat of formation of WCl₆(g) at 298°K is calculated by the second and third law method as -131.8 ± 2.9 kcal/mol and -135.2 kcal/mol, respectively. The third law drift is 2.4 ± 1.9 eu. Unfortunately, the reported equilibrium constants may be seriously in error, since atomic chlorine is the main species at the pressure and temperature studied.

* Enthalpy changes are converted to ΔH_f⁰₂₉₈ for WCl₆(α, c) → WCl₆(g).

** Vapor pressure equations for the crystal (α,β) and the liquid to gas are given.

*** The third law ΔH_f⁰₂₉₈ is used in calculation.

References:

1. F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines Rept. Invest. 6367 (1961).
2. S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
3. J. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. 52, 597 (1943).
4. A. A. Vernon, J. Am. Chem. Soc. 59, 1832 (1937).

Heat Capacity and Entropy.

R. G. Owens and M. W. Lister, Trans. Faraday Soc. 35, 1358 (1939), have determined the octahedral structure for WCl₆(g) by electron diffraction and found the bond length to be 2.26 Å.

The vibrational frequency of ν₃, 375 cm⁻¹, was observed in the infrared spectra by J. C. Evans, The Dow Chemical Company, private communication, Dec. 1, 1966. The values of ν₁, ν₂ and ν₅ (360, 340 and 180 cm⁻¹, respectively) are estimated, based on those of the aqueous ion PtCl₆²⁻ reported by L. A. Woodward and J. A. Creighton, Spectrochim. Acta 17, 594 (1961). The values of ν₄ and ν₆ (140 and 120 cm⁻¹, respectively) are estimated by comparison with those of Wp₆(g).

The three principal moments of inertia are I_A = I_B = I_C = 120.2684 x 10⁻³⁹ g cm².

Dec. 31, 1962; Dec. 31, 1966

T, °K	Cp ^o	S ^o - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH ^o	ΔG ^o	Log Kp
0	+0.00	INFINITE	7.359	-117.586	-117.586	INFINITE
100	22.253	68.286	5.996	-118.469	-118.469	743.733
200	31.228	86.997	3.245	-118.576	-118.576	114.266
298	34.402	100.135	+0.00	-118.000	-97.870	71.740
300	34.439	100.168	-0.04	-97.745	-97.745	71.207
400	35.793	110.486	3.584	-117.551	-91.063	91.754
500	36.468	118.553	7.200	-117.095	-84.492	36.931
600	36.850	125.239	10.868	-116.685	-78.018	29.416
700	37.065	130.618	14.585	-116.263	-71.610	22.358
800	37.239	135.901	18.282	-115.777	-65.272	17.031
900	37.346	140.234	22.012	-115.359	-59.981	14.323
1000	37.423	144.233	25.750	-114.957	-54.742	11.527
1100	37.481	147.902	29.494	-114.566	-49.546	9.246
1200	37.524	151.065	33.240	-114.191	-44.370	7.552
1300	37.558	154.070	36.990	-113.829	-39.214	6.255
1400	37.585	156.855	40.758	-113.480	-34.075	5.291
1500	37.607	159.449	44.517	-113.147	-28.940	4.581
1600	37.625	161.874	48.270	-112.826	-23.806	4.012
1700	37.640	164.158	52.042	-112.523	-18.676	3.574
1800	37.653	166.310	55.807	-112.233	-13.546	3.231
1900	37.663	168.346	59.573	-111.956	-8.416	2.966
2000	37.672	170.278	63.339	-111.700	-3.286	2.766
2100	37.680	172.116	67.107	-111.464	18.088	2.627
2200	37.687	173.869	70.875	-111.239	26.059	2.553
2300	37.693	175.544	74.644	-111.017	34.027	2.473
2400	37.698	177.149	78.414	-110.802	42.000	2.391
2500	37.702	178.688	82.184	-110.648	50.000	2.315
2600	37.704	180.167	85.954	-110.489	58.000	2.247
2700	37.710	181.590	89.724	-110.355	66.000	2.184
2800	37.713	182.961	93.494	-110.226	74.000	2.126
2900	37.716	184.285	97.264	-110.104	82.000	2.072
3000	37.719	185.563	101.040	-110.190	90.000	2.022
3100	37.721	186.800	104.812	-110.268	98.000	1.976
3200	37.723	187.998	108.586	-110.366	106.000	1.934
3300	37.725	189.159	112.356	-110.563	114.000	1.896
3400	37.727	190.285	116.129	-110.840	122.000	1.862
3500	37.729	191.378	119.902	-111.217	130.000	1.832
3600	37.730	192.441	123.675	-111.718	138.000	1.806
3700	37.732	193.475	127.444	-120.465	146.000	1.784
3800	37.733	194.481	131.221	-120.676	154.000	1.764
3900	37.734	195.462	135.004	-120.576	162.000	1.746
4000	37.735	196.417	138.768	-120.544	170.000	1.730
4100	37.736	197.359	142.541	-120.516	178.000	1.716
4200	37.737	198.289	146.314	-120.479	186.000	1.704
4300	37.738	199.166	150.086	-120.468	194.000	1.694
4400	37.739	200.014	153.863	-120.468	202.000	1.686
4500	37.740	200.862	157.636	-120.468	210.000	1.680
4600	37.740	201.691	161.410	-120.469	218.000	1.676
4700	37.741	202.503	165.186	-120.469	226.000	1.672
4800	37.742	203.297	168.959	-120.463	234.000	1.669
4900	37.742	204.076	172.733	-120.463	242.000	1.666
5000	37.743	204.838	176.507	-120.477	250.000	1.664
5100	37.743	205.586	180.281	-120.484	258.000	1.662
5200	37.744	206.321	184.054	-120.484	266.000	1.660
5300	37.744	207.037	187.826	-120.506	274.000	1.658
5400	37.745	207.743	191.605	-120.518	282.000	1.656
5500	37.745	208.436	195.379	-120.531	290.000	1.654
5600	37.745	209.116	199.154	-120.543	298.000	1.652
5700	37.746	209.781	202.926	-120.549	306.000	1.650
5800	37.746	210.431	206.703	-120.571	314.000	1.648
5900	37.746	211.085	210.477	-120.587	322.000	1.646
6000	37.747	211.720	214.259	-120.587	330.000	1.644

Tungsten Pentachloride, Dimeric (W_2Cl_{10})
(Ideal Gas) $GFW = 722.230$

T, K	C_p	S	$-(G^\circ - H^\circ)/T$	$H^\circ - H^\circ_{298}$	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-18,438	-208,490	-208,490	INFINITE
100	97.951	104,851	223,358	-11,451	-209,495	-197,345	431,298
200	58,922	146,124	176,176	-6,010	-204,644	-185,682	202,692
298	62,949	170,521	170,521	0	-207,600	-174,346	127,799
300	43,017	170,911	170,522	6,117	-207,580	-174,140	126,861
400	65,758	203,895	177,758	13,053	-206,529	-163,157	99,145
500	65,758	203,895	177,758	13,053	-205,539	-152,141	86,632
600	66,283	215,934	183,172	19,654	-204,401	-141,639	51,701
700	66,612	224,178	186,602	26,304	-203,387	-131,609	41,080
800	66,830	235,088	193,688	32,976	-202,411	-121,427	33,172
900	67,011	244,644	198,648	39,671	-201,484	-111,357	27,041
1000	67,090	256,032	203,661	46,391	-200,528	-101,401	22,181
1100	67,171	256,430	208,172	53,084	-199,628	-91,533	18,186
1200	67,233	252,278	212,431	59,805	-198,757	-81,744	14,888
1300	67,281	257,661	216,484	66,531	-197,913	-72,027	12,109
1400	67,310	262,610	220,371	73,261	-197,087	-62,377	9,770
1500	67,351	277,295	223,355	79,994	-196,310	-52,779	7,600
1600	67,377	281,642	227,435	86,731	-195,551	-43,234	5,906
1700	67,398	285,728	230,765	93,469	-194,820	-33,731	4,336
1800	67,416	289,590	233,938	100,210	-194,118	-24,281	2,988
1900	67,431	293,241	236,983	106,953	-193,443	-15,875	1,813
2000	67,444	296,685	239,837	113,698	-192,803	-7,475	1,508
2100	67,455	299,976	242,623	120,441	-192,187	3,871	1,403
2200	67,465	303,114	245,302	127,187	-191,609	13,189	1,310
2300	67,473	306,113	247,691	133,934	-191,057	22,594	1,237
2400	67,479	308,987	249,897	140,683	-190,530	31,964	1,173
2500	67,487	311,740	252,768	147,430	-190,033	41,317	1,116
2600	67,493	314,387	255,087	154,179	-189,566	50,555	1,064
2700	67,498	316,934	257,331	160,929	-189,120	59,870	1,014
2800	67,502	319,358	259,504	167,676	-188,695	69,161	967
2900	67,506	321,674	261,610	174,423	-188,290	78,422	922
3000	67,510	324,046	263,653	181,180	-187,901	87,651	876
3100	67,514	326,250	265,637	187,931	-187,528	96,859	830
3200	67,517	328,403	267,565	194,683	-187,170	106,043	784
3300	67,519	330,497	269,440	201,438	-186,826	115,204	739
3400	67,521	332,538	271,266	208,193	-186,494	124,343	694
3500	67,524	334,554	273,063	214,939	-186,176	133,461	649
3600	67,527	336,556	274,775	221,691	-185,870	142,550	604
3700	67,529	338,520	276,495	228,444	-185,570	151,601	559
3800	67,531	340,458	278,131	235,197	-185,276	160,622	514
3900	67,532	342,372	279,704	241,950	-184,987	169,622	469
4000	67,534	344,271	281,296	248,703	-184,703	178,594	424
4100	67,535	345,139	282,832	255,457	-184,424	187,536	379
4200	67,536	346,766	284,335	262,210	-184,150	196,451	334
4300	67,537	348,378	285,800	268,963	-183,880	205,336	289
4400	67,539	349,998	287,206	275,716	-183,614	214,191	244
4500	67,540	351,626	288,655	282,472	-183,352	223,020	199
4600	67,541	352,211	290,035	289,226	-183,094	231,826	154
4700	67,542	353,763	291,399	295,980	-182,840	240,609	109
4800	67,543	355,292	292,711	302,733	-182,590	249,369	64
4900	67,544	356,798	293,974	309,486	-182,342	258,106	19
5000	67,544	358,284	295,124	316,243	-182,096	266,820	-26
5100	67,545	359,880	296,587	322,994	-181,853	275,511	-71
5200	67,546	361,172	297,776	329,752	-181,614	284,179	-126
5300	67,547	362,468	298,914	336,510	-181,378	292,826	-181
5400	67,548	363,781	300,178	343,261	-181,144	301,454	-236
5500	67,548	365,100	301,381	350,016	-180,912	310,064	-291
5600	67,548	366,197	302,498	356,771	-180,682	318,656	-346
5700	67,549	367,593	303,516	363,526	-180,454	327,230	-401
5800	67,550	369,000	304,534	370,281	-180,228	335,786	-456
5900	67,550	369,722	305,618	377,036	-180,004	344,324	-511
6000	67,550	370,858	306,691	383,791	-179,782	352,844	-566

Dec. 31, 1966

$Cl_{10}W_2$

$GFW = 722.230$

TUNGSTEN PENTACHLORIDE, DIMERIC (W_2Cl_{10}) (IDEAL GAS)

Point Group [D_{2h}]
 $S^\circ_{298,15} = [170]$ gibbs/mol
 $\Delta H^\circ_0 = -208.7 \pm 10$ kcal/mol
 $\Delta H^\circ_{298,15} = -207.6 \pm 10$ kcal/mol

Ground State Quantum Weight = [3]

Vibrational Frequencies and Degeneracies

ω , cm^{-1}	ω , cm^{-1}	ω , cm^{-1}
[500] (2)	[150] (2)	[90] (2)
[400] (2)	[125] (4)	[80] (2)
[350] (2)	[100] (6)	[60] (4)
[250] (2)		[40] (2)

Bond Distance: W-Cl = [2.26] Å

Bond Angle: Cl-W-Cl = [90]° W-Cl_{bridge}-W = [90]°

Cl**-W-Cl** = [180]° Cl*-W-Cl** = [90]°

*Equatorial **Axial

Product of the Moments of Inertia: $I_A I_B I_C = [8.638] \times 10^{-110}$ g³ cm⁶

Heat of Formation

The heat of formation, $\Delta H^\circ_{298} (W_2Cl_{10}(g)) = -207.6$ kcal/mol, is calculated from $\Delta H^\circ_{298} = 10.4$ kcal/mol for $WCl_5(g)$, using all JANAF functions (Dec. 31, 1966). The value of ΔH°_{298} is obtained from third law analysis of the partial pressures of $WCl_5(g)$ and $W_2Cl_{10}(g)$ derived from PVT data determined by S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4, Ser. Fiz. i Khim., No. 1, 120 (1959). The second law ΔH°_{298} is 10.4 ± 0.3 kcal/mol.

Heat Capacity and Entropy

The molecular configuration is estimated by analogy with that of Mo_2Cl_{10} reported by D. Z. Sands and A. Zaikin, Acta Cryst. 12, 723 (1959). Chlorine atoms are placed octahedrally around two tungsten atoms and these two octahedra share one common edge with six chlorine and two tungsten atoms in a plane. The bond length is estimated to be the same as that in $WCl_5(g)$. The three principal moments of inertia are $I_A = 210.5 \times 10^{-39}$, $I_B = 576.8 \times 10^{-39}$ and $I_C = 546.8 \times 10^{-39}$ g cm².

All vibrational frequencies are estimated, based on those of WCl_5 , $(AlCl_3)_2$ and Ca_2Cl_6 , such that $S^\circ_{50}(W_2Cl_{10}(g)) = 216.65$ eu. This entropy is derived from $\Delta S^\circ_{50} = 19.92 \pm 0.5$ eu for $W_2Cl_{10}(g) = 2WCl_5(g)$, obtained by second law analysis of the data of Shchukarev et al., loc. cit. The frequencies are not in point group order.

$Cl_{10}W_2$

(REFERENCE STATE)

COBALT (Co)

(Reference State) GFW = 58.9332

T, °K	Cp*	$\frac{\mu\text{bbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	.000	.000	INFINITE	-1.139	.000	.000	.000
100	3.330	1.840	11.990	-1.015	.000	.000	.000
200	5.190	2.490	7.710	.000	.000	.000	.000
298	5.937	2.817	7.180	.011	.000	.000	.000
300	5.937	2.817	7.180	.011	.000	.000	.000
400	6.340	6.980	7.418	.625	.000	.000	.000
500	6.740	10.439	7.680	1.879	.000	.000	.000
600	7.090	11.499	8.416	1.971	.000	.000	.000
700	7.420	12.817	8.946	2.497	.000	.000	.000
800	7.750	13.975	9.559	3.557	.000	.000	.000
900	8.230	14.916	10.075	4.356	.000	.000	.000
1000	8.680	15.415	10.605	5.210	.000	.000	.000
1100	9.520	16.488	11.118	6.127	.000	.000	.000
1200	10.310	17.548	11.618	7.115	.000	.000	.000
1300	11.630	18.424	12.108	8.211	.000	.000	.000
1400	10.570	19.337	12.592	9.443	.000	.000	.000
1500	9.500	20.021	13.065	10.435	.000	.000	.000
1600	9.150	20.629	13.519	11.345	.000	.000	.000
1700	9.030	21.172	13.953	12.272	.000	.000	.000
1800	9.680	21.869	14.407	17.067	.000	.000	.000
1900	9.680	24.813	14.920	14.035	.000	.000	.000
2000	9.680	24.909	15.407	16.008	.000	.000	.000
2100	9.680	25.381	15.871	15.971	.000	.000	.000
2200	9.680	25.832	16.314	20.539	.000	.000	.000
2300	9.680	26.262	16.737	21.907	.000	.000	.000
2400	9.680	26.674	17.143	22.875	.000	.000	.000
2500	9.680	27.069	17.532	23.843	.000	.000	.000
2600	9.680	27.449	17.906	24.811	.000	.000	.000
2700	9.680	27.814	18.270	24.779	.000	.000	.000
2800	9.680	28.166	18.613	24.747	.000	.000	.000
2900	9.680	28.506	18.949	27.715	.000	.000	.000
3000	9.680	28.834	19.273	28.663	.000	.000	.000
3100	9.680	29.151	19.586	28.451	.000	.000	.000
3200	9.680	29.459	19.887	19.437	.000	.000	.000
3300	6.304	27.763	21.246	120.368	.000	.000	.000
3400	6.319	27.959	22.344	120.999	.000	.000	.000
3500	6.333	28.135	23.383	121.632	.000	.000	.000
3600	6.351	28.316	24.381	122.266	.000	.000	.000
3700	6.374	28.498	25.341	122.900	.000	.000	.000
3800	6.396	28.680	26.168	123.540	.000	.000	.000
3900	6.423	28.825	26.983	124.181	.000	.000	.000
4000	6.453	28.988	27.781	124.825	.000	.000	.000
4100	6.487	29.167	28.564	125.472	.000	.000	.000
4200	6.521	29.364	29.329	126.122	.000	.000	.000
4300	6.563	29.608	30.075	126.777	.000	.000	.000
4400	6.605	29.809	30.687	127.435	.000	.000	.000
4500	6.650	29.758	31.292	128.098	.000	.000	.000
4600	6.697	29.905	31.913	128.745	.000	.000	.000
4700	6.746	30.050	32.510	129.437	.000	.000	.000
4800	6.798	30.192	33.049	130.114	.000	.000	.000
4900	6.855	30.333	33.640	130.797	.000	.000	.000
5000	6.907	30.472	34.175	131.485	.000	.000	.000
5100	6.965	30.609	34.692	132.178	.000	.000	.000
5200	7.024	30.745	35.192	132.878	.000	.000	.000
5300	7.085	30.879	35.675	133.583	.000	.000	.000
5400	7.147	31.012	36.163	134.295	.000	.000	.000
5500	7.210	31.144	36.596	135.013	.000	.000	.000
5600	7.275	31.275	37.036	135.737	.000	.000	.000
5700	7.340	31.406	37.482	136.466	.000	.000	.000
5800	7.404	31.532	37.926	137.205	.000	.000	.000
5900	7.474	31.659	38.378	137.949	.000	.000	.000
6000	7.541	31.786	38.849	138.700	.000	.000	.000

Sept. 30, 1967

See crystal, liquid and monatomic gas tables for details.

Cobalt (Co)

Co

(Crystal)

GFW = 58.9332

GFW = 58.9332

COBALT (Co)

(CRYSTAL)

T, °K	C _p ^o	S ^o - (C _p ^o - H _{298.15})/T	H ^o - H _{298.15}	ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	1.139	0.000	0.000	0.000
100	3.330	1.040	11.990	0.000	0.000	0.000
200	5.340	4.920	7.710	0.000	0.000	0.000
298	5.930	7.180	0.000	0.000	0.000	0.000
300	5.937	7.217	0.111	0.000	0.000	0.000
400	6.740	8.680	7.419	0.000	0.000	0.000
500	6.740	10.439	1.279	0.000	0.000	0.000
600	7.090	11.699	8.414	0.000	0.000	0.000
700	7.420	12.617	8.964	0.000	0.000	0.000
800	7.720	13.315	9.797	0.000	0.000	0.000
900	8.000	13.815	10.075	0.000	0.000	0.000
1000	8.240	15.415	5.210	0.000	0.000	0.000
1100	9.520	16.688	11.118	0.000	0.000	0.000
1200	10.330	17.548	11.618	0.000	0.000	0.000
1300	11.670	18.437	12.595	0.000	0.000	0.000
1400	12.590	19.437	13.065	0.000	0.000	0.000
1500	9.500	20.021	10.435	0.000	0.000	0.000
1600	9.150	20.422	13.519	0.000	0.000	0.000
1700	9.030	21.172	13.953	0.000	0.000	0.000
1800	9.000	21.976	14.366	0.000	0.000	0.000
1900	9.000	22.436	14.976	0.000	0.000	0.000
2000	9.000	22.436	14.976	0.000	0.000	0.000
2100	9.000	23.075	15.516	4.095	0.747	0.078
2200	9.000	23.494	16.776	4.163	0.960	0.092
2300	9.000	23.577	16.537	4.259	1.453	0.132
2400	9.000	24.445	16.854	4.367	1.693	0.148
2500	9.000	24.445	16.854	4.367	1.693	0.148

S_{298.15} = 7.18 ± 0.1 gibbs/molΔH_f^o = 0 kcal/molΔH_f^o_{298.15} = 0 kcal/molΔH_f^o = 0.108 kcal/molΔH_m^o = 3.87 ± 0.06 kcal/molΔH_f^o_{298.15} = 101.5 ± 0.5 kcal/mol

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity of Co(c) is adopted from Hultgren et al. (1). Their selected values are based on the data from nineteen investigations. The entropy values are based on S₁^o = 0.0011 eu. The heat capacity has a maximum value of 13.14 gibbs/mol at the Curie point (1394°K).

Transition Data

The exact nature of the α(hcp)-β(fcc) transition is yet to be clearly elucidated. Three investigations (2,3,4) indicate that it is not a simple time- and temperature-dependent phenomenon. Crystalline cobalt exists as pure β-phase above 700°K whereas mixtures of alpha and beta cobalt commonly coexist in varying proportions below this temperature. The values of T_c^o and ΔH_t^o are those selected by Hultgren et al. (1).

Melting Data

The temperature and heat of melting are those selected by Hultgren et al. (1).

Heat of Sublimation

The heat of sublimation is calculated from the data of Edwards et al. (5). See Co(g) table for details.

References

1. R. Hultgren, R. L. Orr and K. K. Kelley "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," University of California, Berkeley, Calif., (1966).
2. O. S. Edwards and H. Lipson, J. Inst. Metals 89, 177 (1943).
3. A. R. Troiano and J. L. Tokich, Trans. Am. Inst. Mining Met. Engrs. 175, 728 (1948).
4. P. R. Rao, Proc. Indian Acad. Sci. Sect. A, 61, 230 (1965).
5. J. W. Edwards, H. L. Johnston and W. E. Dittmars, J. Am. Chem. Soc. 73, 4779 (1951).

Cobalt (Co)

GFW = 58.9332

(Liquid)

COBALT (Co) (LIQUID)

GFW = 58.9332

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100						
200						
298						
300	5.930	9.793	9.793	.000	3.524	2.593
400	5.937	9.830	9.793	.011	3.519	2.564
500	6.340	11.593	10.031	.625	3.258	1.760
600	6.740	13.052	10.493	1.279	4.303	1.310
700	7.090	14.312	11.027	1.971	2.735	.996
800	7.380	15.426	11.577	2.664	2.473	.772
900	7.750	16.434	12.122	3.450	2.228	.609
1000	8.250	17.375	12.654	4.249	1.982	.481
1100	8.840	18.274	13.172	5.103	1.736	.379
1200	9.520	19.148	13.675	6.020	1.490	.294
1300	9.560	19.978	14.166	6.974	1.246	.227
1400	9.600	20.745	14.643	7.932	1.007	.169
1500	9.640	21.458	15.105	8.894	3.754	.122
1600	9.680	22.124	15.551	9.860	3.728	.084
1700	9.680	22.740	15.981	10.828	3.746	.050
1800	9.680	23.316	16.397	11.794	3.827	.019
1900	9.680	23.850	16.798	12.746	.000	.000
2000	9.680	24.349	17.185	13.732	.000	.000
2100	9.680	24.809	17.559	14.700	.000	.000
2200	9.680	25.341	17.920	15.648	.000	.000
2300	9.680	25.832	18.270	16.596	.000	.000
2400	9.680	26.282	18.608	17.604	.000	.000
2500	9.680	26.674	18.935	18.572	.000	.000
2600	9.680	27.069	19.253	19.540	.000	.000
2700	9.680	27.460	19.561	20.508	.000	.000
2800	9.680	27.814	19.860	21.426	.000	.000
2900	9.680	28.166	20.150	22.444	.000	.000
3000	9.680	28.506	20.433	23.412	.000	.000
3100	9.680	28.834	20.707	24.380	.000	.000
3200	9.680	29.151	20.974	25.348	.000	.000
3300	9.680	29.459	21.235	26.316	.000	.000
3400	9.680	29.757	21.489	27.284	.000	.000
3500	9.680	30.045	21.736	28.252	.000	.000
3600	9.680	30.326	21.977	29.220	.000	.000
3700	9.680	30.599	22.213	30.188	.000	.000
3800	9.680	30.864	22.448	31.156	.000	.000
3900	9.680	31.122	22.648	32.124	.000	.000
4000	9.680	31.374	22.888	33.092	.000	.000
4100	9.680	31.619	23.104	34.060	.000	.000
4200	9.680	31.859	23.299	35.028	.000	.000
4300	9.680	32.094	23.484	36.000	.000	.000
4400	9.680	32.324	23.659	36.972	.000	.000
4500	9.680	32.549	23.824	37.944	.000	.000
4600	9.680	32.769	23.989	38.916	.000	.000
4700	9.680	32.984	24.154	39.888	.000	.000
4800	9.680	33.194	24.319	40.860	.000	.000
4900	9.680	33.399	24.484	41.832	.000	.000
5000	9.680	33.604	24.649	42.804	.000	.000
5100	9.680	33.809	24.814	43.776	.000	.000
5200	9.680	34.014	24.979	44.748	.000	.000
5300	9.680	34.219	25.144	45.720	.000	.000
5400	9.680	34.424	25.309	46.692	.000	.000
5500	9.680	34.629	25.474	47.664	.000	.000
5600	9.680	34.834	25.639	48.636	.000	.000
5700	9.680	35.039	25.804	49.608	.000	.000
5800	9.680	35.244	25.969	50.580	.000	.000
5900	9.680	35.449	26.134	51.552	.000	.000
6000	9.680	35.654	26.299	52.524	.000	.000
6100	9.680	35.859	26.464	53.496	.000	.000
6200	9.680	36.064	26.629	54.468	.000	.000
6300	9.680	36.269	26.794	55.440	.000	.000
6400	9.680	36.474	26.959	56.412	.000	.000
6500	9.680	36.679	27.124	57.384	.000	.000
6600	9.680	36.884	27.289	58.356	.000	.000
6700	9.680	37.089	27.454	59.328	.000	.000
6800	9.680	37.294	27.619	60.300	.000	.000
6900	9.680	37.499	27.784	61.272	.000	.000
7000	9.680	37.704	27.949	62.244	.000	.000
7100	9.680	37.909	28.114	63.216	.000	.000
7200	9.680	38.114	28.279	64.188	.000	.000
7300	9.680	38.319	28.444	65.160	.000	.000
7400	9.680	38.524	28.609	66.132	.000	.000
7500	9.680	38.729	28.774	67.104	.000	.000
7600	9.680	38.934	28.939	68.076	.000	.000
7700	9.680	39.139	29.104	69.048	.000	.000
7800	9.680	39.344	29.269	70.020	.000	.000
7900	9.680	39.549	29.434	70.992	.000	.000
8000	9.680	39.754	29.599	71.964	.000	.000
8100	9.680	39.959	29.764	72.936	.000	.000
8200	9.680	40.164	29.929	73.908	.000	.000
8300	9.680	40.369	30.094	74.880	.000	.000
8400	9.680	40.574	30.259	75.852	.000	.000
8500	9.680	40.779	30.424	76.824	.000	.000
8600	9.680	40.984	30.589	77.796	.000	.000
8700	9.680	41.189	30.754	78.768	.000	.000
8800	9.680	41.394	30.919	79.740	.000	.000
8900	9.680	41.599	31.084	80.712	.000	.000
9000	9.680	41.804	31.249	81.684	.000	.000
9100	9.680	42.009	31.414	82.656	.000	.000
9200	9.680	42.214	31.579	83.628	.000	.000
9300	9.680	42.419	31.744	84.600	.000	.000
9400	9.680	42.624	31.909	85.572	.000	.000
9500	9.680	42.829	32.074	86.544	.000	.000
9600	9.680	43.034	32.239	87.516	.000	.000
9700	9.680	43.239	32.404	88.488	.000	.000
9800	9.680	43.444	32.569	89.460	.000	.000
9900	9.680	43.649	32.734	90.432	.000	.000
10000	9.680	43.854	32.899	91.404	.000	.000

Sept. 30, 1967

Co

$$\Delta H_f^{298.15} = 4.303 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 3.87 \pm 0.06 \text{ kcal/mol}$$

$$\Delta H_v^\circ = 89.219 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 9.79 \text{ gibbs/mol}$$

$$T_m = 1768^\circ\text{K}$$

$$T_b = 3170.29^\circ\text{K}$$

Heat of Formation

The heat of formation (ΔH_f°) of Co(l) is obtained from that of the crystal by adding ΔH_m° and the differences between $H_{1768}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity of Co(l) selected by Hultgren et al. (1) is used at temperatures above 1768°K. The heat capacities at temperatures below the melting point are estimated by assuming a glass transition at 1100°K and heat capacities similar to those of the crystal below 1100°K.

Melting Data

See Co(c) table for details.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen heat of sublimation at 298°K so that the free energy functions calculated by integration of the crystal liquid data and by statistical methods from the gas phase are equal at the boiling point.

Reference

1. R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," University of California, Berkeley, Calif. (1966).

Cobalt (Co)
(Ideal Gas)

GFV = 58.9332

T, °K	Cp ^b	S ^c	-(C _p ^b - H ^o)/T	H ^o - H ²⁹⁸	ΔH ^o	ΔG ^f	Log K ^p
0	0.000	INFINITE	0.000	0.000	0.000	0.000	INFINITE
100	6.270	37.290	47.521	1.023	97.947	97.947	-214.665
200	5.127	40.764	43.369	-0.521	94.368	94.368	-103.121
298	5.503	42.879	42.879	0.000	90.857	90.857	-66.600
300	5.510	42.813	42.870	0.100	90.791	90.791	-66.141
400	5.257	45.481	43.527	0.959	87.297	87.297	-39.375
500	5.077	48.461	45.527	1.177	83.677	83.677	-29.575
600	4.886	51.000	48.015	1.171	80.140	80.140	-29.191
700	4.686	53.234	50.248	1.243	76.617	76.617	-23.921
800	4.479	55.163	52.177	1.296	73.187	73.187	-19.977
900	4.259	56.793	53.807	1.333	69.858	69.858	-16.465
1000	4.029	58.163	55.177	1.356	66.625	66.625	-13.465
1100	3.793	59.309	56.313	1.368	62.760	62.760	-10.473
1200	3.559	60.250	57.254	1.370	58.388	58.388	-7.416
1300	3.327	61.000	57.900	1.368	53.503	53.503	-4.318
1400	3.097	61.571	58.369	1.356	48.117	48.117	-1.200
1500	2.871	62.000	58.667	1.333	42.234	42.234	0.304
1600	2.649	62.300	58.833	1.300	35.858	35.858	1.516
1700	2.431	62.479	58.886	1.256	29.086	29.086	2.516
1800	2.217	62.534	58.833	1.200	21.917	21.917	3.375
1900	2.007	62.479	58.667	1.133	14.358	14.358	4.029
2000	1.800	62.309	58.313	1.056	6.403	6.403	4.500
2100	1.600	61.934	57.800	0.971	-1.846	-1.846	4.800
2200	1.400	61.463	57.143	0.879	-8.281	-8.281	4.934
2300	1.200	60.900	56.357	0.771	-15.817	-15.817	4.900
2400	1.000	60.250	55.443	0.649	-23.454	-23.454	4.734
2500	0.800	59.521	54.400	0.506	-31.181	-31.181	4.443
2600	0.600	58.625	53.229	0.343	-38.998	-38.998	4.029
2700	0.400	57.571	51.934	0.163	-46.906	-46.906	3.500
2800	0.200	56.369	50.521	0.000	-54.917	-54.917	2.871
2900	0.000	55.000	48.900	0.000	-63.034	-63.034	2.143
3000	0.000	53.500	47.071	0.000	-71.259	-71.259	1.317
3100	0.000	51.857	45.034	0.000	-79.598	-79.598	0.400
3200	0.000	50.000	42.793	0.000	-88.053	-88.053	-0.500
3300	0.000	48.000	40.357	0.000	-96.625	-96.625	-1.350
3400	0.000	45.857	37.729	0.000	-105.317	-105.317	-2.071
3500	0.000	43.571	34.900	0.000	-114.129	-114.129	-2.671
3600	0.000	41.143	31.869	0.000	-123.054	-123.054	-3.150
3700	0.000	38.571	28.629	0.000	-132.093	-132.093	-3.517
3800	0.000	35.857	25.186	0.000	-141.246	-141.246	-3.771
3900	0.000	33.000	21.543	0.000	-150.517	-150.517	-3.917
4000	0.000	30.000	17.714	0.000	-160.000	-160.000	-3.950
4100	0.000	26.857	13.714	0.000	-169.693	-169.693	-3.871
4200	0.000	23.571	9.357	0.000	-179.598	-179.598	-3.686
4300	0.000	20.143	4.629	0.000	-189.717	-189.717	-3.393
4400	0.000	16.571	-0.400	0.000	-200.054	-200.054	-2.993
4500	0.000	12.857	-5.250	0.000	-210.717	-210.717	-2.493
4600	0.000	9.000	-10.000	0.000	-221.717	-221.717	-1.893
4700	0.000	5.000	-14.643	0.000	-233.054	-233.054	-1.193
4800	0.000	0.857	-19.143	0.000	-244.717	-244.717	-0.400
4900	0.000	-3.250	-23.400	0.000	-256.717	-256.717	0.400
5000	0.000	-7.500	-27.357	0.000	-269.054	-269.054	1.143
5100	0.000	-11.857	-31.000	0.000	-281.717	-281.717	1.843
5200	0.000	-16.357	-34.357	0.000	-294.717	-294.717	2.493
5300	0.000	-20.900	-37.429	0.000	-308.054	-308.054	3.093
5400	0.000	-25.500	-40.214	0.000	-321.717	-321.717	3.643
5500	0.000	-30.143	-42.714	0.000	-335.717	-335.717	4.143
5600	0.000	-34.857	-44.929	0.000	-350.054	-350.054	4.593
5700	0.000	-39.629	-46.857	0.000	-364.717	-364.717	4.993
5800	0.000	-44.457	-48.500	0.000	-379.717	-379.717	5.343
5900	0.000	-49.343	-49.857	0.000	-395.054	-395.054	5.643
6000	0.000	-54.286	-50.929	0.000	-410.717	-410.717	5.893

Sept. 30, 1967

COBALT, MONATOMIC (Co)

Ground State Configuration

$4f^7 5s^2$

$S^{\circ}_{298.15} = 42.88 \text{ gibbs/mol}$

(IDEAL GAS)

GFV = 58.9332

$\Delta H^{\circ}_0 = 101.1 \pm 0.5 \text{ kcal/mol}$

$\Delta H^{\circ}_{298.15} = 101.5 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Multiplicities

ϵ_i cm ⁻¹	g_i	ϵ_j cm ⁻¹	g_j	ϵ_i cm ⁻¹	g_i	ϵ_j cm ⁻¹	g_j	ϵ_i cm ⁻¹	g_i	ϵ_j cm ⁻¹	g_j
0	10	5076	4	15774	4	18775	2	23184	10	29488	36
816	8	7442	8	16186	2	20501	4	23208	8	30107	20
1407	6	8461	6	16467	10	21216	2	24466	42	33100	144
1809	4	13796	6	17234	8	21780	12	25590	30	42245	268
3483	10	14036	4	16471	4	22475	10	25987	54	48000	694
4343	8	14399	2	16778	6	21921	6	27883	10	50000	782
4690	6	15184	6	18390	4	23153	4	28975	28	[18000]	24

Heat of Formation

The heat of formation is the heat of sublimation at 298°K. The adopted value is that reported by Edwards et al. (1). Their value is used because their vapor pressure measurements for Fe (1) and Cu (2) have proved to be very reliable. The results obtained by Vintaikin and Tomash (3) are rejected because their vapor pressure data for Fe (4) resulted in a value for the heat of sublimation which was higher than the accepted value (see JANAF Fe(4) Table for details). The remaining vapor pressure data are rejected either because the drift was too large or because there were not enough points. Second and third law analyses of the available vapor pressure data gave the following results, with reaction A corresponding to $\text{Co}(c) = \text{Co}(g)$ and reaction B corresponding to $\text{Co}(l) = \text{Co}(g)$.

Source	Reaction	Method	No. Pts.	Range, T°K	$\Delta H^{\circ}_{298.15}$	2nd Law	3rd Law	Drift, eu	ΔH°_{298}
Edwards (1)	A	Langmuir	9	1363-1522	101.0 ± 1.0	101.54	101.54	+0.4 ± 0.7	101.54
Kornev (5)	A	Knudsen	8*	1373-1523	98.8 ± 0.8	95.37	95.37	-2.4 ± 0.6	95.37
Dancy (6)	B	Langmuir	1	1823	--	90.61	90.61	--	94.82
Ruff (7)	B	Boiling Pt.	1	2648	--	99.35	99.35	--	103.66
Nesmeyanov (8)	A	Knudsen	3	1391-1540	82.4 ± 2.4	82.31	82.31	-0.1 ± 1.6	82.31
Nesmeyanov (9)	A	Knudsen	12*	1345-1541	91.7 ± 2.4	83.19	83.19	-5.9 ± 1.7	83.19
Vintaikin (3)	A	Knudsen	Eqn.	1373-1523	102.9	103.34	103.34	+0.3	103.34

*One point rejected due to failure of a statistical test.

**Calculation based on third law ΔH°_{298} .

Heat Capacity and Entropy

The electronic levels are taken from Moore (10). Levels above 25,000 cm⁻¹ are averaged. Unobserved levels below 20,000 cm⁻¹ are estimated.

References

1. J. W. Edwards, H. L. Johnston and W. E. Dittmar, J. Am. Chem. Soc. **73**, 4729 (1951).
2. J. W. Edwards, H. L. Johnston and W. E. Dittmar, J. Am. Chem. Soc. **75**, 2467 (1953).
3. E. Z. Vintaikin and Ya. Tomash, Russ. J. Phys. Chem. (English Transl.) **35**, 1042 (1961).
4. E. Z. Vintaikin, Dokl. Akad. Nauk SSSR **117**, 832 (1957).
5. Iu. V. Kornev and V. N. Golubkin, Dokl. Akad. Nauk SSSR **99**, 565 (1954).
6. T. E. Dancy, J. Iron Steel Inst. (London) **167**, 160 (1951).
7. O. Ruff and F. Keilig, Z. Anorg. Chem. **129**, 321 (1914).
8. An. N. Nesmeyanov and D. D. Man, Dokl. Akad. Nauk SSSR **123**, 1064 (1959).
9. An. N. Nesmeyanov and D. D. Man, Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk, No. 1 (1960).
10. C. E. Moore, U. S. Natl. Bur. Std. Circ. **467** (1949).

Sept. 30, 1967

$$\Delta H_f^\circ = 282.50 \pm 0.5 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 284.34 \pm 0.5 \text{ kcal/mol}$$

Ground State Configuration $3F_4$

$$S^\circ_{298.15} = 42.6 \pm 0.1 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	8	13261	5	27484	7
950	7	13405	3	28112	5
1597	5	13594	1	27585	3
3351	11	17772	7	41738	25
4029	9	18032	5	45972	35
4561	7	18339	3	47667	69
4950	5	24075	5	49865	48
5205	3	24268	3	52230	15
9813	9	24412	1	56011	5
10708	7	24887	5	62670	58
11322	5	26000	4	84127	131

Heat of Formation

The heat of formation, ΔH_f° , is calculated from the equation $\text{Co}(g) \rightarrow e^- + \text{Co}^+(g)$ with the JANAF auxiliary value for $\text{Co}(g)$; using an ionization potential of 6348 cm⁻¹ (181.377 kcal/mol) obtained from C. E. Moore, "Atomic Energy Levels," Vol. II, U. S. Natl. Bur. Std. Circ. 467, 1949. The value of $H^\circ - H^\circ_{298}$ is -1.504 kcal/mol.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, loc. cit. Levels above 30,000 cm⁻¹ are averaged.

T, °K	C_p°	S°	$-(C^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	$\log K_p$
200	5.123	42.599	62.599	.000	284.341	272.293	-199.596
250	5.129	42.632	62.599	.010	284.349	272.219	-198.311
300	5.142	42.665	62.609	.059	284.781	268.110	-186.608
350	5.170	42.695	62.624	.135	285.200	263.894	-175.348
400	5.200	42.719	62.637	.230	285.600	259.595	-164.557
450	5.230	42.743	62.649	.337	285.977	255.228	-154.228
500	5.260	42.767	62.661	.457	286.333	250.803	-144.353
550	5.287	42.781	62.673	.587	286.552	246.343	-134.938
600	5.311	42.794	62.685	.724	286.698	241.904	-125.968
650	5.335	42.807	62.697	.867	286.772	237.490	-117.447
700	5.358	42.819	62.709	1.015	286.788	233.100	-109.366
750	5.380	42.831	62.721	1.167	286.748	228.732	-101.722
800	5.401	42.843	62.733	1.322	286.663	224.385	-94.513
850	5.421	42.855	62.745	1.480	286.533	220.057	-87.722
900	5.440	42.867	62.757	1.639	286.368	215.738	-81.343
950	5.458	42.879	62.769	1.800	286.168	211.428	-75.372
1000	5.475	42.891	62.781	1.962	285.933	207.128	-69.802
1100	5.500	42.916	62.806	2.287	285.500	202.738	-63.422
1200	5.523	42.939	62.829	2.612	284.967	198.268	-57.042
1300	5.545	42.961	62.851	2.937	284.333	193.718	-50.662
1400	5.566	42.983	62.873	3.262	283.600	189.088	-44.282
1500	5.587	42.995	62.885	3.587	282.767	184.378	-37.902
1600	5.607	43.007	62.897	3.912	281.833	179.588	-31.522
1700	5.626	43.019	62.909	4.237	280.800	174.718	-25.142
1800	5.644	43.031	62.921	4.562	279.667	169.768	-18.762
1900	5.661	43.043	62.933	4.887	278.433	164.738	-12.382
2000	5.678	43.055	62.945	5.212	277.100	159.628	-6.002
2100	5.694	43.067	62.957	5.537	275.667	154.438	3.378
2200	5.709	43.079	62.969	5.862	274.133	149.168	8.758
2300	5.723	43.091	62.981	6.187	272.500	143.818	14.138
2400	5.737	43.103	62.993	6.512	270.767	138.388	19.518
2500	5.750	43.115	63.005	6.837	268.933	132.878	24.898
2600	5.763	43.127	63.017	7.162	267.000	127.288	30.278
2700	5.775	43.139	63.029	7.487	264.967	121.618	35.658
2800	5.787	43.151	63.041	7.812	262.833	115.868	41.038
2900	5.799	43.163	63.053	8.137	260.600	109.938	46.418
3000	5.811	43.175	63.065	8.462	258.267	103.828	51.798
3100	5.823	43.187	63.077	8.787	255.833	97.538	57.178
3200	5.835	43.199	63.089	9.112	253.300	91.168	62.558
3300	5.847	43.211	63.101	9.437	250.667	84.718	67.938
3400	5.859	43.223	63.113	9.762	247.933	78.188	73.318
3500	5.871	43.235	63.125	10.087	245.100	71.578	78.698
3600	5.883	43.247	63.137	10.412	242.167	64.888	84.078
3700	5.895	43.259	63.149	10.737	239.133	58.118	89.458
3800	5.907	43.271	63.161	11.062	236.000	51.268	94.838
3900	5.919	43.283	63.173	11.387	232.767	44.338	100.218
4000	5.931	43.295	63.185	11.712	229.433	37.328	105.598
4100	5.943	43.307	63.197	12.037	226.000	30.238	110.978
4200	5.955	43.319	63.209	12.362	222.467	23.068	116.358
4300	5.967	43.331	63.221	12.687	218.833	15.818	121.738
4400	5.979	43.343	63.233	13.012	215.100	8.488	127.118
4500	5.991	43.355	63.245	13.337	211.267	1.078	132.498
4600	6.003	43.367	63.257	13.662	207.333	-6.412	137.878
4700	6.015	43.379	63.269	13.987	203.300	-13.822	143.258
4800	6.027	43.391	63.281	14.312	199.167	-21.152	148.638
4900	6.039	43.403	63.293	14.637	194.933	-28.402	153.918
5000	6.051	43.415	63.305	14.962	190.600	-35.572	159.198
5100	6.063	43.427	63.317	15.287	186.167	-42.672	164.478
5200	6.075	43.439	63.329	15.612	181.633	-49.702	169.758
5300	6.087	43.451	63.341	15.937	176.933	-56.672	175.038
5400	6.099	43.463	63.353	16.262	172.067	-63.582	180.318
5500	6.111	43.475	63.365	16.587	167.033	-70.432	185.598
5600	6.123	43.487	63.377	16.912	161.833	-77.222	190.878
5700	6.135	43.499	63.389	17.237	156.467	-83.952	196.158
5800	6.147	43.511	63.401	17.562	150.933	-90.622	201.438
5900	6.159	43.523	63.413	17.887	145.233	-97.232	206.718
6000	6.171	43.535	63.425	18.212	139.367	-103.782	211.998

COBALT DIFLUORIDE (CoF₂)

GFW = 96.9300

(CRYSTAL)

$$\Delta H_f^\circ = -160.2 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -160.5 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 14.058 \pm 3.0 \text{ kcal/mol}$$

$$\Delta H_s^\circ = 75.3 \pm 3.0 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 19.60 \pm 0.10 \text{ gibbs/mol}$$

$$T_m = 1400^\circ\text{K}$$

Cobalt Difluoride (CoF₂)

(Crystal)

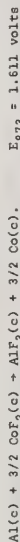
GFW = 96.9300

T, °K	Cp ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	INFINITE	INFINITE	2.978	-160.229	-160.229	INFINITE
100	6.005	5.976	32.192	2.652	-160.692	-157.036	343.201
200	13.763	13.563	21.032	1.494	-160.721	-153.341	167.563
298	16.470	16.605	19.605	1.000	-160.500	-149.760	109.777
300	16.501	19.701	19.605	0.931	-160.494	-149.694	109.052
400	18.096	24.701	20.275	1.770	-160.139	-146.144	79.849
500	18.864	28.430	21.586	3.652	-159.748	-142.691	62.370
600	19.309	32.312	23.091	5.533	-159.361	-139.316	50.746
700	19.516	36.244	24.631	7.450	-158.977	-136.009	41.000
800	19.616	37.944	26.131	9.450	-158.787	-132.730	36.260
900	19.679	40.287	27.576	11.440	-158.432	-129.497	31.446
1000	20.115	42.400	28.954	13.445	-158.166	-126.298	27.602
1100	20.231	44.322	30.265	15.463	-157.957	-123.122	24.462
1200	20.279	46.076	31.521	17.509	-157.775	-119.969	21.840
1300	20.278	47.679	32.736	19.579	-157.615	-116.834	19.642
1400	20.216	49.236	33.824	21.576	-157.467	-113.654	17.742
1500	20.599	50.654	34.899	23.632	-157.314	-110.561	16.100
1600	20.578	51.966	35.926	25.696	-157.195	-107.561	14.665
1700	20.427	53.076	36.909	27.686	-157.094	-104.640	13.370
1800	20.427	54.036	37.849	29.617	-156.986	-101.754	12.200
1900	20.499	55.558	38.751	31.933	-156.692	-97.735	11.242
2000	20.969	56.632	39.619	34.026	-156.494	-94.425	10.318

June 30, 1970

Heat of Formation

Heus and Egan (1) measured the electromotive force of a solid state galvanic cell which involved the reactions



$$E_{973} = 1.611 \text{ volts}$$



$$E_{973} = 2.231 \text{ volts}$$

Combining these results with auxiliary thermodynamic data (2) for the reactants and products, we derive $\Delta H_f^\circ(\text{CoF}_2, \text{c}) = -160.2$ and -159.5 kcal/mol .

Several equilibrium studies (3, 4, 5) involving CoF₂(c) have been reported in the literature. Second and third law analyses of these equilibrium data are summarized below, auxiliary data for Co(c) and CoCl₂(c) are from (6).

Reference	Chemical Reaction	Temp. Range °K	Points	ΔH_{298}° kcal/mol	2nd law gibbs/mol	3rd law gibbs/mol	Drift kcal/mol	$\Delta H_f^\circ(\text{CoF}_{2.1}\text{c})$ kcal/mol
(3)	CoF ₂ (c) + 2HCl(g) \rightleftharpoons CoCl ₂ (c) + 2HF(g)	588-805	3	4.1	1.75±0.4	-1.7±0.1	-162.6±2.0	
(4)	CoF ₂ (c) + H ₂ (g) \rightleftharpoons Co(c) + 2HF(g)	673-873	3	35.2	31.5±1.0	-4.2±3.5	-161.8±2.0	
(5)	CoF ₂ (c) + H ₂ O(g) \rightleftharpoons CoO(c) + 2HF(g)	773-1023	5	30.2	31.1±0.2	0.8±0.3	-160.4±2.0	

*Third law values except for the first reaction.

We note that Heus and Egan (1), in the same paper, measured $\Delta H_{298}^\circ(\text{AlF}_3, \text{c}) = -360.2 \text{ kcal}$ in excellent agreement with the JANAF value (2). Domange (5) also measured similar equilibria for MgF₂ and CaF₂, which were very consistent with the JANAF heats of formation (2). Jellinek and Rudat (4) reported similar equilibria for PbF₂(c), which show excellent consistency with the JANAF heat of formation (2). Thus, it is apparent that these three sets are probably quite reliable, and we adopt $\Delta H_{298.15}^\circ(\text{CoF}_2, \text{c}) = -160.5 \pm 1 \text{ kcal/mol}$.

Heat Capacity and Entropy

Catalano and Stout (7) measured low temperature heat capacities in the temperature range 10° to 300°K. Heat capacity data above 300°K are calculated from the high temperature (468-1400°K) enthalpy data of Binford et al. (8). Both sets of data were smoothed by computer and joined at 298.15°K.

The value of $S_{298.15}^\circ$ is obtained from the low temperature heat capacity data of Catalano and Stout (7) and is based on $S_{10}^\circ = 0.013 \text{ gibbs/mol}$.

Melting Data

$T_m = 1400^\circ\text{K}$ is from the high temperature enthalpy studies of Binford et al. (8). ΔH_m is calculated from their enthalpy data. Premelting of the sample is assumed to be responsible for the rapid rise in the enthalpy near the melting point. This enthalpy is included in ΔH_m .

Heat of Sublimation

Kana'an et al. (9) made sublimation studies of CoF₂ using Knudsen and Langmuir techniques over the temperature range 972°-1241°K. Second and third law analyses of these sublimation pressures are summarized below.

Method	Temp. Range °K	No. of Points	ΔH_{298}° kcal/mol	Drift gibbs/mol
Knudsen	1058-1242	17	75.0	75.1±0.1
Langmuir	972-1032	8	72.8	75.5±0.2

The selected value is $\Delta H_{298}^\circ = 75.3 \pm 3.0 \text{ kcal/mol}$.

References

1. R. J. Heus and J. J. Egan, *Z. Phys. Chem.*, **193**, 38 (1966).
2. JANAF Thermochemical Tables; AlF₃ dated 6-30-70; MgF₂ dated 3-31-66; PbF₂ dated 6-30-69; CaF₂ dated 12-31-68.
3. K. Jellinek and R. Koop, *Z. Phys. Chem.*, **A145**, 305 (1928).
4. K. Jellinek and A. Rudat, *Z. Anorg. Chem.*, **175**, 281 (1928).
5. L. Domange, *Ann. Chim.*, **7**, 225 (1937).
6. U. S. Natl. Bur. Std. Techn. Note 270-4, 1969.
7. E. Catalano and J. W. Stout, *J. Chem. Phys.*, **23**, 1803 (1955).
8. J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, *J. Phys. Chem.*, **71**, 2404 (1967).
9. A. S. Kana'an, G. Besenbruch, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **28**, 1035 (1966).

Cobalt Difluoride (CoF₂)

(Liquid)

GFW = 96.9300

COBALT DIFLUORIDE (CoF₂)

(LIQUID)

GFW = 96.9300

$$S_{298.15}^{\circ} = 20.61 \pm 2.5 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -152.412 \pm 4.0 \text{ kcal/mol}$$

$$T_m = 1400^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 14.058 \pm 3.0 \text{ kcal/mol}$$

$$T_b = 12012^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = [48.0] \text{ kcal/mol}$$

Heat of Formation

$\Delta H_f^{\circ}(l)$ is calculated from $\Delta H_f^{\circ}(c)$ by adding the heat of melting and the difference in ($H_{1400-H_{298}}$) between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid CoF₂ is estimated by comparison with those for FeCl₂(l), MgF₂(l), and PbF₂(l) and is assumed constant in the temperature range 298°-3000°K. Binford et al. (1) reported $C_p = 30.3$ gibbs/mol for liquid CoF₂ at 1444°K. This value is based on only two enthalpy points near the melting point and appears high in comparison with heat capacities for other liquid metal dihalides. Therefore, the value is not adopted.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the CoF₂(c) table for details.

Vaporization Data

T_b is the temperature at which the Gibbs energy change for the process CoF₂(l) + CoF₂(g) approaches zero. The difference between the heat of formation of the gas and liquid at T_b is ΔH_v° .

Reference

1. J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem., **71**, 2404 (1967).

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	25.000	20.611	20.611	.000	-152.412	-141.972	104.066
300	25.000	20.766	20.611	.046	-152.391	-141.906	103.360
400	25.000	27.958	21.592	2.546	-151.275	-138.593	95.741
500	25.000	33.536	23.484	5.046	-150.236	-135.552	87.201
600	25.000	38.094	25.517	7.546	-149.260	-132.684	80.330
700	25.000	41.948	27.596	10.046	-148.337	-129.995	74.566
800	25.000	45.286	29.604	12.546	-147.463	-127.421	69.810
900	25.000	48.231	31.513	15.046	-146.736	-124.952	65.943
1000	25.000	50.865	33.319	17.546	-146.177	-122.574	62.705
1100	25.000	53.248	35.024	20.046	-145.286	-120.268	59.895
1200	25.000	55.423	36.634	22.546	-144.671	-118.020	57.494
1300	25.000	57.424	38.158	25.046	-144.170	-115.821	55.471
1400	25.000	59.277	39.601	27.546	-143.800	-113.656	53.792
1500	25.000	61.002	40.971	30.046	-143.212	-111.520	52.446
1600	25.000	62.615	42.274	32.546	-142.557	-109.429	51.497
1700	25.000	64.131	43.515	35.046	-141.882	-107.378	50.804
1800	25.000	65.560	44.701	37.546	-141.099	-105.300	50.365
1900	25.000	66.911	45.834	40.046	-140.491	-103.105	50.160
2000	25.000	68.194	46.921	42.546	-140.000	-100.900	50.100
2100	25.000	69.413	47.963	45.046	-139.284	-98.810	50.283
2200	25.000	70.576	48.964	47.546	-138.685	-96.707	50.607
2300	25.000	71.688	49.928	50.046	-138.088	-94.629	51.022
2400	25.000	72.752	50.857	52.546	-137.494	-92.579	51.430
2500	25.000	73.772	51.754	55.046	-136.903	-90.553	51.816
2600	25.000	74.753	52.620	57.546	-136.314	-88.550	52.183
2700	25.000	75.696	53.457	60.046	-135.727	-86.570	52.537
2800	25.000	76.605	54.268	62.546	-135.142	-84.613	52.880
2900	25.000	77.483	55.053	65.046	-134.560	-82.674	53.210
3000	25.000	78.330	55.815	67.546	-133.961	-80.760	53.523

GF_W = 96.9300

(IDEAL GAS)

COBALT DIFLUORIDE (CoF₂)Point Group [C_{2v}] $\Delta H_f^\circ = -85.0 \pm 3.0$ kcal/mol $\Delta H_{298.15}^\circ = -85.2 \pm 3.0$ kcal/mol $S_{298.15}^\circ = [66.42 \pm 3.0]$ gibbs/molGround State Configuration [³F₂]Cobalt Difluoride (CoF₂)

(Ideal Gas)

GF_W = 96.9300

T, K	Cp	$S^\circ - (G^\circ - H^\circ_{298})/T$	gibbs/mol	$H^\circ - H^\circ_{298}$	kcal/mol	ΔH°	ΔG°	Log Kp
0	.000	INFINITE	INFINITE	-3.093	-	-85.044	-	INFINITE
100	9.821	54.354	76.866	-2.231	-	-85.001	-	186.353
200	11.016	61.166	83.016	-1.812	-	-85.000	-	195.439
298	12.239	66.421	88.421	-1.000	-	-85.000	-	195.439
300	12.232	66.427	88.427	-1.023	-	-85.202	-	64.827
400	12.793	70.102	92.102	-1.277	-	-85.332	-	48.069
500	13.126	72.996	94.996	-1.584	-	-85.466	-	39.567
600	13.341	75.409	96.912	-1.909	-	-85.695	-	33.332
700	13.494	77.478	98.691	-2.241	-	-85.930	-	28.687
800	13.613	79.288	100.261	-2.576	-	-86.161	-	25.205
900	13.713	80.897	101.660	-2.904	-	-86.388	-	22.681
1000	13.803	82.347	102.917	-3.226	-	-86.611	-	20.773
1100	13.885	83.660	104.040	-3.543	-	-86.830	-	19.041
1200	13.960	84.877	105.040	-3.856	-	-87.045	-	17.590
1300	14.029	85.998	105.915	-4.165	-	-87.256	-	16.355
1400	14.093	87.040	106.662	-4.469	-	-87.463	-	15.286
1500	14.150	88.014	107.291	-4.768	-	-87.666	-	14.357
1600	14.202	88.929	107.815	-5.062	-	-87.865	-	13.538
1700	14.250	89.781	108.240	-5.351	-	-88.060	-	12.812
1800	14.293	90.607	108.575	-5.635	-	-88.251	-	12.156
1900	14.331	91.361	108.831	-5.914	-	-88.438	-	11.549
2000	14.366	92.117	109.017	-6.188	-	-88.622	-	10.999
2100	14.397	92.819	109.159	-6.457	-	-88.803	-	10.500
2200	14.425	93.469	109.266	-6.721	-	-88.980	-	10.044
2300	14.450	94.131	109.340	-6.980	-	-89.153	-	9.625
2400	14.473	94.746	109.381	-7.234	-	-89.322	-	9.240
2500	14.493	95.337	109.398	-7.483	-	-89.487	-	8.883
2600	14.510	95.900	109.387	-7.727	-	-89.648	-	8.553
2700	14.526	96.454	109.346	-7.966	-	-89.805	-	8.245
2800	14.539	96.983	109.276	-8.200	-	-89.958	-	7.959
2900	14.550	97.489	109.181	-8.429	-	-90.107	-	7.690
3000	14.561	97.967	109.066	-8.653	-	-90.252	-	7.439
3100	14.569	98.404	108.934	-8.872	-	-90.393	-	7.202
3200	14.576	98.827	108.787	-9.087	-	-90.530	-	6.973
3300	14.582	99.237	108.626	-9.297	-	-90.663	-	6.759
3400	14.586	99.611	108.453	-9.502	-	-90.792	-	6.557
3500	14.589	100.234	108.234	-9.702	-	-90.917	-	6.367
3600	14.591	100.645	108.045	-9.897	-	-91.038	-	6.187
3700	14.592	101.044	107.860	-10.087	-	-91.155	-	6.016
3800	14.592	101.438	107.660	-10.271	-	-91.268	-	5.853
3900	14.591	101.813	107.446	-10.450	-	-91.376	-	5.696
4000	14.590	102.162	107.212	-10.624	-	-91.480	-	5.543
4100	14.588	102.542	106.963	-10.793	-	-91.580	-	5.393
4200	14.585	102.894	106.691	-10.957	-	-91.676	-	5.245
4300	14.581	103.237	106.402	-11.116	-	-91.769	-	5.100
4400	14.577	103.572	106.097	-11.270	-	-91.858	-	4.957
4500	14.573	103.900	105.776	-11.419	-	-91.943	-	4.816
4600	14.568	104.220	105.440	-11.563	-	-92.024	-	4.677
4700	14.563	104.533	105.088	-11.702	-	-92.101	-	4.540
4800	14.557	104.840	104.721	-11.836	-	-92.174	-	4.404
4900	14.551	105.140	104.340	-11.965	-	-92.243	-	4.269
5000	14.545	105.434	103.947	-12.089	-	-92.308	-	4.135
5100	14.539	105.722	103.542	-12.208	-	-92.369	-	4.001
5200	14.532	106.004	103.127	-12.322	-	-92.426	-	3.867
5300	14.526	106.281	102.702	-12.431	-	-92.479	-	3.733
5400	14.519	106.552	102.267	-12.535	-	-92.528	-	3.600
5500	14.512	106.816	101.822	-12.634	-	-92.573	-	3.467
5600	14.505	107.080	101.367	-12.728	-	-92.615	-	3.334
5700	14.498	107.337	100.902	-12.817	-	-92.654	-	3.201
5800	14.491	107.589	100.427	-12.901	-	-92.690	-	3.068
5900	14.483	107.836	99.942	-12.980	-	-92.723	-	2.935
6000	14.476	108.080	99.447	-13.054	-	-92.753	-	2.802

June 30, 1970

Electronic Levels and Quantum Weights

E_e, cm^{-1}	g_e
-----------------------	-------

0

{300}

{4000}

{3000}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

{4}

Vibrational Frequencies and Degeneracies

 ω_e, cm^{-1}

{600}

{1511}

{762}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

{1}

Bond Distance: Co-F = [1.72] Å
Bond Angle: F-Co-F = [165°]
Product of Moments of Inertia: $I_{AB}I_C = 6.5424 \times 10^{-116} \text{ g}^3 \text{ cm}^6$ $\sigma = 2$

Heat of Formation

The heat of formation of gaseous CoF_2 , $\Delta H_f^\circ = -88.1 \pm 7.0$ kcal/mol, is calculated from the heat of formation of the crystal, $\Delta H_{298}^\circ = -163.4 \pm 4.0$ kcal/mol, and the heat of sublimation, $\Delta H_{298}^\circ = 75.3 \pm 3.0$ kcal/mol. The sublimation value is determined from a third law analysis of the vapor pressure data for CoF_2 reported by Kana'an et al. (1). See $\text{CoF}_2(\text{c})$ table for details.

Heat Capacity and Entropy

Büchler et al. (2) investigated the deflection of a molecular beam of $\text{CoF}_2(\text{g})$ by an electric field and found that within the sensitivity of the apparatus the molecule was nonpolar and consequently possessed a linear structure. Hartie et al. (3) recently investigated the infrared absorption spectra of several transition metal difluorides through the use of matrix isolation techniques. Isotopic shift measurements for matrix isolated NiF_2 , ZnF_2 , and CuF_2 in neon and argon indicated that these species were slightly bent. Based upon these results, the authors estimated the F-Co-F angle as 165° . This value is adopted here. The bond length was estimated by Brewer et al. (4). Individual moments of inertia are $I_A = 0.1925 \times 10^{-39}$, $I_B = 18.341 \times 10^{-39}$, and $I_C = 18.533 \times 10^{-39} \text{ g cm}^2$.
Hartie et al. (3) isolated CoF_2 in neon and argon matrices and observed the ν_3 fundamental at 762 cm^{-1} . They also calculated $\nu_1 = 600 \text{ cm}^{-1}$ by a valence force field method and estimated ν_2 as 151 cm^{-1} by applying the variation in the frequencies for the chlorides of Co, Ni, Cu, and Zn to the fluorides. The electronic levels and quantum weights are estimated by comparison with the electronic energy levels for $\text{Co}^{2+}(\text{g})$ ion (5) and those for $\text{CoF}_2(\text{g})$ observed by Hough et al. (6).

References

1. A. S. Kana'an, G. Besenbruch, and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **28**, 1035 (1966).
2. A. Büchler, J. L. Stauffer, and W. Kienperger, *J. Chem. Phys.*, **40**, 3471 (1964).
3. J. W. Hartie, R. H. Hauge, and J. L. Margrave, *High Temperature Science*, **1**, 76 (1969).
4. L. Brewer, R. R. Somayajulu, and E. Brackett, *Chem. Rev.*, **63**, 111 (1963).
5. C. E. Moore, *U. S. Natl. Bur. Std. Circ.*, **467**, Vol. II, 1952.
6. J. T. Hough, G. E. Leroy, and T. C. James, *J. Chem. Phys.*, **34**, 1670 (1961).

Cesium (Cs)

(Reference State) GFW = 132.905

CESIUM (Cs)

(REFERENCE STATE)

GFW = 132.905

T, K	Cp ^o	S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	ΔH ^o	ΔG ^o	Log Kp
0	.000	.000	INFINITE	1.844	.000	.000	.000
100	6.16v	13.134	26.443	1.331	.000	.000	.000
200	6.65v	17.556	21.007	.690	.000	.000	.000
298	7.265	20.351	.000	.000	.000	.000	.000
400	7.733	20.359	20.351	.014	.000	.000	.000
500	7.933	24.26v	21.05v	1.276	.000	.000	.000
600	7.946	25.920	21.871	2.025	.000	.000	.000
800	7.805v	27.278	22.662	2.761	.000	.000	.000
900	7.355v	28.945	24.005	3.507	.000	.000	.000
1000	7.39v	29.402	24.094	4.247	.000	.000	.000
1500	7.13v	30.673	24.233	4.986	.000	.000	.000
1000	4.568	47.354	26.148	21.807	.000	.000	.000

See crystal, liquid and monatomic gas tables for details.

0 to 301.55°K Crystal
301.55 to 951.6°K Liquid
951.6 to 6000°K Ideal Monatomic Gas

June 30, 1968

T, °K	Cp°	S°	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	-1.844	.000	.000	INFINITE
100	6.169	13.134	26.443	-1.331	.000	.000	.000
200	7.495	17.356	21.097	.000	.000	.000	.000
298	7.495	26.351	26.351	.000	.000	.000	.000
300	7.495	26.351	26.351	.014	.000	.000	.000
400	8.620	22.775	20.669	.842	.434	.156	.585
500	8.890	24.733	21.292	1.720	.305	.289	.126
600	8.670	26.361	22.005	2.614	.153	.394	.144
700	8.590	27.746	22.729	3.512	.005	.473	.148
800	8.595	28.947	23.433	4.411	.184	.528	.144
900	8.600	30.006	24.106	5.311	.325	.565	.137
1000	8.600	30.955	24.764	6.211	15.586	1.404	.307

CESIUM (Cs)

(CRYSTAL)

GFW = 132.905

$\Delta H_f^\circ = 0 \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = 0 \text{ kcal/mol}$
 $\Delta H_m^\circ = 0.499 \pm 0.001 \text{ kcal/mol}$
 $\Delta H_m^\circ_{298.15} = 18.32 \text{ kcal/mol}$

$S^\circ_{298.15} = 20.351 \pm 0.05 \text{ gibbs/mol}$
 $T_m = 301.55 \pm 0.01^\circ\text{K}$

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities, 0.19-301.55°K, have been measured by Dauphinee (1), McCollum (2), Martin (3), Lien (4), Filby (5), and Morgan (6). The adopted values are derived based on the Cp data reported by Filby (5) and Lien (4). Lien measured the heat capacities in the temperature range 0.1874 to 1.20°K in the adiabatic demagnetization cryostat and at higher temperatures, 1.2 to 4.09°K, in the liquid-helium temperature cryostat. The Cs sample was obtained from a commercial source of 99.8 per cent purity. Filby determined the Cp values in the temperature ranges 0.4-1.5°K, 3-26°K and 20-320°K, using commercial samples of 99.9 per cent purity. These two sets of measurements are joined smoothly at 4°K. $S^\circ_{298.15}$ is derived from the adopted heat capacities, based on $S^\circ_{0.20} = 0.0002 \text{ eu}$.

Dauphinee (1) determined the heat capacities of Cs(c) employing a sample badly contaminated with oxygen. In the temperature range of approximately 100 to 200°K, an anomaly of Cp curve somewhat similar to those found for sodium and potassium was reported. This anomaly was not observed by Filby who used the higher purity cesium sample. The Cp values reported by Dauphinee are lower than the adopted ones by about 0.5 to 1.5 per cent in the temperatures 55 to 220°K; above 270°K his reported heat capacities are unreasonably high. Therefore the data are not adopted for evaluation. McCollum (2) calculated the Debye θ values from the measured low temperature heat capacities and plotted them, since no numerical data were reported these were not used. The low temperature Cp values determined by Martin (3) and Morgan (6) are in good agreement with the adopted ones.

Melting Data

See Cs(l) table for details.

Heat of Sublimation

 $\Delta H_m^\circ_{298.15}$ is calculated as the difference between $\Delta H_f^\circ_{298.15}$ for Cs(g) and Cs(c).

References

1. T. M. Dauphinee, D. L. Martin and H. Preston-Thomas, Proc. Roy. Soc. (London) **A233**, 214 (1955), 20-320°K.
2. D. C. McCollum, Jr. and H. B. Silsbee, Phys. Rev. **127**, 119 (1962), 1.3-12°K.
3. B. D. Martin, D. A. Zych and C. V. Heer, Phys. Rev. **135**, A671 (1964), 0.36-1.63°K.
4. W. H. Lien and N. E. Phillips, Phys. Rev. **133**, A1370 (1964), 0.18-4.09°K.
5. J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A284**, 83 (1965), 0.7-320°K.
6. J. A. Morgan and J. C. Thompson, J. Chem. Phys. **47**, 4607 (1967), 2.1-4.2°K.

(Liquid) GFW = 132.905

T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
100							
200							
298	7.753	22.005	22.005	.000	.499	.006	.004
300	7.747	22.053	22.005	.014	.499	.003	.002
400	7.533	24.250	22.306	.777	.000	.000	.000
500	7.486	25.920	22.669	1.526	.000	.000	.000
600	7.409	27.274	23.494	2.248	.000	.000	.000
700	7.395	28.415	24.117	3.008	.000	.000	.000
800	7.363	29.402	24.716	3.748	.000	.000	.000
900	7.359	30.273	25.287	4.467	.000	.000	.000
1000	7.469	31.053	25.826	5.228	16.080	.821	.179
1100	7.692	31.740	26.334	6.040	15.635	2.450	.487
1200	7.837	32.407	26.813	6.902	15.341	5.791	.974
1300	7.894	33.003	27.267	7.857	15.341	9.406	1.156
1400	7.872	33.546	27.696	8.203	15.093	9.005	1.312
1500	7.881	34.072	28.104	8.651	14.842		

CESIUM (Cs)

(LIQUID)

GFW = 132.905

S°_{298.15} = 22.005 gibbs/molT_m = 301.55 ± 0.01°KT_b = 951.6°KΔH_f°_{298.15} = 0.499 kcal/molΔH_m° = 0.499 ± 0.001 kcal/molΔH_v° = 16.198 kcal/mol

Heat of Formation

The heat of formation is obtained from ΔH_f°₂₉₈(c) by adding ΔH_m° and the difference between H°_{301.55} - H°₂₉₈ for Cs(l) and Cs(s).

Heat Capacity and Entropy

The enthalpies of Cs(l) have been measured by Tepper et al. (1), Achener (2), and Lemmon et al. (3), using drop calorimetry. Lemmon et al. used a cesium sample of 99.994 per cent purity and encapsulated in Nb-12p alloy. They found that Cs(l) does not behave as a normal liquid from about 100-300°C. The thermal conductivity measurements of Cs(l) show a change of slope at about 200°C and its electrical resistivity also shows scatter in this region. The heat capacities, 301.55-1435.2°K, derived from the reported enthalpies (corrected for vapor condensation), are consistent with the low temperature heat capacity data on Cs(c) at 298°K and are adopted.

Tepper et al. measured the enthalpies in the temperature range 351.1-1228°K. The reported enthalpy values are considerably higher, over 20 per cent, at the lower end of the measured temperature range than the adopted ones. However, the agreement becomes better at the higher temperature end. Achener determined the enthalpies of Cs(l) at the temperatures 340.1-1175.7°K. Using the reported enthalpies, the average heat capacity is derived to be 8.75 gibbs/mol, which is unreasonably high by comparison with those for the other alkali metals. The above two sets of data are not used for evaluation. The enthalpies of Cs(l), 773-1423°K, were also measured by Shapiro (4) and quoted by (3). The derived constant heat capacity, 7.60 gibbs/mol, is in reasonable agreement with the adopted ones.

Heat capacities of Cs(l), 301.55-373.2°K, were reported by Filby (5), 301.55-320°K, Dauphinee (6), 310-320°K, and Rengade (7), 301.7-373.2°K. The values obtained are consistent with the adopted ones.

S°_{298.15} is derived in a manner analogous to that of the heat of formation.

Melting Data

The melting point and heat of melting have been determined by many investigators. The results reported are presented in the table below. The adopted T_m and ΔH_m° are obtained from (5). The two determinations of fraction melted against temperature are in very good agreement with one another and lead to a linear plot of reciprocal fraction melted against temperature thus indicating that the major impurity is solid insoluble. This is confirmed by a graph of excess heat capacity against the reciprocal of (T₀-T), where T₀ is the melting point, which indicates an impurity (mainly oxygen) concentration of 0.06 atomic per cent.

T _m , °K	ΔH _m °, kcal/mol
299.52	0.496
301.35	-
301.60±0.05	0.500
301.75	-
301.75	-
301.45	-
301.95±0.1	-
301.75	-
301.79±0.17	-
-	0.510
301.67	0.470
301.55±0.01	0.499±0.01

References

- M. Eckardt and E. Graefe, Z. Anorg. Chem. **23**, 378 (1900).
- A. Guntz and W. Broniewski, J. Chim. Phys. **7**, 474 (1909).
- E. Rengade (7).
- J. H. Boer, J. Broos and H. Emmens, Z. Anorg. Chem. **191**, 118 (1930).
- Z. Rindk, Compt. Rend. **193**, 1217 (1934).
- L. Lonana, Gazz. Chim. Ital. **65**, 855 (1935).
- J. B. Taylor and J. Langmuir, Phys. Rev. **51**, 759 (1937).
- K. Clusius and H. Stern, Z. Angew. Physik **6**, 194 (1954).
- W. D. Weatherford, Jr., et al., WADD Tech. Rept. 61-96, November 1961.
- A. W. Lemmon et al. (3).
- J. D. Filby and D. L. Martin (5).

Vaporization Data

T_b is the temperature at which the Gibbs energy change (ΔG°) for the reaction Cs(l) = Cs(g) approaches zero. The difference between ΔH_f°(Cs, g) and ΔH_f°(Cs, l) at T_b is ΔH_v°. Due to the presence of dimer (Cs₂) in the vapor (see Cs(g) and Cs₂(g) tables for details), the real boiling point of Cs(l) is calculated to be 941.3°K at which the vapor mixture contains 0.835 mol of monomer/mol of Cs(l) vaporized, or 9.0 per cent of dimer. The corresponding heat of vaporization is evaluated as 15.26 kcal/mol of vapor mixture.

References

- F. Tepper, A. Murchison, J. Zelenak, and F. Roellich, "Thermophysical Properties of Rubidium and Cesium," RTD-TDR-63-4018, Part I, MSA Research Corporation, Callery, Pennsylvania, November 1963.
- P. Y. Achener, "The Determination of the Latent Heat of Vaporization, Vapor Pressure, Enthalpy, Specific Heat, and Density of Liquid Rubidium and Cesium up to 1800°K," AGH-6050, Aerojet-General Nuclear, January 1964.
- A. W. Lemmon, Jr., H. W. Deem, E. A. Eldridge, E. H. Hall, J. Matolich, Jr., and J. F. Walling, "The Specific Heat, Thermal Conductivity, and Viscosity of Liquid Cesium," BART-4673-77, Battelle Memorial Institute, February 1964.
- A. Shapiro and C. J. Meisl, General Electric Company, Flight Propulsion Laboratory Department Report No. RGOPD358-A, Nov. 9, 1960.
- J. D. Filby and D. L. Martin, Proc. Roy. Soc. (London) **A284**, 83 (1965).
- T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas, Proc. Roy. Soc. (London) **A233**, 214 (1955).
- E. Rengade, Compt. Rend. **156**, 1897 (1913); Bull. Soc. Chim. France **15**, 130 (1914).

June 30, 1968

T, °K	Cp*	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞	∞
100	4.968	36.515	46.359	1.481	18.583	18.583	18.583	INFINITE
200	4.968	39.959	42.397	1.488	18.583	18.583	18.583	INFINITE
298	4.968	41.942	41.942	1.488	18.583	18.583	18.583	INFINITE
300	4.968	41.973	41.942	1.488	18.583	18.583	18.583	INFINITE
400	4.968	43.402	42.137	1.506	17.550	9.889	5.403	8.628
500	4.968	44.511	42.505	1.503	17.298	8.002	3.498	5.403
600	4.968	45.417	42.917	1.500	17.053	6.167	2.246	3.498
700	4.968	46.182	43.310	1.496	16.809	4.372	1.365	2.246
800	4.968	46.846	43.729	1.493	16.566	2.611	0.713	1.365
900	4.968	47.431	44.109	1.490	16.324	0.985	0.214	0.713
1000	4.968	47.958	44.468	1.487	16.082	0.000	0.000	0.000
1100	4.968	48.428	44.804	1.484	15.840	0.000	0.000	0.000
1200	4.968	48.860	45.127	1.480	15.600	0.000	0.000	0.000
1300	4.968	49.258	45.429	1.477	15.360	0.000	0.000	0.000
1400	4.975	49.627	45.716	1.475	15.120	0.000	0.000	0.000
1500	4.981	49.970	45.988	1.472	14.880	0.000	0.000	0.000
1600	4.992	50.292	46.247	1.467	14.640	0.000	0.000	0.000
1700	5.006	50.595	46.494	1.461	14.400	0.000	0.000	0.000
1800	5.031	50.882	46.730	1.453	14.160	0.000	0.000	0.000
1900	5.062	51.154	46.956	1.444	13.920	0.000	0.000	0.000
2000	5.102	51.415	47.172	1.433	13.680	0.000	0.000	0.000
2100	5.154	51.665	47.380	1.420	13.440	0.000	0.000	0.000
2200	5.218	51.906	47.591	1.405	13.200	0.000	0.000	0.000
2300	5.295	52.140	47.774	1.388	12.960	0.000	0.000	0.000
2400	5.385	52.367	47.940	1.369	12.720	0.000	0.000	0.000
2500	5.491	52.589	48.101	1.348	12.480	0.000	0.000	0.000
2600	5.613	52.807	48.256	1.324	12.240	0.000	0.000	0.000
2700	5.752	53.021	48.407	1.297	12.000	0.000	0.000	0.000
2800	5.908	53.233	48.552	1.268	11.760	0.000	0.000	0.000
2900	6.085	53.444	48.694	1.236	11.520	0.000	0.000	0.000
3000	6.282	53.653	48.832	1.203	11.280	0.000	0.000	0.000
3100	6.502	53.863	48.974	1.168	11.040	0.000	0.000	0.000
3200	6.747	54.073	49.128	1.131	10.800	0.000	0.000	0.000
3300	7.018	54.285	49.296	1.092	10.560	0.000	0.000	0.000
3400	7.317	54.498	49.472	1.050	10.320	0.000	0.000	0.000
3500	7.647	54.715	49.656	1.005	10.080	0.000	0.000	0.000
3600	8.008	54.936	49.858	0.958	9.840	0.000	0.000	0.000
3700	8.403	55.160	49.998	0.908	9.600	0.000	0.000	0.000
3800	8.831	55.390	50.137	0.855	9.360	0.000	0.000	0.000
3900	9.294	55.625	50.275	0.798	9.120	0.000	0.000	0.000
4000	9.790	55.867	50.411	0.738	8.880	0.000	0.000	0.000
4100	10.318	56.115	50.548	0.675	8.640	0.000	0.000	0.000
4200	10.876	56.370	50.693	0.608	8.400	0.000	0.000	0.000
4300	11.461	56.633	50.818	0.538	8.160	0.000	0.000	0.000
4400	12.069	56.903	50.954	0.465	7.920	0.000	0.000	0.000
4500	12.694	57.182	51.069	0.388	7.680	0.000	0.000	0.000
4600	13.331	57.468	51.224	0.308	7.440	0.000	0.000	0.000
4700	13.972	57.761	51.360	0.225	7.200	0.000	0.000	0.000
4800	14.612	58.062	51.497	0.138	6.960	0.000	0.000	0.000
4900	15.242	58.370	51.634	0.048	6.720	0.000	0.000	0.000
5000	15.855	58.684	51.772	0.000	6.480	0.000	0.000	0.000
5100	16.443	59.004	51.910	0.000	6.240	0.000	0.000	0.000
5200	16.999	59.328	52.050	0.000	6.000	0.000	0.000	0.000
5300	17.516	59.657	52.190	0.000	5.760	0.000	0.000	0.000
5400	17.999	59.989	52.332	0.000	5.520	0.000	0.000	0.000
5500	18.441	60.323	52.474	0.000	5.280	0.000	0.000	0.000
5600	18.740	60.658	52.617	0.000	5.040	0.000	0.000	0.000
5700	19.051	60.994	52.761	0.000	4.800	0.000	0.000	0.000
5800	19.343	61.328	52.906	0.000	4.560	0.000	0.000	0.000
5900	19.536	61.660	53.052	0.000	4.320	0.000	0.000	0.000
6000	19.666	61.990	53.198	0.000	4.080	0.000	0.000	0.000

June 30, 1968

Ground State Configuration $2s^2_{1/2}$ $S^{\circ}_{298.15} = 41.942 \pm 0.01$ gibbs/mol

(IDEAL GAS)

GFW = 132.905

 $\Delta H^{\circ}_f = 18.68 \pm 0.5$ kcal/mol $\Delta H^{\circ}_{298.15} = 18.32 \pm 0.5$ kcal/mol

Electronic Levels and Quantum Weights

g_i , cm ⁻¹	g_i , cm ⁻¹	g_i , cm ⁻¹	g_i
0.00	22588.89	4	72
11178.24	22631.83	6	38
11732.35	24317.17	2	28
14499.49	24472.29	8	[66]
14597.08	24472.46	6	[96]
18535.51	24784.23	6	[130]
21765.65	26616.40	26	[168]
21946.66	27363.68	34	

Heat of Formation

The total pressures of Cs(g) and Cs₂(g) over Cs(l) in the temperature range 738.6 to 1268.3°K have been measured, using the boiling point method, by Bonilla (4), Tepper (3) and Achener (2); using the static method, by Kröner (10), Scott (7) and Stone (11); and the positive ion method by Taylor (6). Fichtbauer (8) and Hacksapill (9) have determined the vapor pressures of Cs(l) by a spectroscopic method and P-V-T relationships, respectively. Based on the reported total pressures, the partial pressures of Cs(g) and Cs₂(g) are evaluated by use of dimer-monomer ratios calculated from JANAF free energy functions and $\Delta H^{\circ}_{298.15} = 11.24$ kcal/mol for the reaction $Cs_2(g) = 2Cs(g)$. The value of $\Delta H^{\circ}_{298.15}$ is adopted such that the derived monomer partial pressures give consistent second and third law heats of vaporization. The results are presented in the table below.

Stone et al. (1) measured the vapor pressures of Cs(l) at temperatures 920-1682°K and pressures 0.811-33.53 atm in both the saturation and superheat regions, using a static method and a refractory metal apparatus with a diaphragm as a null-point detector. These vapor pressures reported at temperatures 920-1267.3°K and total pressure below 10 atm are used for evaluation and are reasonably represented by a mixture of monomer and dimer ideal gases. The value of ΔH°_{298} (Cs, g) is adopted as 18.3240.5 kcal/mol which is derived based on the vapor pressures reported by Stone et al. The results obtained are in reasonable agreement with the values derived from the other vapor pressure sets.

Investigator	Temperature, °K	Points	Second Law	Third Law	Drift, eu	ΔH°_{298} , kcal/mol*
1. Stone (1966)	920.6-1267.7	79	18.19±0.02	17.82	-0.37±0.02	18.32
2. Achener (1964)	752.1-1144.3	15	18.15±0.04	17.88	-0.30±0.05	18.38
3. Tepper (1963)	729.3-1268.3	21	18.11±0.02	17.86	-0.27±0.02	18.36
4. Bonilla (1962)	674.3-1199.2	41	18.16±0.03	17.76	-0.42±0.03	18.26
5. Weathford (1961)	722.2-1277.8	11	18.01±0.01	18.09	0.08±0.01	18.59
6. Taylor (1937)	238.6-298.5	8	18.41±0.03	18.35	-0.22±0.11	18.35
	303.3-345.8	6	17.75±0.10	17.86	0.32±0.31	18.36
7. Scott (1924)	321.4-386.5	8	17.28±0.28	17.13	-0.43±0.79	17.63
8. Fichtbauer (1921)	464.1-505.5	4	17.20±0.74	18.10	1.86±1.54	18.60
9. Hacksapill (1913)	503.2-670.2	10	18.33±0.47	18.00	-0.56±0.80	18.50
10. Kröner (1913)	522.7-628.7	12	18.67±0.44	18.10	-1.00±0.76	18.60

*Calculation based on the third law ΔH°_{298} and $\Delta H^{\circ}_{298} = 0$ and 0.499 kcal/mol for Cs(l) and Cs(g), respectively.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights ($n \leq 10$) are obtained from Moore (11). The electronic levels above 25000 cm⁻¹ are average values calculated from those given by Moore. The missing electronic levels, where quantum number $n = 7, 8, 9$ and 10, and the corresponding quantum weights are estimated according to the method recommended by Gurvich (12). The calculated values at 6000°K, e.g. Cp = 19.668 gibbs/mol and S° = 61.980 eu, are not significantly different from the corresponding values, Cp = 19.650 gibbs/mol and S° = 61.871 eu, obtained from using all the electronic levels reported by Moore for calculation without cutting or adding any levels.

References

1. J. P. Stone, C. T. Ewing, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, J. Chem. Eng. Data **11**, 309 and 315 (1966).
2. F. Y. Achener, Aerojet-General Nuclear, AGN-8090, January 1964.
3. R. Tepper, A. Hurchison, J. Zelenak, and F. Koehlich, NSA Research Corporation, Calvery, Pennsylvania, RTD-TDR-63-4018, 1963.
4. J. Bonilla, D. Swamy and M. Wakana, J. Chem. Phys. **36**, 169 (1962).
5. Vapor pressure data measured by W. D. Weatherford, Jr., and quoted by Tepper (2).
6. J. B. Taylor and I. Langmuir, Phys. Rev. **53**, 753 (1937).
7. D. H. Scott, Phil. Mag. **47**, 32 (1924).
8. C. Fichtbauer, and H. Bartels, Z. Physik **4**, 337 (1921).
9. A. Hacksapill, Ann. Phys. **40**, 438 (1913).
10. A. Kröner, Ann. Phys. **40**, 438 (1913).
11. C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, 1958.
12. L. V. Gurvich, V. A. Kvitidze, and N. P. Riancheva, Russ. J. Phys. Chem. **36**, 108 (1962).

T, °K	Cp ^a	S ^b - (C ^a - H [°])/T	H [°] - H [°] ₂₉₈	ΔH ^c	ΔG ^d	Log K ^e
100						
200	4.568	40.545	0.000	108.100	108.566	73.732
298	4.568	40.545	0.000	108.100	108.566	73.732
300	4.568	40.545	0.000	108.100	108.566	73.732
400	4.568	40.545	0.000	108.100	108.566	73.732
500	4.568	40.545	0.000	108.100	108.566	73.732
600	4.568	40.545	0.000	108.100	108.566	73.732
700	4.568	40.545	0.000	108.100	108.566	73.732
800	4.568	40.545	0.000	108.100	108.566	73.732
900	4.568	40.545	0.000	108.100	108.566	73.732
1000	4.568	40.545	0.000	108.100	108.566	73.732
1100	4.568	40.545	0.000	108.100	108.566	73.732
1200	4.568	40.545	0.000	108.100	108.566	73.732
1300	4.568	40.545	0.000	108.100	108.566	73.732
1400	4.568	40.545	0.000	108.100	108.566	73.732
1500	4.568	40.545	0.000	108.100	108.566	73.732
1600	4.568	40.545	0.000	108.100	108.566	73.732
1700	4.568	40.545	0.000	108.100	108.566	73.732
1800	4.568	40.545	0.000	108.100	108.566	73.732
1900	4.568	40.545	0.000	108.100	108.566	73.732
2000	4.568	40.545	0.000	108.100	108.566	73.732
2100	4.568	40.545	0.000	108.100	108.566	73.732
2200	4.568	40.545	0.000	108.100	108.566	73.732
2300	4.568	40.545	0.000	108.100	108.566	73.732
2400	4.568	40.545	0.000	108.100	108.566	73.732
2500	4.568	40.545	0.000	108.100	108.566	73.732
2600	4.568	40.545	0.000	108.100	108.566	73.732
2700	4.568	40.545	0.000	108.100	108.566	73.732
2800	4.568	40.545	0.000	108.100	108.566	73.732
2900	4.568	40.545	0.000	108.100	108.566	73.732
3000	4.568	40.545	0.000	108.100	108.566	73.732
3100	4.568	40.545	0.000	108.100	108.566	73.732
3200	4.568	40.545	0.000	108.100	108.566	73.732
3300	4.568	40.545	0.000	108.100	108.566	73.732
3400	4.568	40.545	0.000	108.100	108.566	73.732
3500	4.568	40.545	0.000	108.100	108.566	73.732
3600	4.568	40.545	0.000	108.100	108.566	73.732
3700	4.568	40.545	0.000	108.100	108.566	73.732
3800	4.568	40.545	0.000	108.100	108.566	73.732
3900	4.568	40.545	0.000	108.100	108.566	73.732
4000	4.568	40.545	0.000	108.100	108.566	73.732
4100	4.568	40.545	0.000	108.100	108.566	73.732
4200	4.568	40.545	0.000	108.100	108.566	73.732
4300	4.568	40.545	0.000	108.100	108.566	73.732
4400	4.568	40.545	0.000	108.100	108.566	73.732
4500	4.568	40.545	0.000	108.100	108.566	73.732
4600	4.568	40.545	0.000	108.100	108.566	73.732
4700	4.568	40.545	0.000	108.100	108.566	73.732
4800	4.568	40.545	0.000	108.100	108.566	73.732
4900	4.568	40.545	0.000	108.100	108.566	73.732
5000	4.568	40.545	0.000	108.100	108.566	73.732
5100	4.568	40.545	0.000	108.100	108.566	73.732
5200	4.568	40.545	0.000	108.100	108.566	73.732
5300	4.568	40.545	0.000	108.100	108.566	73.732
5400	4.568	40.545	0.000	108.100	108.566	73.732
5500	4.568	40.545	0.000	108.100	108.566	73.732
5600	4.568	40.545	0.000	108.100	108.566	73.732
5700	4.568	40.545	0.000	108.100	108.566	73.732
5800	4.568	40.545	0.000	108.100	108.566	73.732
5900	4.568	40.545	0.000	108.100	108.566	73.732
6000	4.568	40.545	0.000	108.100	108.566	73.732

June 30, 1968

Cs⁺Ground State Configuration ¹S₀S[°]_{298.15} = 40.565 ± 0.0005 gibbs/molΔH[°]_f = 108.5 ± 1 kcal/molΔH[°]_{f,298.15} = 108.1 ± 1 kcal/mol

Electronic Levels and Quantum Weights

$$\frac{g_i, \text{cm}^{-1}}{0} \frac{g_i}{1}$$

Heat of Formation

The ionization potential of Cs(g) was reported as 3.893 eV or 89.776 kcal/mol by C. E. Moore, U. S. Natl. Bur. Std. Circ. 467, 1958. Based on this data we derived ΔH[°]_{f,298.15} = 108.1 ± 1 kcal/mol for Cs⁺(g).

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights were reported by Moore, loc. cit. However, the lowest electronic level above ground state is given as 107392.33 cm⁻¹ which is so high that the evaluated thermodynamic properties of Cs⁺(g) will not be affected if we disregard all of these higher levels for calculation. Therefore we do not use them. The H[°]₂₉₈ value at 0°K is -1.481 kcal/mol.

Cesium Fluoride (CsF)

CsF

(Crystal)

GFW = 151.9034

T, °K	Cp°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(C^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{H^\circ - H^\circ_{298}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
100							
200							
298	12.420	21.100	21.100	.000	-132.570	-125.571	92.046
300	12.420	21.177	21.100	.063	-132.568	-125.538	91.667
400	12.420	21.503	21.503	1.267	-132.951	-123.034	87.223
500	12.420	21.724	21.724	2.593	-132.797	-120.573	82.702
600	13.710	30.183	23.611	3.983	-132.606	-118.144	73.034
700	14.130	32.328	24.707	5.335	-132.379	-115.751	66.139
800	14.590	34.582	26.789	6.765	-132.119	-113.419	60.184
900	15.100	37.056	29.016	8.273	-131.819	-111.071	54.572
1000	15.660	39.663	31.416	9.743	-131.485	-108.763	49.595
1100	16.280	42.400	33.983	11.200	-131.119	-106.491	45.069
1200	16.960	45.263	36.722	12.657	-130.726	-104.263	40.841
1300	17.690	48.253	39.625	14.114	-130.309	-102.086	36.951
1400	18.470	51.372	42.693	15.571	-129.868	-99.951	33.351
1500	19.300	54.622	45.923	17.028	-129.404	-97.861	29.991
1600	16.430	45.121	32.987	19.414	-123.610	-85.179	11.635
1700	16.470	46.118	33.730	21.059	-123.924	-81.587	10.484
1800	16.480	47.060	34.445	22.857	-124.259	-78.003	9.458
1900	16.480	47.953	35.118	24.700	-124.614	-74.433	8.558
2000	16.500	48.798	35.795	26.607	-124.977	-70.866	7.746

CESIUM FLUORIDE (CsF)

(CRYSTAL)

GFW = 151.9034

 $\Delta H^\circ_f = \text{Unknown}$ $\Delta H^\circ_{298,15} = -132.57 \pm 0.5 \text{ kcal/mol}$ $\Delta H_m^\circ = 5.19 \text{ kcal/mol}$ $\Delta H^\circ_{298,15}(\text{to monomer}) = 47.37 \text{ kcal/mol}$ $S^\circ_{298,15} = [21.1 \pm 2] \text{ gibbs/mol}$ $T_m = 976^\circ\text{K}$

Heat of Formation

The enthalpy of solution (ΔH_{soln}) of CsF(c) in water at 298.15°K has been carefully determined with an adiabatic calorimeter by Somsen (1). Based on the reported value, $\Delta H_{\text{soln},298} = -8.62 \pm 0.04 \text{ kcal/mol}$ and $\Delta H^\circ_{298} = -61.69$ (2) and -79.5 kcal/mol (3) for Cs⁺(aq, H₂O) and F⁻(aq, H₂O), respectively, the heat of formation for CsF(c) is calculated to be -132.57 kcal/mol which is adopted. The value, $\Delta H_{\text{soln},298} = -8.81 \pm 0.2 \text{ kcal/mol}$ for CsF(c), was reported by Parker (1), which is in agreement with the value measured by Somsen (1).

Heat Capacity and Entropy

The heat capacities of CsF(c) are estimated according to the method of Kristov (5), based on $H^\circ_{298} - H^\circ_{298} = 9.4 \text{ kcal/mol}$ reported by Dworin (6). The entropy (S°_{298}) is estimated such that the calculated and observed vapor pressures are in good agreement (see CsF(g) and Cs₂F₂(g) tables for details).

Melting Data

T_m and ΔH_m° are obtained from Bredig (7) and Dworin (8). Bukhalova (9) reported $T_m = 958^\circ\text{K}$, which is not adopted.

Heat of Sublimation

ΔH°_{298} is calculated as the difference between ΔH°_{298} for CsF(g) and CsF(c).

References

1. G. Somsen and L. Weeda, Rec. Trav. Chim. **83**, 810 (1964).
2. S. R. Gunn, J. Phys. Chem. **71**, 1386 (1967).
3. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
4. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-NBS 2, 1965.
5. G. A. Kristov, Izv. Vych. Uchebn. Zavedeni, SSR, Khim. i Khim. Techn. No. 5, 751, 1964.
6. A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1, 1964.
7. M. A. Bredig, H. R. Bronstein and W. T. Smith, Jr., J. Am. Chem. Soc. **77**, 1484 (1955).
8. A. S. Dworin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960).
9. G. A. Bukhalova and D. V. Sementsova, Russ. J. Inorg. Chem. (English Transl.) **10**, 1027 (1965).

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	17.700	21.534	21.534	0.000	-129.983	-123.114	90.245
300	17.700	21.648	21.535	+0.33	-129.971	-123.071	89.657
400	17.700	26.736	22.229	1.803	-129.848	-120.701	85.948
500	17.700	30.685	23.540	3.573	-129.231	-118.487	51.791
600	17.700	33.913	25.008	5.343	-128.619	-116.395	42.397
700	17.700	36.641	26.480	6.883	-127.917	-112.503	30.735
800	17.700	38.979	27.952	8.423	-126.824	-110.674	26.675
900	17.700	41.089	29.263	10.623	-125.223	-108.091	23.673
1000	17.700	42.944	30.531	12.623	-123.316	-105.691	21.130
1100	17.700	44.641	31.739	14.193	-121.490	-104.708	20.803
1200	17.700	46.168	32.867	15.723	-119.844	-104.161	16.502
1300	17.700	47.561	33.910	17.203	-118.366	-104.161	14.828
1400	17.700	48.910	34.979	18.503	-117.025	-94.886	13.385
1500	17.700	50.131	35.949	21.273	-115.808	-91.868	13.385
1600	17.700	51.273	36.871	23.043	-114.739	-88.806	12.130
1700	17.700	52.346	37.750	24.613	-113.776	-82.831	10.057
1800	17.700	53.358	38.580	26.083	-112.910	-79.910	9.192
1900	17.700	54.319	39.362	27.353	-112.134	-77.032	8.418
2000	17.700	55.223	40.161	30.123	-110.474	-74.196	7.722
2100	17.700	56.066	40.899	31.693	-108.920	-71.501	7.031
2200	17.700	56.840	41.580	33.163	-107.463	-68.931	6.521
2300	17.700	57.557	42.204	34.533	-106.093	-66.481	6.001
2400	17.700	58.210	42.769	35.803	-104.803	-64.141	5.525
2500	17.700	58.803	43.273	36.973	-103.587	-61.901	5.088
2600	17.700	59.336	43.726	38.043	-102.439	-59.761	4.688
2700	17.700	60.535	44.129	40.743	-101.354	-57.721	4.315
2800	17.700	61.588	44.482	42.283	-100.328	-55.778	3.971
2900	17.700	62.491	44.786	43.653	-99.356	-53.928	3.652
3000	17.700	63.250	45.019	44.883	-98.433	-52.168	3.352
				47.823	-126.739	-	

June 30, 1968

CsF

CESIUM FLUORIDE (CsF)

(LIQUID)

GFW = 151.9034

 $S_{298.15}^{\circ} = [21.534] \text{ gibbs/mol}$ $\Delta H_f^{\circ} 298.15 = -129.983 \text{ kcal/mol}$ $\Delta H_m^{\circ} = 5.19 \text{ kcal/mol}$ $\Delta H_v^{\circ} = 27.6 \text{ kcal/mol of liquid}$ $T_m = 976^{\circ}\text{K}$ $T_b = 1504^{\circ}\text{K}$

Heat of Formation

 $\Delta H_f^{\circ} 298(4)$ is obtained from $\Delta H_f^{\circ} 298(c)$ by adding ΔH_m° and the difference between H_{298}° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

Dorbin (1) measured the heat capacity of CsF(l) at the melting point to be 17.7 gibbs/mol which is adopted and assumed to be constant in the temperature range 298 - 3000°K. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See CsF(c) for details.

Vaporization Data

T_b is the temperature at which the calculated vapor pressures of CsF(g) and Cs₂F₂(g) equal one atmosphere. The vapor composition at T_m is calculated as CsF 80.3 per cent and Cs₂F₂ 19.7 per cent. The heat required to vaporize one mole of liquid to the above vapor mixture at T_m is ΔH_v° .

T_b has been observed as 1524 and 1526°K by Wartenberg (1) and Ruff (2), respectively, which are in fair agreement with the calculated one, 1504°K.

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. **27**, 568 (1921).
2. O. Ruff, G. Schmidt and S. Wogdan, Z. Anorg. Allgem. Chem. **123**, 83 (1922).

Cesium Fluoride (CsF)

CsF

(Ideal Gas) GFW = 151.9034

CESIUM FLUORIDE (CsF) (IDEAL GAS) GFW = 151.9034

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
10	7.500	0.000	INFINITE	-2.308	-84.605	-84.605	INFINITE
100	7.591	45.399	84.764	-1.602	-84.764	-84.355	186.779
200	8.176	54.754	58.876	-0.824	-84.977	-85.011	96.011
288	8.565	58.102	56.102	-0.000	-85.200	-85.233	65.410
300	8.570	58.155	56.102	0.016	-85.205	-85.258	45.024
400	8.750	60.648	58.491	0.883	-85.585	-90.403	40.364
500	8.848	62.612	59.066	1.763	-86.257	-91.477	39.985
600	8.909	64.231	56.812	2.651	-86.527	-92.495	33.691
700	8.952	65.608	60.524	3.544	-86.600	-93.466	29.162
800	9.000	66.812	61.931	4.441	-86.500	-94.388	25.102
900	9.035	68.016	62.573	5.341	-87.353	-95.301	23.142
1000	9.056	69.678	63.180	6.248	-103.714	-95.349	20.839
1100	9.056	69.678	63.180	7.148	-103.751	-94.510	18.777
1200	9.055	70.487	63.755	8.055	-103.790	-93.668	17.059
1300	9.055	71.296	64.329	8.973	-103.872	-92.825	15.562
1400	9.110	71.859	64.816	9.873	-103.872	-91.975	14.358
1500	9.126	72.488	65.308	10.785	-103.812	-91.123	13.277
1600	9.142	73.087	65.776	11.699	-103.955	-90.270	12.330
1700	9.158	73.652	66.222	12.618	-103.999	-89.413	11.495
1800	9.167	74.187	66.658	13.548	-104.098	-88.552	10.767
1900	9.172	74.692	67.084	14.488	-104.146	-87.692	10.107
2000	9.202	75.134	67.450	15.368	-104.146	-86.827	9.498
2100	9.217	75.583	67.827	16.289	-104.203	-85.960	8.946
2200	9.231	76.032	68.198	17.211	-104.266	-85.091	8.453
2300	9.243	76.481	68.569	18.133	-104.331	-84.223	7.999
2400	9.250	76.817	68.875	19.060	-104.412	-83.341	7.589
2500	9.274	77.195	69.200	19.987	-104.500	-82.461	7.209
2600	9.288	77.559	69.515	20.915	-104.599	-81.578	6.857
2700	9.302	77.910	69.819	21.844	-104.710	-80.698	6.531
2800	9.316	78.246	70.111	22.772	-104.831	-79.819	6.229
2900	9.329	78.576	70.401	23.707	-104.977	-78.940	5.946
3000	9.343	78.892	70.678	24.641	-105.138	-78.060	5.682
3100	9.357	79.199	70.948	25.576	-105.319	-77.092	5.435
3200	9.371	79.496	71.211	26.512	-105.524	-76.116	5.203
3300	9.385	79.784	71.466	27.448	-105.745	-75.139	4.983
3400	9.399	80.065	71.715	28.389	-106.011	-74.130	4.778
3500	9.412	80.337	71.957	29.330	-106.301	-73.393	4.583
3600	9.426	80.603	72.194	30.272	-106.624	-72.449	4.398
3700	9.439	80.863	72.428	31.215	-106.983	-71.423	4.223
3800	9.452	81.117	72.658	32.160	-107.375	-70.333	4.058
3900	9.467	81.365	72.870	33.106	-107.833	-69.255	3.898
4000	9.481	81.599	73.045	34.053	-108.326	-68.166	3.746
4100	9.494	81.833	73.286	35.002	-108.871	-67.066	3.602
4200	9.508	82.064	73.502	35.953	-109.470	-65.952	3.463
4300	9.522	82.290	73.702	36.903	-110.121	-64.827	3.329
4400	9.535	82.505	73.901	37.856	-110.841	-63.676	3.203
4500	9.549	82.719	74.095	38.811	-111.617	-62.415	3.080
4600	9.563	82.929	74.285	39.766	-112.456	-61.134	2.962
4700	9.576	83.137	74.463	40.723	-113.356	-60.015	2.847
4800	9.590	83.337	74.633	41.683	-114.326	-58.875	2.737
4900	9.603	83.535	74.833	42.641	-115.356	-57.725	2.630
5000	9.617	83.729	75.009	43.602	-116.446	-56.561	2.527
5100	9.631	83.920	75.181	44.564	-117.600	-55.331	2.427
5200	9.645	84.108	75.348	45.529	-118.821	-54.083	2.332
5300	9.658	84.291	75.514	46.503	-120.107	-52.825	2.245
5400	9.671	84.471	75.678	47.482	-121.463	-51.558	2.163
5500	9.685	84.649	75.844	48.467	-122.798	-50.283	2.083
5600	9.698	84.823	76.003	49.457	-124.133	-49.005	1.995
5700	9.712	84.994	76.158	50.453	-125.476	-47.726	1.915
5800	9.726	85.164	76.313	51.455	-126.828	-46.446	1.835
5900	9.739	85.331	76.464	52.462	-128.198	-45.166	1.755
6000	9.753	85.494	76.613	53.487	-129.592	-43.879	1.675

June 30, 1968

Ground State Configuration 1_s²+S°_{298.15} = 58.10 ± 0.01 gibbs/mol

(IDEAL GAS)

ΔH°₀ = -84.6 ± 0.5 kcal/molΔH°_{298.15} = -85.2 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	1
ω _e X = 1.23 cm ⁻¹	
ω _e = 0.001105 cm ⁻¹	
ω _e = 353 ± 4 cm ⁻¹	
B _e = 0.18437 cm ⁻¹	
σ = 1	
x _e = 2.345 Å	

Heat of Formation

The vapor pressures of CsF(c) and CsF(g) were measured by the manometric method (A) by Martenberg (1), Ruff (2) and Cantor (3); the torsion-fiber effusion method (B) by Pugh (4); and the Knudsen effusion method (C) by Scheer (5). Based on the reported total pressures, the corresponding partial pressures of CsF(g) and Cs₂F₂(g) were evaluated using the adjusted heats of vaporization and Gibbs free energy functions such that the calculated and observed total pressures are in reasonable agreement, and the derived enthalpy changes by the second and third law methods are consistent. The results obtained are presented in the table below. The value of ΔH°₂₉₈ (CsF, g) is adopted as -82.5 ± 0.5 kcal/mol.

The dissociation energy (D₀) of CsF(g) has been reported using the spectroscopic convergence limit as 5.65 eV (130.3 kcal/mol) and 5.56 eV (126.8 kcal/mol) by Herzberg (6) and Gaydon (7), respectively. Based on the above two D₀ values, and ΔH°₀ = 18.68 and 18.36 for Cs(g) and F(g), we obtain the corresponding value for ΔH°₂₉₈ (CsF, g) as -93.85 and -90.39 kcal/mol, which are not adopted.

Investigator	Reaction*	Method	ΔH° ₂₉₈ , kcal/mol	Drift eu	ΔH° ₂₉₈ , kcal/mol**
1. Martenberg (1921)	2	A	45.39±0.15	44.98	-0.28±0.10
2. Ruff (1922)	2	A	44.78±1.70	44.94	-0.11±1.18
3. Cantor (1958)	2	A	44.83	44.89	0.05±0.04
4. Pugh (1958)	1	B	48.52±0.03	47.57	-1.18±0.04
5. Scheer (1962)	1	C	48.43±0.27	46.61	-2.35±0.35

*1 represents the reaction CsF(c) = CsF(g); 2, the reaction CsF(l) = CsF(g).

**Calculation based on the third law ΔH°₂₉₈ and ΔH°₂₉₈ = -132.57 and -129.983 kcal/mol for CsF(c) and CsF(l), respectively.

Heat Capacity and Entropy

The ground state configuration was reported by Herzberg (6). The molecular constants are obtained from Honig (2), who observed the microwave spectra of CsF(g) at temperatures of about 700°C. Based on the J = 1 + 2 transition, the molecular constants are derived. The vibrational frequency (ω_e) has been reported, from different kinds of spectra, in the range 270 - 385 cm⁻¹ by many investigators, e.g., radiofrequency, infrared, ultraviolet, microwave, etc. The value of ω_e adopted was reported by Balikov (8), who also reviewed the ω_e values obtained by the earlier investigators.

References

1. H. von Martenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921), 1391 - 1524°K, 6 points. Two data points at 1228 and 1319°K are not adopted for evaluation due to the inconsistency with the other data.
2. O. Ruff, G. Schmidt and S. Mugdan, Z. Anorg. Allgem. Chem. 133, 83 (1922), 1308 - 1528°K, 7 points.
3. S. Cantor and F. Blankenship, "Vapor Pressure of the Alkali Fluorides," Oak Ridge National Laboratory, Oak Ridge, Tennessee, September 1958, 1009 - 1380°K, 7 points calculated using the given vapor pressure equation.
4. A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958), 753 - 856°K, 6 points.
5. M. D. Scheer and J. Fine, J. Chem. Phys. 36, 1647 (1962), 677 - 878°K, 32 points. Evaluation based on the reported data points.
6. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
7. A. Honig, M. Mandel, M. L. Stiche and C. H. Townes, Phys. Rev. 96, 629 (1954).
8. V. I. Balikov and K. P. Vasilievskii, Opt. Spectry. (USSR) (English Transl.) 22, 198 (1967).
9. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

CsF

GFW = 148.9044

(IDEAL GAS)

CESIUM MONOXIDE (CsO)

Ground State Configuration $[2^1P_1]$ $\Delta H_f^\circ = [15.5 \pm 10] \text{ kcal/mol}$ $\Delta H_f^{*298.15} = [15.0 \pm 10] \text{ kcal/mol}$ $S_{298.15}^\circ = [61 \pm 1] \text{ gibbs/mol}$

Electronic Levels and Quantum Heights

$$\frac{e_1, \text{ cm}^{-1}}{0} = \frac{g_1}{[4]}$$

$$\omega_e = [280] \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = [0.199] \text{ cm}^{-1} \quad \alpha_e = [0.001] \text{ cm}^{-1}$$

$$r_e = [2.40] \text{ \AA}$$

Heat of Formation

The heat of formation is estimated from three calculated values. The methods of estimation are described as follows. Brewer and Margrave (1) suggested that the ΔH_f value for HO(g) from the gaseous ions can be taken as the mean of the corresponding ΔH_f values for the alkali fluoride and chloride with a maximum uncertainty of 10 kcal/mol. Adopting $\Delta H_f^{*298} = -131.1$ and -109.6 kcal/mol for the reaction $\text{Cs}^+(g) + \text{F}^-(g) = \text{CsF(g)}$ and $\text{Cs}^+(g) + \text{Cl}^-(g) = \text{CsCl(g)}$, respectively, we obtain $\Delta H_f^{*298} = -120.4$ kcal/mol for $\text{Cs}^+(g) + \text{O}^-(g) = \text{CsO(g)}$ which leads to $\Delta H_f^{*298}(\text{CsO, g}) = 12.0$ kcal/mol. The ΔH_f^{*298} values of the above species used for calculation are taken from the respective JANAF Thermochemical Tables.

Based on the assumption that $\text{D(Cs-O)} = 1/2[\text{D(Ca}_2\text{)} + \text{D(O}_2\text{)}]$, we derive $D_{298}(\text{Cs-O}) = 85.2$ kcal/mol and $\Delta H_f^{*298} = 12.7$ kcal/mol for CsO(g) .

Adopting the Cs-O bond energy as half of the atomization energy of Cs_2O , we calculate $\text{D(Cs-O)} = 60 \pm 10$ kcal/mol and $\Delta H_f^{*298}(\text{CsO, g}) = 17 \pm 10$ kcal/mol.

The heat of formation for CsO(g) is tentatively selected as 15 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of the isoelectronic molecule OH(g) . ω_e is estimated from those of LiO(g) , CaF(g) , and CsCl(g) . The bond distance is taken from that in CsOH(g) reported by Lide and Kuczkowski (2). ω_e is estimated by comparison with those of the other alkali oxides. The values of B_e and α_e are calculated from r_e , ω_e and ω_e^2 by the method suggested by Herzberg (3). The moment of inertia is $1.413 \times 10^{-38} \text{ g cm}^2$.

References

1. L. Brewer and J. L. Margrave, *J. Phys. Chem.*, **59**, 421 (1955).
2. D. R. Lide, Jr. and R. L. Kuczkowski, *J. Chem. Phys.*, **45**, 4768 (1967).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

Cesium Monoxide (CsO)

GFW = 148.9044

(Ideal Gas)

T, °K	C_p°	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H^\circ_{298})/T}$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	7.000	INFINITE	2.361	15.920	15.920	INFINITE
100	7.484	52.461	1.161	15.526	15.526	7.409
200	7.924	61.830	0.844	15.169	15.169	12.892
298	8.119	61.049	0.000	15.000	10.171	7.456
300	8.122	61.103	-0.016	14.996	10.141	7.386
400	8.454	63.632	0.566	14.258	9.723	6.766
500	8.527	65.616	1.163	14.033	7.385	5.219
600	8.676	67.249	2.680	13.603	6.053	3.201
700	9.013	68.635	4.521	13.578	4.779	1.492
800	9.043	69.841	6.237	13.343	3.536	0.066
900	9.069	70.907	8.020	13.102	2.362	-0.265
1000	9.093	71.664	9.568	3.224	1.182	-0.589
1100	9.115	72.732	66.160	3.229	2.482	-0.493
1200	9.137	73.526	66.760	3.236	3.001	-0.547
1300	9.157	74.258	67.309	3.249	3.582	-0.592
1400	9.177	74.937	67.829	3.402	4.042	-0.631
1500	9.196	75.571	68.325	3.276	4.565	-0.665
1600	9.216	76.165	68.796	3.293	5.088	-0.695
1700	9.239	76.724	69.246	3.311	5.612	-0.722
1800	9.253	77.253	69.677	3.333	6.137	-0.745
1900	9.272	77.753	70.069	3.356	6.665	-0.767
2000	9.290	78.280	70.484	3.386	7.193	-0.786
2100	9.307	78.843	70.929	3.424	7.723	-0.804
2200	9.327	79.117	71.229	3.467	8.254	-0.820
2300	9.345	79.532	71.561	3.516	8.788	-0.835
2400	9.363	79.630	71.921	3.576	9.325	-0.849
2500	9.381	80.312	72.249	21.035	9.863	-0.862
2600	9.399	80.681	72.566	3.729	10.405	-0.875
2700	9.417	81.036	72.873	3.825	10.951	-0.886
2800	9.435	81.379	73.171	3.937	11.500	-0.898
2900	9.458	81.710	73.460	4.065	12.044	-0.908
3000	9.471	82.031	73.740	4.214	12.613	-0.918
3100	9.489	82.342	74.012	25.820	13.177	-0.929
3200	9.507	82.643	74.277	4.577	13.745	-0.939
3300	9.525	82.936	74.535	4.797	14.320	-0.948
3400	9.543	83.221	74.787	26.675	14.904	-0.958
3500	9.561	83.498	75.032	5.045	15.494	-0.967
3600	9.579	83.767	75.271	30.587	16.093	-0.977
3700	9.597	84.030	75.504	5.640	16.702	-0.987
3800	9.614	84.286	75.732	32.507	17.322	-0.996
3900	9.632	84.536	75.954	33.469	17.950	-1.006
4000	9.650	84.780	76.172	34.433	18.591	-1.016
4100	9.668	85.019	76.385	35.399	19.245	-1.026
4200	9.686	85.252	76.593	36.367	19.912	-1.036
4300	9.703	85.480	76.797	37.336	20.586	-1.047
4400	9.721	85.703	76.997	38.307	21.263	-1.058
4500	9.739	85.922	77.193	39.280	22.008	-1.069
4600	9.757	86.136	77.385	40.255	22.743	-1.081
4700	9.775	86.346	77.573	41.232	23.494	-1.092
4800	9.792	86.552	77.758	42.210	24.266	-1.105
4900	9.810	86.754	77.940	43.190	25.055	-1.118
5000	9.828	86.953	78.118	44.172	25.866	-1.131
5100	9.846	87.147	78.293	45.156	26.705	-1.144
5200	9.864	87.339	78.465	46.141	27.561	-1.158
5300	9.881	87.527	78.634	47.129	28.445	-1.173
5400	9.899	87.712	78.801	48.118	29.349	-1.188
5500	9.917	87.893	78.965	49.109	30.281	-1.203
5600	9.935	88.072	79.126	50.101	31.234	-1.219
5700	9.952	88.248	79.284	51.095	32.214	-1.235
5800	9.970	88.421	79.440	52.092	33.221	-1.252
5900	9.988	88.594	79.594	53.089	34.249	-1.269
6000	10.006	88.760	79.745	54.089	35.306	-1.286

Dec. 31, 1968

Cesium, Dimeric (Cs₂)

(Ideal Gas) GFW = 265.810

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	enthalpy/mol H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	8.000	58.000	2.435	26.453	29.453	14.711
100	8.542	58.007	75.521	26.271	23.057	14.711
200	9.046	58.043	66.669	25.869	20.063	14.711
298	9.112	67.667	1.000	25.400	17.301	12.582
300	9.114	67.623	0.917	25.386	17.251	12.587
400	9.176	70.554	45.225	23.779	14.957	12.587
500	9.237	72.608	66.904	23.202	12.818	12.587
600	9.297	74.597	66.466	22.645	10.795	12.587
700	9.357	75.735	70.433	22.097	8.864	12.587
800	9.416	76.106	71.846	21.563	6.924	12.587
900	9.476	76.510	72.557	21.033	4.984	12.587
1000	9.536	76.942	73.557	20.503	3.044	12.587
1100	9.597	77.404	74.894	20.000	1.104	12.587
1200	9.659	77.894	76.465	19.525	-0.835	12.587
1300	9.721	78.410	78.265	19.075	-2.775	12.587
1400	9.783	78.950	80.295	18.650	-4.725	12.587
1500	9.846	79.514	82.555	18.250	-6.675	12.587
1600	9.909	80.102	85.045	17.875	-8.625	12.587
1700	9.972	80.714	87.765	17.525	-10.575	12.587
1800	10.035	81.350	90.715	17.200	-12.525	12.587
1900	10.098	82.010	93.895	16.895	-14.475	12.587
2000	10.161	82.694	97.305	16.615	-16.425	12.587
2100	10.224	83.402	100.945	16.360	-18.375	12.587
2200	10.287	84.134	104.815	16.125	-20.325	12.587
2300	10.350	84.890	108.915	15.900	-22.275	12.587
2400	10.413	85.670	113.245	15.685	-24.225	12.587
2500	10.476	86.474	117.805	15.485	-26.175	12.587
2600	10.539	87.294	122.595	15.295	-28.125	12.587
2700	10.602	88.134	127.615	15.115	-30.075	12.587
2800	10.665	88.994	132.865	14.945	-32.025	12.587
2900	10.728	89.874	138.345	14.785	-33.975	12.587
3000	10.791	90.774	144.055	14.635	-35.925	12.587
3100	10.854	91.694	149.995	14.495	-37.875	12.587
3200	10.917	92.634	156.165	14.365	-39.825	12.587
3300	10.980	93.594	162.565	14.245	-41.775	12.587
3400	11.043	94.574	169.195	14.135	-43.725	12.587
3500	11.106	95.574	176.045	14.035	-45.675	12.587
3600	11.169	96.594	183.115	13.945	-47.625	12.587
3700	11.232	97.634	190.405	13.865	-49.575	12.587
3800	11.295	98.694	197.915	13.795	-51.525	12.587
3900	11.358	99.774	205.645	13.735	-53.475	12.587
4000	11.421	100.874	213.595	13.685	-55.425	12.587
4100	11.484	101.994	221.765	13.645	-57.375	12.587
4200	11.547	103.134	230.155	13.615	-59.325	12.587
4300	11.610	104.294	238.765	13.595	-61.275	12.587
4400	11.673	105.474	247.595	13.585	-63.225	12.587
4500	11.736	106.674	256.645	13.585	-65.175	12.587
4600	11.799	107.894	265.915	13.595	-67.125	12.587
4700	11.862	109.134	275.405	13.615	-69.075	12.587
4800	11.925	110.394	285.115	13.645	-71.025	12.587
4900	11.988	111.674	295.045	13.685	-72.975	12.587
5000	12.051	112.974	305.195	13.735	-74.925	12.587
5100	12.114	114.294	315.565	13.795	-76.875	12.587
5200	12.177	115.634	326.155	13.865	-78.825	12.587
5300	12.240	116.994	336.965	13.945	-80.775	12.587
5400	12.303	118.374	347.995	14.035	-82.725	12.587
5500	12.366	119.774	359.345	14.135	-84.675	12.587
5600	12.429	121.194	370.915	14.245	-86.625	12.587
5700	12.492	122.634	382.705	14.365	-88.575	12.587
5800	12.555	124.094	394.715	14.495	-90.525	12.587
5900	12.618	125.574	406.945	14.635	-92.475	12.587
6000	12.681	127.074	419.395	14.785	-94.425	12.587

CESIUM, DIMERIC (Cs₂)

Ground State Configuration 1²S_g

S⁰_{298.15} = [67.87] gibbs/mol

(IDEAL GAS)

GFW = 265.810

ΔHf° = 26.45 ± 1.0 kcal/mol

ΔHf°_{298.15} = 25.40 ± 1.0 kcal/mol

Electronic Levels and Quantum Weights

State	E _i , cm ⁻¹	g _i
1 _g ⁺	0	1
1 _g ⁺	9000	1
1 _g ⁺	13043.87	2
1 _g ⁺	16066.03	[1]
1 _g ⁺	16175.80	[2]

ω_eX_e = 0.08005 cm⁻¹

B_e = [0.01283] cm⁻¹

α_e = [0.000035] cm⁻¹

σ = 2

r_e = [4.48] Å

Heat of Formation

The vapor pressures of Cs(g) and Cs₂(g) over Cs(l) have been measured by many investigators (see Cs(g) table for details). For internal consistency, the vapor pressures determined at temperatures 980-1684°K and pressures 1.1-7.5 atm by Stone (1) are employed for evaluation. The P-T data on cesium reported by Tepper (2) are employed for comparison. Using the reported pressures, the JANAF free energy functions and ΔHf°₂₉₈ = 11.24 kcal/mol for the reaction Cs₂(g) = 2Cs(g), the equilibrium constants for this reaction are evaluated. From the derived equilibrium constants, the enthalpy change of the reaction Cs₂(g) = 2Cs(g) is calculated by the second and third law methods. The results are presented in the table below. The value of ΔHf°₂₉₈(Cs₂, g) is adopted as 25.40 ± 1.0 kcal/mol. The D₀(Cs-Cs) was reported as 0.45 eV or 10.38 kcal/mol by Gaydon (3) and Herzberg (3), yielding ΔHf°₂₉₈ = 25.93 ± 0.92 kcal/mol for Cs₂(g) which is in agreement with the adopted value, within the experimental uncertainty.

Expt. No.	Points	Temperature, °K	Pressure, atm	ΔHf° ₂₉₈ , kcal/mol	ΔHf° ₂₉₈ , kcal/mol
28 (1)	23	1151-1680	4.7-7.5	12.39±0.10	11.63
30 (1)	24	980-1684	1.1-2.0	10.90±0.16	11.24
38 (1)	19	1100-1657	3.2-5.2	12.28±0.22	11.22
1-6, 8, 10 (2)	54	955-1375	1.0-5.4	12.35±0.70	11.47

*Calculation based on the third law ΔHf°₂₉₈ and ΔHf°₂₉₈(Cs, g) = 18.32 kcal/mol.

Heat Capacity and Entropy

The ground state configuration, electronic levels and quantum weights, ω_e and ω_x, are obtained from Herzberg (3). The second electronic level is reported as 8800-11000 cm⁻¹ and the value 9000 cm⁻¹ is chosen for calculation. The last two electronic states are estimated by comparison with those for K₂(g) given by (3). The bond distance r_e is calculated from ω based on the method suggested by Guggenheimer (4). The values of B_e and α_e are calculated (3). The moment of inertia is 2.2145 x 10⁻³⁷ g cm².

References

1. J. P. Stone, C. T. Ewing, J. R. Spann, E. W. Steinkuller, D. D. Williams, and R. R. Miller, J. Chem. Eng. Data 11, 309 (1966).
2. F. Tepper, J. Zelenak, F. Roehlich and V. May, "Thermophysical and Transport Properties of Liquid Metals," NSR 84-116, Third Quarterly Progress Rept. July - Sept. 1964, NSA Research Corp., Callery, Pennsylvania, October 19, 1964.
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
4. K. M. Guggenheimer, Proc. Phys. Soc. (London) 58, 456 (1946).
5. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

June 30, 1968

CESIUM FLUORIDE, DIMERIC (Cs₂F₂) (IDEAL GAS)

GFW = 303.8068

Point Group [D_{2h}]
S_{298.15} = (84 ± 2) gibbs/mol
Ground State Quantum Weight = (1)

ΔH_{f,0}^o = -211.55 ± 2.0 kcal/mol
ΔH_{f,298.15}^o = -212.74 ± 2.0 kcal/mol

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
[200] (1)	[120] (1)
[110] (1)	[220] (1)
[210] (1)	[230] (1)

Bond Angle: Cs-F = (2.35) Å

Bond Distance: F-Cs-F = (85°)

Product of the Moments of Inertia: I_AI_BI_C = {3.126 × 10⁻¹¹²} g³ cm⁶

Heat of Formation

Evidence from the velocity distribution in molecular beams (1) has shown that alkali halide vapors contain significant amounts of polymeric species. Using the same method Eisenstadt (2) determined the molecular composition of CsF vapor in the temperature range 838 - 919°K. Based on the reported equilibrium constants for the reaction (CsF)₂(g) = 2CsF(g), we evaluate the enthalpy change (ΔH_{f,298}^o) by the second and third law methods to be 40.53 ± 1.75 and 42.34 ± 0.26 kcal/mol, respectively. Employing ΔH_{f,298}^o = 42.34 and ΔH_{f,298}^o(CsF, g) = -85.2 kcal/mol, we obtained ΔH_{f,298}^o = -212.74 kcal/mol for Cs₂F₂(g), which is adopted.

Heat Capacity and Entropy

The Cs₂F₂ molecule is assumed to have a rhombic configuration of symmetry D_{2h} as Cs₂Cl₂(3). The Cs-F bond distance is taken as the same as that in CsF(g). The bond angles and vibrational frequencies are estimated by comparison with those of other dimeric alkali halides (3, 4). The three principal moments of inertia are: I_A = 1.590 × 10⁻³⁸, I_B = 1.325 × 10⁻³⁷ and I_C = 1.484 × 10⁻³⁷ g cm².

References

1. R. C. Miller and P. Kusch, J. Chem. Phys. **23**, 860 (1955); *ibid.* **27**, 981 (1957).
2. M. Eisenstadt, G. M. Rothberg and P. Kusch, J. Chem. Phys. **23**, 787 (1958).
3. J. Berkowitz, J. Chem. Phys. **23**, 1386 (1958).
4. J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).

T, °K	Cp ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log Kp
0	16.000	45.000	INFINITE	-3.606	-211.548	-211.548	INFINITE
100	16.239	76.707	65.004	1.440	-212.485	-211.501	21.350
200	16.478	107.414	85.004	1.000	-212.740	-211.495	23.339
298	16.603	127.059	107.059	0.000	-212.740	-211.495	25.456
300	16.603	127.059	107.059	0.000	-212.740	-211.495	25.456
400	16.839	147.697	127.697	0.035	-212.747	-211.249	153.894
500	16.968	168.335	148.335	1.064	-212.747	-211.249	153.894
600	17.097	188.973	168.973	3.016	-212.747	-211.249	153.894
700	17.226	209.610	189.610	5.079	-212.747	-211.249	153.894
800	17.355	230.247	210.247	7.142	-212.747	-211.249	153.894
900	17.484	250.884	230.884	9.205	-212.747	-211.249	153.894
1000	17.613	271.521	251.521	11.268	-212.747	-211.249	153.894
1100	17.742	292.158	272.158	13.331	-212.747	-211.249	153.894
1200	17.871	312.795	292.795	15.394	-212.747	-211.249	153.894
1300	17.999	333.432	313.432	17.457	-212.747	-211.249	153.894
1400	18.128	354.069	334.069	19.520	-212.747	-211.249	153.894
1500	18.257	374.706	354.706	21.583	-212.747	-211.249	153.894
1600	18.386	395.343	375.343	23.646	-212.747	-211.249	153.894
1700	18.515	415.980	395.980	25.709	-212.747	-211.249	153.894
1800	18.644	436.617	416.617	27.772	-212.747	-211.249	153.894
1900	18.773	457.254	437.254	29.835	-212.747	-211.249	153.894
2000	18.902	477.891	457.891	31.898	-212.747	-211.249	153.894
2100	19.031	498.528	478.528	33.961	-212.747	-211.249	153.894
2200	19.160	519.165	499.165	36.024	-212.747	-211.249	153.894
2300	19.289	539.802	519.802	38.087	-212.747	-211.249	153.894
2400	19.418	560.439	540.439	40.150	-212.747	-211.249	153.894
2500	19.547	581.076	561.076	42.213	-212.747	-211.249	153.894
2600	19.676	601.713	581.713	44.276	-212.747	-211.249	153.894
2700	19.805	622.350	602.350	46.339	-212.747	-211.249	153.894
2800	19.934	642.987	622.987	48.402	-212.747	-211.249	153.894
2900	20.063	663.624	643.624	50.465	-212.747	-211.249	153.894
3000	20.192	684.261	664.261	52.528	-212.747	-211.249	153.894
3100	20.321	704.898	684.898	54.591	-212.747	-211.249	153.894
3200	20.450	725.535	705.535	56.654	-212.747	-211.249	153.894
3300	20.579	746.172	726.172	58.717	-212.747	-211.249	153.894
3400	20.708	766.809	746.809	60.780	-212.747	-211.249	153.894
3500	20.837	787.446	767.446	62.843	-212.747	-211.249	153.894
3600	20.966	808.083	788.083	64.906	-212.747	-211.249	153.894
3700	21.095	828.720	808.720	66.969	-212.747	-211.249	153.894
3800	21.224	849.357	829.357	69.032	-212.747	-211.249	153.894
3900	21.353	869.994	849.994	71.095	-212.747	-211.249	153.894
4000	21.482	890.631	870.631	73.158	-212.747	-211.249	153.894
4100	21.611	911.268	891.268	75.221	-212.747	-211.249	153.894
4200	21.740	931.905	911.905	77.284	-212.747	-211.249	153.894
4300	21.869	952.542	932.542	79.347	-212.747	-211.249	153.894
4400	21.998	973.179	953.179	81.410	-212.747	-211.249	153.894
4500	22.127	993.816	973.816	83.473	-212.747	-211.249	153.894
4600	22.256	1014.453	994.453	85.536	-212.747	-211.249	153.894
4700	22.385	1035.090	1015.090	87.599	-212.747	-211.249	153.894
4800	22.514	1055.727	1035.727	89.662	-212.747	-211.249	153.894
4900	22.643	1076.364	1056.364	91.725	-212.747	-211.249	153.894
5000	22.772	1097.001	1077.001	93.788	-212.747	-211.249	153.894
5100	22.901	1117.638	1097.638	95.851	-212.747	-211.249	153.894
5200	23.030	1138.275	1118.275	97.914	-212.747	-211.249	153.894
5300	23.159	1158.912	1138.912	99.977	-212.747	-211.249	153.894
5400	23.288	1179.549	1159.549	102.040	-212.747	-211.249	153.894
5500	23.417	1200.186	1180.186	104.103	-212.747	-211.249	153.894
5600	23.546	1220.823	1200.823	106.166	-212.747	-211.249	153.894
5700	23.675	1241.460	1221.460	108.229	-212.747	-211.249	153.894
5800	23.804	1262.097	1242.097	110.292	-212.747	-211.249	153.894
5900	23.933	1282.734	1262.734	112.355	-212.747	-211.249	153.894
6000	24.062	1303.371	1283.371	114.418	-212.747	-211.249	153.894

June 30, 1968

GFW = 281.8094

(IDEAL GAS)

DICESIUM MONOXIDE (Cs₂O) $\Delta H_f^\circ = -20.6 \pm 10$ kcal/mol $\Delta H_f^\circ_{298.15} = -22.0 \pm 10$ kcal/molPoint Group C_{2v} $S^\circ_{298.15} = [76 \pm 2]$ gibbs/mol

Ground State Quantum Weight = [1]

Dicesium Monoxide (Cs₂O)
(Ideal Gas) GFW = 281.8094

T, °K	Cp*	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	3.331	20.604	20.604	INFINITE
100	10.503	62.790	77.259	2.444	21.091	22.674	49.554
200	12.536	71.816	77.181	1.822	21.572	24.156	68.805
300	13.238	75.998	77.198	1.000	22.000	25.216	81.836
400	13.245	76.079	75.998	0.24	22.010	25.238	88.386
500	13.521	79.933	76.521	1.365	23.549	25.905	14.194
600	13.657	82.966	77.518	2.724	24.053	26.436	11.555
700	13.732	85.464	78.640	4.094	24.545	26.965	9.764
800	13.779	87.584	79.770	5.470	25.038	27.212	8.496
900	13.809	89.426	80.864	6.849	25.538	27.491	7.510
1000	13.830	91.034	81.908	8.231	26.041	27.703	6.727
1100	13.845	92.512	82.897	9.615	26.542	27.871	6.070
1200	13.856	93.832	83.832	11.000	27.045	28.000	5.543
1300	13.865	95.038	84.716	12.384	27.548	28.100	5.040
1400	13.872	96.148	85.553	13.773	28.050	28.180	4.558
1500	13.877	97.176	86.347	15.161	28.549	28.240	4.096
1600	13.881	98.134	87.101	16.548	29.045	28.290	3.654
1700	13.885	99.030	87.819	17.937	29.537	28.330	3.232
1800	13.888	99.872	88.504	19.325	30.025	28.360	2.828
1900	13.890	100.666	89.156	20.714	30.508	28.380	2.442
2000	13.892	101.417	89.783	22.103	30.985	28.390	2.074
2100	13.894	102.129	90.393	23.493	31.457	28.390	1.724
2200	13.895	102.807	90.956	24.882	31.924	28.380	1.392
2300	13.897	103.454	91.512	26.272	32.385	28.360	1.076
2400	13.898	104.071	92.061	27.661	32.840	28.330	0.776
2500	13.899	104.663	92.598	29.051	33.289	28.290	0.492
2600	13.900	105.230	93.124	30.441	33.732	28.240	0.224
2700	13.901	105.775	93.633	31.831	34.169	28.180	0.000
2800	13.902	106.300	94.124	33.221	34.600	28.110	-0.280
2900	13.902	106.806	94.600	34.611	35.025	28.030	-0.564
3000	13.903	107.293	95.074	36.002	35.444	27.940	-0.852
3100	13.903	107.765	95.531	37.392	35.856	27.840	-1.144
3200	13.903	108.231	95.970	38.782	36.261	27.730	-1.440
3300	13.904	108.682	96.398	40.173	36.659	27.610	-1.744
3400	13.904	109.120	96.815	41.563	37.050	27.480	-2.056
3500	13.904	109.545	97.228	42.953	37.433	27.340	-2.376
3600	13.905	109.958	97.636	44.344	37.809	27.190	-2.700
3700	13.905	110.360	98.034	45.734	38.178	27.030	-3.028
3800	13.905	110.752	98.418	47.125	38.540	26.860	-3.360
3900	13.906	111.133	98.796	48.515	38.895	26.680	-3.696
4000	13.906	111.508	99.168	49.906	39.244	26.490	-4.036
4100	13.906	111.876	99.531	51.297	39.587	26.290	-4.380
4200	13.906	112.238	99.885	52.687	39.924	26.080	-4.728
4300	13.906	112.593	100.231	54.078	40.254	25.860	-5.080
4400	13.907	112.941	100.566	55.469	40.578	25.630	-5.436
4500	13.907	113.283	100.890	56.859	40.895	25.390	-5.796
4600	13.907	113.620	101.208	58.250	41.206	25.140	-6.160
4700	13.907	113.952	101.521	59.641	41.511	24.880	-6.528
4800	13.907	114.279	101.829	61.031	41.811	24.610	-6.896
4900	13.907	114.601	102.133	62.422	42.106	24.330	-7.264
5000	13.908	114.918	102.433	63.813	42.396	24.040	-7.632
5100	13.908	115.231	102.728	65.204	42.681	23.740	-8.000
5200	13.908	115.540	103.018	66.594	42.961	23.430	-8.368
5300	13.908	115.845	103.303	67.985	43.236	23.110	-8.736
5400	13.908	116.146	103.583	69.376	43.506	22.780	-9.104
5500	13.908	116.442	103.858	70.767	43.771	22.440	-9.472
5600	13.908	116.735	104.129	72.157	44.031	22.090	-9.840
5700	13.908	117.024	104.395	73.548	44.286	21.730	-10.208
5800	13.908	117.309	104.657	74.939	44.536	21.360	-10.576
5900	13.908	117.590	104.914	76.330	44.781	20.980	-10.944
6000	13.908	117.867	105.167	77.721	45.021	20.590	-11.312
6100	13.908	118.141	105.416	79.112	45.256	20.190	-11.680
6200	13.908	118.412	105.661	80.503	45.486	19.780	-12.048
6300	13.908	118.680	105.902	81.894	45.711	19.360	-12.416
6400	13.908	118.945	106.139	83.285	45.931	18.930	-12.784
6500	13.908	119.208	106.372	84.676	46.146	18.490	-13.152
6600	13.908	119.468	106.601	86.067	46.356	18.040	-13.520
6700	13.908	119.725	106.826	87.458	46.561	17.580	-13.888
6800	13.908	119.979	107.047	88.849	46.761	17.110	-14.256
6900	13.908	120.230	107.264	90.240	46.956	16.640	-14.624
7000	13.908	120.479	107.477	91.631	47.146	16.160	-14.992
7100	13.908	120.725	107.686	93.022	47.331	15.670	-15.360
7200	13.908	120.969	107.891	94.413	47.511	15.170	-15.728
7300	13.908	121.210	108.093	95.804	47.686	14.660	-16.096
7400	13.908	121.449	108.291	97.195	47.856	14.140	-16.464
7500	13.908	121.685	108.486	98.586	48.021	13.610	-16.832
7600	13.908	121.918	108.678	99.977	48.181	13.070	-17.200
7700	13.908	122.149	108.867	101.368	48.336	12.520	-17.568
7800	13.908	122.378	109.053	102.759	48.486	11.960	-17.936
7900	13.908	122.604	109.236	104.150	48.631	11.390	-18.304
8000	13.908	122.828	109.416	105.541	48.771	10.810	-18.672
8100	13.908	123.049	109.593	106.932	48.906	10.220	-19.040
8200	13.908	123.268	109.767	108.323	49.041	9.620	-19.408
8300	13.908	123.484	109.938	109.714	49.171	9.010	-19.776
8400	13.908	123.698	110.106	111.105	49.296	8.390	-20.144
8500	13.908	123.909	110.271	112.496	49.416	7.760	-20.512
8600	13.908	124.118	110.433	113.887	49.531	7.120	-20.880
8700	13.908	124.325	110.589	115.278	49.641	6.470	-21.248
8800	13.908	124.529	110.742	116.669	49.746	5.810	-21.616
8900	13.908	124.731	110.893	118.060	49.846	5.140	-21.984
9000	13.908	124.931	111.042	119.451	49.941	4.460	-22.352
9100	13.908	125.129	111.189	120.842	50.031	3.780	-22.720
9200	13.908	125.325	111.333	122.233	50.116	3.090	-23.088
9300	13.908	125.518	111.474	123.624	50.196	2.390	-23.456
9400	13.908	125.709	111.613	125.015	50.271	1.680	-23.824
9500	13.908	125.898	111.750	126.406	50.341	0.960	-24.192
9600	13.908	126.084	111.884	127.797	50.406	0.240	-24.560
9700	13.908	126.268	112.016	129.188	50.466	-0.480	-24.928
9800	13.908	126.449	112.146	130.579	50.521	-1.190	-25.296
9900	13.908	126.628	112.273	131.970	50.571	-1.890	-25.664
10000	13.908	126.804	112.398	133.361	50.616	-2.580	-26.032

Dec. 31, 1968

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	3.826	2.392	12.749	1.036	∞.000	∞.000	∞.000
200	5.399	5.061	8.437	∞.555	∞.000	∞.000	∞.000
298	5.843	7.913	7.913	∞.000	∞.000	∞.000	∞.000
300	5.846	7.949	7.943	∞.11	∞.000	∞.000	∞.000
400	6.077	9.665	8.166	∞.608	∞.000	∞.000	∞.000
500	6.250	11.040	8.591	1.224	∞.000	∞.000	∞.000
600	6.394	12.193	9.068	1.857	∞.000	∞.000	∞.000
700	6.513	13.163	9.502	2.502	∞.000	∞.000	∞.000
800	6.620	14.068	10.116	3.159	∞.000	∞.000	∞.000
900	6.725	14.850	10.598	3.826	∞.000	∞.000	∞.000
1000	6.822	15.564	11.060	4.504	∞.000	∞.000	∞.000
1100	6.910	16.218	11.500	5.190	∞.000	∞.000	∞.000
1200	7.000	16.818	11.918	5.890	∞.000	∞.000	∞.000
1300	7.088	17.367	12.318	6.590	∞.000	∞.000	∞.000
1400	7.150	20.263	12.772	10.288	∞.000	∞.000	∞.000
1500	7.500	20.780	13.288	11.238	∞.000	∞.000	∞.000
1600	7.500	21.264	13.772	11.988	∞.000	∞.000	∞.000
1700	7.500	21.716	14.236	12.688	∞.000	∞.000	∞.000
1800	7.500	22.148	14.654	13.488	∞.000	∞.000	∞.000
1900	7.500	22.553	15.060	14.238	∞.000	∞.000	∞.000
2000	7.500	22.938	15.444	14.988	∞.000	∞.000	∞.000
2100	7.500	23.304	15.810	15.738	∞.000	∞.000	∞.000
2200	7.500	23.654	16.166	16.488	∞.000	∞.000	∞.000
2300	7.500	23.984	16.491	17.238	∞.000	∞.000	∞.000
2400	7.500	24.305	16.810	17.988	∞.000	∞.000	∞.000
2500	7.500	24.612	17.116	18.738	∞.000	∞.000	∞.000
2600	7.500	24.906	17.410	19.488	∞.000	∞.000	∞.000
2700	7.500	25.192	17.695	20.238	∞.000	∞.000	∞.000
2800	7.500	25.469	17.968	20.988	∞.000	∞.000	∞.000
2900	5.892	51.236	18.686	94.396	∞.000	∞.000	∞.000
3000	6.010	51.438	19.774	94.591	∞.000	∞.000	∞.000
3100	6.131	51.637	20.799	95.598	∞.000	∞.000	∞.000
3200	6.251	51.834	21.768	96.604	∞.000	∞.000	∞.000
3300	6.373	52.028	22.680	96.849	∞.000	∞.000	∞.000
3400	6.496	52.220	23.546	97.492	∞.000	∞.000	∞.000
3500	6.616	52.410	24.368	98.148	∞.000	∞.000	∞.000
3600	6.732	52.598	25.149	98.815	∞.000	∞.000	∞.000
3700	6.846	52.784	25.894	100.184	∞.000	∞.000	∞.000
3800	6.959	52.968	26.594	101.184	∞.000	∞.000	∞.000
3900	7.059	53.150	27.282	100.885	∞.000	∞.000	∞.000
4000	7.158	53.330	27.931	101.596	∞.000	∞.000	∞.000
4100	7.251	53.508	28.553	102.316	∞.000	∞.000	∞.000
4200	7.339	53.684	29.149	103.046	∞.000	∞.000	∞.000
4300	7.426	53.859	29.722	103.782	∞.000	∞.000	∞.000
4400	7.498	54.029	30.272	104.530	∞.000	∞.000	∞.000
4500	7.568	54.198	30.802	105.283	∞.000	∞.000	∞.000
4600	7.633	54.365	31.312	106.043	∞.000	∞.000	∞.000
4700	7.693	54.530	31.805	106.812	∞.000	∞.000	∞.000
4800	7.749	54.693	32.279	107.592	∞.000	∞.000	∞.000
4900	7.797	54.853	32.739	108.389	∞.000	∞.000	∞.000
5000	7.842	55.011	33.183	109.141	∞.000	∞.000	∞.000
5100	7.884	55.167	33.612	109.927	∞.000	∞.000	∞.000
5200	7.925	55.320	34.026	110.752	∞.000	∞.000	∞.000
5300	7.964	55.471	34.426	111.512	∞.000	∞.000	∞.000
5400	7.999	55.620	34.822	112.309	∞.000	∞.000	∞.000
5500	8.016	55.767	35.202	113.109	∞.000	∞.000	∞.000
5600	8.043	55.912	35.570	113.912	∞.000	∞.000	∞.000
5700	8.069	56.054	35.929	114.717	∞.000	∞.000	∞.000
5800	8.094	56.193	36.278	115.520	∞.000	∞.000	∞.000
5900	8.118	56.334	36.616	116.336	∞.000	∞.000	∞.000
6000	8.142	56.470	36.945	117.149	∞.000	∞.000	∞.000

Dec. 31, 1965

(REFERENCE STATE)

COPPER (Cu)

0 to 1356.6°K. Crystal
1356.6 to 2848°K. Liquid
2848 to 6000°K. Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

AT. WT. = 63.54

Cu

Cu

Copper (Cu)
(Crystal)

At. Wt. = 63.54

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	3.826	2.392	12.749	0.000	0.000	∞.000
200	5.399	5.661	8.437	0.000	0.000	∞.000
298	5.853	7.913	0.000	0.000	0.000	∞.000
300	5.846	7.949	0.011	0.000	0.000	∞.000
400	6.077	9.665	8.146	0.000	0.000	∞.000
500	6.250	11.040	8.591	0.000	0.000	∞.000
600	6.394	12.193	9.098	0.000	0.000	∞.000
700	6.516	13.188	9.613	0.000	0.000	∞.000
800	6.620	14.064	10.116	0.000	0.000	∞.000
900	6.725	14.850	10.599	0.000	0.000	∞.000
1000	6.822	15.564	11.060	0.000	0.000	∞.000
1100	6.910	16.218	11.500	0.000	0.000	∞.000
1200	6.998	16.823	11.918	0.000	0.000	∞.000
1300	7.086	17.387	12.318	0.000	0.000	∞.000
1400	7.174	17.915	12.699	0.000	0.000	∞.000
1500	7.262	18.413	13.063	0.000	0.000	∞.000
1600	7.350	18.886	13.413	0.000	0.000	∞.000
1700	7.438	19.333	13.748	0.000	0.000	∞.000
1800	7.526	19.761	14.070	0.000	0.000	∞.000
1900	7.614	20.170	14.380	0.000	0.000	∞.000
2000	7.702	20.563	14.680	0.000	0.000	∞.000

(CRYSTAL)

COPPER (Cu)

AT. WT. = 63.54

$$\Delta H_f^\circ 0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ 298.15 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 3.17 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^\circ 298.15 = 81 \pm 0.4 \text{ kcal. mole}^{-1}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The low temperature specific heat of copper has been measured by several workers and generally there is good agreement. The selected values lie close to the determinations of J. A. Kok and W. H. Keesom (1.2-20°K), Physica 3, 1035 (1936); D. L. Martin (20-300°K), Can. J. Phys. 38, 17 (1960); C. B. Satterthwaite, R. S. Creig and W. E. Wallace, J. Am. Chem. Soc. 76, 232 (1954), and S. M. Dookerty, Can. J. Research 2, 84 (1933) and 15B, 59 (1937). Several other workers have reported values of C_p slightly higher than the adopted values especially W. F. Glaue and P. F. Heads, J. Am. Chem. Soc. 63, 1897 (1941), however these measurements were not used for reasons discussed by Martin. The heat capacity above room temperature has been determined directly by several workers, the values of R. E. Pawel and E. E. Stansbury, J. Phys. Chem. Solids 26, 607 (1965) join well with the low temperature data and are adopted. These values lie within 1% of the values adopted by R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley and Sons, Inc., New York, 1963. Several determinations of the solid enthalpy are also in good agreement with selected heat capacity curve. For references to these determinations refer to Hultgren et al. loc. cit.

Melting Data.

The melting point of copper is well established and the recent determination of W. Heyne, Exptl. Tech. Physik. 12, 87 (1964) is adopted. The heat of fusion was obtained from the calculated enthalpy of the solid at the melting point and the liquid enthalpy measurements of F. Wust, A. Meuthen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1918). The liquid enthalpies of I. B. Fieldhouse, J. C. Hedge, J. I. Lang and T. E. Waterman, ASTIA Doc. No. A. D. 150954 are somewhat higher than the adopted values.

Sublimation Data.

See Cu(g) for details.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔF _T ⁰	Log K _p
100					
200					
298	8.663	8.663	0.000	2.000	-1.466
300	8.709	8.663	+0.14	1.999	-1.456
400	10.867	8.957	+0.44	1.980	-1.456
500	12.951	9.513	+1.514	1.763	-1.771
600	13.908	10.135	2.264	1.602	-1.983
700	15.064	10.759	3.014	1.423	-2.444
800	16.066	11.361	3.764	1.227	-3.335
900	16.842	11.934	4.492	1.047	-4.493
1000	17.359	12.475	5.204	0.869	-5.177
1100	18.454	12.987	6.014	0.588	-6.117
1200	19.107	13.470	6.764	0.361	-7.066
1300	19.707	13.927	7.514	0.132	-8.022
1400	20.263	14.360	8.264	0.000	-9.000
1500	20.780	14.771	9.014	0.000	-10.000
1600	21.264	15.162	9.764	0.000	-11.000
1700	21.719	15.534	10.514	0.000	-12.000
1800	22.148	15.890	11.264	0.000	-13.000
1900	22.548	16.230	12.014	0.000	-14.000
2000	22.918	16.556	12.764	0.000	-15.000
2100	23.304	16.869	13.514	0.000	-16.000
2200	23.653	17.169	14.264	0.000	-17.000
2300	23.986	17.458	15.014	0.000	-18.000
2400	24.305	17.737	15.764	0.000	-19.000
2500	24.611	18.006	16.514	0.000	-20.000
2600	24.906	18.266	17.264	0.000	-21.000
2700	25.189	18.517	18.014	0.000	-22.000
2800	25.461	18.760	18.764	0.000	-23.000
2900	25.725	18.996	19.514	0.000	-24.000
3000	25.979	19.224	20.264	0.000	-25.000
3100	26.225	19.446	21.014	6.417	-4.52
3200	26.463	19.662	21.764	72.229	8.958
3300	26.694	19.871	22.514	72.111	11.491
3400	26.918	20.075	23.264	72.006	14.023
3500	27.135	20.274	24.014	71.910	16.552
3600	27.346	20.467	24.764	71.827	19.080
3700	27.552	20.656	25.514	71.756	21.602
3800	27.752	20.840	26.264	71.696	24.125
3900	27.947	21.020	27.014	71.647	26.645
4000	28.136	21.195	27.764	71.608	29.168

Dec. 31, 1965

COPPER (Cu)

(LIQUID)

At. Wt. = 63.54

$$\Delta H_f^0 = 8.663 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 298.15 = 2.224 \text{ kcal. mole}^{-1}$$

$$\eta_m^0 = 1356.6^\circ \text{K.}$$

$$\Delta H_m^0 = 3.17 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\eta_b^0 = 2848^\circ \text{K.}$$

$$\Delta H_b^0 = 72.743 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m^0 and the difference between $H_{1356.6}^0 - H_{298}^0$ for (c) and (l).

Heat Capacity and Entropy.

The heat capacity was calculated from the enthalpy data of P. Kist, A. Mathen and R. Durrer, Forsch. Geb. Ingenieurw. VDI-Forsch. 204 (1916). The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Copper (Cu)

(Ideal Gas) At. Wt. = 63.54

COPPER (Cu)

(IDEAL GAS)

AT. WT. = 63.54

Ground State Configuration $2s^2 3s^2 3p^6 3d^{10}$ $\Delta H_f^\circ 0 = 80.714 \pm 0.5 \text{ kcal. mole}^{-1}$ $\Delta H_f^\circ 298.15 = 81.0 \pm 0.5 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = 39.744 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Quantum Weight

$E_1, \text{ cm.}^{-1}$	g_1	$E_2, \text{ cm.}^{-1}$	g_2	$E_3, \text{ cm.}^{-1}$	g_3	$E_4, \text{ cm.}^{-1}$	g_4
0	2	4406.0	4	5478.7	4	5784.7	4
1120.0	2	4454.2	4	5527.7	4	5834.7	4
1324.5	4	4495.6	6	5537.7	6	5884.7	6
3053.5	2	43726.2	6	55391.3	6	57905.2	6
3763.7	2	44963.2	8	55426.3	8	57908.7	8
39018.7	6	45821.0	2	55429.8	6	58568.9	2
40344.9	2	46579.8	4	56050.9	6	58569.9	2
40809.1	10	46598.4	6	56343.7	4	58725.5	4
41153.4	8	49383.0	4	58364.7	2	59323.2	2
41562.9	6	49383.3	2	58651.5	6	59647.9	2
42302.5	4	49395.2	4	58690.9	4	60070.0	16
43137.2	2	49442.1	2	58711.4	2	60595.0	16
43514.0	8	52846.8	2	61150.0	2		

Heat of Formation.

The heat of sublimation has been determined by second and third law analysis of the vapor pressure data of a large number of investigators. The results are summarized below:

Ref.	Range ^a , K.	Method	Points	$\Delta H_{\text{subl.}}^\circ 298.15 \text{ kcal. mole}^{-1}$	3rd law	Drift
1.	1242-1340	Knudsen	6	80.6 \pm 0.2	81.39 \pm 0.04	0.3 \pm 0.2
2.	1347-1523	Knudsen	18*	80.6 \pm 0.6	80.22 \pm 0.3	-1.9 \pm 0.2
3.	1605-1879	Transport	21*	79.7 \pm 0.6	80.55 \pm 0.25	0.5 \pm 0.4
4.	1192-1360	Knudsen	13	80.6 \pm 0.4	81.16 \pm 1.2	0.4 \pm 3.1
5.	1143-1292	Langmuir	5	81.3 \pm 1.0	80.61 \pm 0.2	-0.6 \pm 0.8
6.	1475-1707	Knudsen	8	85.2 \pm 1.3	81.05 \pm 0.4	-1.4 \pm 0.8
7.	1356-1356	Knudsen	15	93.1 \pm 2.3	92.36 \pm 1.7	2.7 \pm 2.0
8.	1268-1320	Langmuir	7*	92.5 \pm 3.3	81.26 \pm 0.5	-8.9 \pm 2.6
9.	1419-1463	Knudsen	9	76.6 \pm 1.0	80.30 \pm 0.4	2.3 \pm 0.6
10.	1419-1463	Knudsen	7	85.0 \pm 11.7	81.84 \pm 0.8	12.9 \pm 8.2
11.	1083-2643	Transport	1	93.5 \pm 4.3	79.2 \pm 2.8	-5.3 \pm 1.7
12.	2138-2573	Boiling	5	76.3 \pm 13.8	75.0 \pm 2.0	-1.6 \pm 1.3
13.	2253-2583	Boiling	6	66.2 \pm 2.5	73.5 \pm 1.3	-0.9 \pm 5.9
14.	1768-2116	Boiling	6	66.2 \pm 2.5	73.5 \pm 1.3	3.5 \pm 1.3

*1 Point rejected due to failure of statistical test.

References:

- H. H. Herzog, J. Am. Chem. Soc. 75, 1529 (1953)
- J. Knapowski and J. Kolonel, Bull. Acad. Polon. Sci. Ser. Sci. Tech. 12, 69 (1964)
- A. N. Nemyanov, L. A. Shakhin and V. I. Lebedev, Zhur. Fiz. Khim. 33, 598 (1959)
- J. W. Edwards, H. L. Johnston and W. E. Dilmore, J. Am. Chem. Soc. 75, 2467 (1953)
- J. R. B. McConach, J. R. Myers and R. K. Saker, J. Chem. Eng. Data, 10, 319 (1965)
- R. B. McConach, J. R. Myers and R. K. Saker, J. Chem. Eng. Data, 10, 319 (1965)
- R. B. Marshall, J. R. Myers and R. K. Saker, J. Chem. Eng. Data, 10, 319 (1965)
- P. J. Zettervall, J. R. Myers and R. K. Saker, J. Chem. Eng. Data, 10, 319 (1965)
- P. J. Zettervall, J. R. Myers and R. K. Saker, J. Chem. Eng. Data, 10, 319 (1965)
- E. Mack, G. Osterhof and H. M. Kramer, J. Am. Chem. Soc. 45, 617 (1923)
- O. Ruff and M. Bergdahl, Z. Elektrochem. 52, 515 (1926)
- O. Ruff and M. Bergdahl, Z. Anorg. Allgem. Chem. 106, 76 (1939)
- C. Greenwood, Z. Physik. Chem. 126, 484 (1928)
- E. Bur and N. Brunner, Helv. Chim. Acta, 17, 956 (1934)

The first eight references may be considered to have reasonable drifts and second and third law agreement. The three Langmuir values are grouped closely together at about 80.3 kcal. mole⁻¹. The Knudsen values all lie a little higher averaging 81.4 kcal. mole⁻¹, the single transport determination is at 80.55 kcal. mole⁻¹. If the evaporation coefficient is not unity in the Langmuir experiments then one would observe lower pressures and higher heats of sublimation, thus it appears that the coefficient must be unity and that all techniques are measuring valid heats of sublimation. A value of 81 \pm 0.5 kcal. mole⁻¹ has been chosen weighted toward the more precise Knudsen work of Herzog.

Heat Capacity and Entropy.

The electronic ground state configuration and higher electronic levels were taken from C. E. Moore "Atomic Energy Levels", Natl. Bur. Stds. Circular 467, Washington 1952.

Dec. 31, 1965

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S ^o -(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈ kcal. mole ⁻¹	ΔH_f°	ΔF_f°	Log K _p
0	4.000	INFINITE	80.714	80.714	80.714	INFINITE
100	34.317	44.161	0.984	81.052	77.859	-170.153
200	4.968	37.760	0.888	81.067	74.648	-81.567
298	4.968	39.744	0.000	81.000	71.510	-52.415
300	4.968	39.774	0.009	80.998	71.450	-52.049
400	4.968	41.204	3.039	80.898	68.282	-37.306
500	4.968	42.313	4.0307	80.779	65.142	-28.472
600	4.968	43.218	4.0719	80.643	62.028	-22.592
700	4.968	43.968	4.0719	80.500	58.943	-18.720
800	4.968	44.648	4.0719	80.334	55.867	-15.720
900	4.968	45.231	4.0719	80.164	52.819	-12.681
1000	4.968	45.756	4.2269	79.983	49.791	-10.881
1100	4.969	46.230	4.2608	79.794	46.781	-9.294
1200	4.970	46.658	4.2813	79.598	43.781	-7.918
1300	4.972	47.060	4.3231	79.388	40.813	-6.841
1400	4.977	47.429	4.3516	79.167	37.887	-5.925
1500	4.985	47.772	4.3780	78.935	35.007	-5.135
1600	4.997	48.094	4.4049	78.692	32.166	-4.447
1700	5.016	48.398	4.4322	78.438	29.361	-3.851
1800	5.041	48.685	4.4592	78.176	26.591	-3.345
1900	5.074	48.959	4.4858	77.907	23.857	-2.925
2000	5.116	49.220	4.5123	77.633	21.163	-2.597
2100	5.168	49.471	4.5383	77.355	18.503	-2.337
2200	5.229	49.711	4.5633	77.072	15.877	-2.130
2300	5.300	49.947	4.5877	76.784	13.283	-1.964
2400	5.380	50.174	4.6116	76.491	10.721	-1.834
2500	5.468	50.395	4.6354	76.193	8.193	-1.731
2600	5.565	50.612	4.6587	75.891	5.705	-1.654
2700	5.668	50.823	4.6816	75.584	3.257	-1.604
2800	5.778	51.032	4.7040	75.272	0.849	-1.574
2900	5.892	51.236	4.7259	74.956	-1.529	-1.554
3000	6.010	51.438	4.7474	74.635	-3.860	-1.544
3100	6.131	51.637	4.7688	74.309	-6.174	-1.544
3200	6.253	51.834	4.7898	73.978	-8.471	-1.554
3300	6.375	52.028	4.8103	73.643	-10.751	-1.564
3400	6.496	52.220	4.8303	73.303	-13.015	-1.574
3500	6.616	52.410	4.8500	72.958	-15.263	-1.584
3600	6.732	52.598	4.8693	72.608	-17.495	-1.594
3700	6.846	52.784	4.8882	72.253	-19.711	-1.604
3800	6.954	52.968	4.9067	71.893	-21.911	-1.614
3900	7.059	53.150	4.9248	71.530	-24.095	-1.624
4000	7.158	53.330	4.9424	71.163	-26.263	-1.634
4100	7.251	53.508	4.9595	70.791	-28.415	-1.644
4200	7.339	53.684	4.9761	70.414	-30.551	-1.654
4300	7.421	53.858	4.9922	70.032	-32.671	-1.664
4400	7.498	54.029	5.0078	69.645	-34.775	-1.674
4500	7.568	54.198	5.0229	69.253	-36.863	-1.684
4600	7.633	54.365	5.0375	68.856	-38.935	-1.694
4700	7.693	54.529	5.0516	68.454	-40.991	-1.704
4800	7.747	54.693	5.0652	68.047	-43.031	-1.714
4900	7.797	54.853	5.0784	67.635	-45.055	-1.724
5000	7.842	55.011	5.0911	67.218	-47.063	-1.734
5100	7.884	55.167	5.1033	66.796	-49.055	-1.744
5200	7.921	55.320	5.1150	66.369	-51.031	-1.754
5300	7.955	55.471	5.1262	65.937	-52.991	-1.764
5400	7.987	55.620	5.1369	65.500	-54.935	-1.774
5500	8.016	55.767	5.1471	65.058	-56.863	-1.784
5600	8.043	55.912	5.1568	64.611	-58.775	-1.794
5700	8.069	56.054	5.1660	64.160	-60.671	-1.804
5800	8.094	56.195	5.1747	63.704	-62.551	-1.814
5900	8.118	56.334	5.1830	63.243	-64.415	-1.824
6000	8.142	56.470	5.1908	62.777	-66.263	-1.834

Copper Unifpositive Ion (Cu⁺)
(Ideal Gas) At. Wt. = 63.53945

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.968	38.367	38.367	•000	260.668	250.101	- 183.320
100	4.968	38.397	38.367	•009	260.675	250.035	- 182.142
200	4.968	38.462	38.462	•506	261.072	246.428	- 134.636
300	4.968	40.935	38.493	1.003	261.450	242.724	- 106.089
400	4.968	41.841	39.362	1.500	261.811	238.944	- 87.031
500	4.968	42.607	39.755	1.996	262.158	235.105	- 73.400
600	4.968	43.270	40.154	2.493	262.495	231.217	- 63.162
700	4.968	43.855	40.533	2.990	262.822	227.288	- 55.190
800	4.968	44.379	40.892	3.487	263.138	223.322	- 48.805
900	4.968	44.852	41.231	3.984	263.446	219.327	- 43.574
1000	4.968	45.285	41.551	4.481	263.744	215.302	- 39.210
1100	4.968	45.682	41.854	4.977	264.032	211.254	- 35.513
1200	4.968	46.050	42.140	5.474	264.312	207.266	- 32.357
1300	4.968	46.393	42.413	5.971	264.584	203.330	- 29.636
1400	4.968	46.714	42.672	6.468	264.850	199.558	- 27.257
1500	4.968	47.013	42.916	6.965	265.112	195.974	- 25.154
1600	4.968	47.294	43.154	7.461	265.370	192.573	- 23.283
1700	4.968	47.558	43.379	7.958	265.624	189.346	- 21.608
1800	4.969	47.803	43.595	8.455	265.874	186.282	- 20.098
1900	4.970	48.029	43.802	8.952	266.120	183.372	- 18.731
2000	4.971	48.236	44.001	9.449	266.362	180.593	- 17.488
2100	4.973	48.417	44.193	9.946	266.599	177.934	- 16.351
2200	4.976	48.573	44.377	10.444	266.832	175.386	- 15.308
2300	4.978	48.709	44.556	10.942	267.061	172.948	- 14.347
2400	4.981	48.828	44.728	11.440	267.286	170.619	- 13.460
2500	4.984	48.934	44.894	11.939	267.507	168.396	- 12.638
2600	4.986	49.028	45.055	12.439	267.724	166.276	- 11.873
2700	4.988	49.112	45.212	12.941	267.937	164.258	- 11.261
2800	4.990	49.187	45.363	13.444	268.146	162.339	- 10.717
2900	4.992	49.254	45.510	13.950	268.350	160.516	- 10.235
3000	4.994	49.312	45.654	14.458	268.550	158.789	- 9.809
3100	4.996	49.361	45.793	14.970	268.746	157.160	- 9.449
3200	4.998	49.401	45.928	15.486	268.937	155.634	- 9.151
3300	4.999	49.434	46.058	16.006	269.124	154.209	- 8.912
3400	5.000	49.461	46.189	16.532	269.307	152.886	- 8.734
3500	5.001	49.483	46.316	17.065	269.486	151.666	- 8.617
3600	5.002	49.500	46.439	17.604	269.661	150.546	- 8.547
3700	5.003	49.514	46.560	18.152	269.832	149.524	- 8.527
3800	5.004	49.524	46.678	18.709	269.999	148.600	- 8.547
3900	5.005	49.531	46.794	19.276	270.162	147.772	- 8.604
4000	5.006	49.536	46.907	19.853	270.321	147.044	- 8.697
4100	5.007	49.539	47.019	20.443	270.476	146.416	- 8.827
4200	5.008	49.541	47.129	21.045	270.627	145.886	- 8.991
4300	5.009	49.542	47.236	21.661	270.774	145.459	- 9.231
4400	5.010	49.543	47.343	22.292	270.917	145.132	- 9.547
4500	5.011	49.544	47.447	22.938	271.056	144.804	- 9.941
4600	5.012	49.545	47.550	23.600	271.191	144.476	- 10.417
4700	5.013	49.546	47.652	24.278	271.321	144.146	- 10.974
4800	5.014	49.547	47.753	24.974	271.446	143.814	- 11.614
4900	5.015	49.548	47.852	25.688	271.566	143.481	- 12.331
5000	5.016	49.549	47.950	26.420	271.681	143.146	- 13.137
5100	5.017	49.550	48.047	27.171	271.791	142.811	- 14.037
5200	5.018	49.551	48.144	27.941	271.896	142.476	- 15.037
5300	5.019	49.552	48.239	28.731	272.000	142.141	- 16.141
5400	5.020	49.553	48.336	29.539	272.100	141.806	- 17.351
5500	5.021	49.554	48.432	30.367	272.200	141.471	- 18.671
5600	5.022	49.555	48.528	31.214	272.300	141.136	- 20.111
5700	5.023	49.556	48.624	32.080	272.400	140.801	- 21.671
5800	5.024	49.557	48.719	32.965	272.500	140.466	- 23.351
5900	5.025	49.558	48.815	33.869	272.600	140.131	- 25.151
6000	5.026	49.559	48.911	34.794	272.700	139.796	- 27.071

Dec. 31, 1965

Dec. 31, 1965

AT. WT. = 63.53945

(IDEAL GAS)

COPPER UNIPosITIVE ION (Cu⁺)

Ground State Configuration ¹S₀
ΔH_f⁰ = 28.367 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ 298.15 = 260.668 ± 0.5 kcal. mole⁻¹

Electronic Levels and Quantum Weight

E _i , cm. ⁻¹	g _i	E _i , cm. ⁻¹	g _i
0.0	1	66694.7	39
21928.6	7	72085.4	42
22847.0	5	85389.8	5
23998.3	3	88505.7	9
26264.5	5	95565.7	9

Heat of Formation.

The heat of formation was obtained from the dissociation limit of Cu(g) which was given as 6237.2 cm.⁻¹ (or 178.187 kcal. mole⁻¹) by C. E. Moore "Atomic Energy Levels", Nat. Bur. Stds. Circ. 467, Washington 1952. This value applies to 0°K. the enthalpy of Cu, Cu⁺ and e⁻ between 298°K. and zero are all 1.481 kcal. mole⁻¹, thus at 298°K. the dissociation energy is 179.668 kcal. mole⁻¹. The heat of formation was then obtained from the reaction Cu(g) → Cu⁺ + e⁻ as ΔH_f⁰ 298.15 = 260.668 ± 0.5 kcal. mole⁻¹, the uncertainty is that due to Cu(g).

Heat Capacity and Entropy.

The ground state configuration and higher electronic levels were taken from C. E. Moore, loc. cit. Levels above 100,000 cm.⁻¹ were not included since they do not affect the thermodynamic function, levels above 30,000 cm.⁻¹ were averaged.

Cu⁺

Copper Monofluoride (CuF)

CuF

(Crystal) GFW = 82.5384

T, °K	Cp ^o	gibbs/mol S ^o - (G ^o - H ^o ₂₉₈)/T	cal/mol H ^o - H ^o ₂₉₈	cal/mol ΔH ^o	ΔG ^o	Log Kp
100						
200						
298	10.720	15.500	15.500	46.000	41.040	30.083
300	10.790	15.567	15.500	45.998	41.010	29.875
400	12.920	16.577	15.953	45.782	39.374	21.513
500	13.820	17.387	16.769	45.461	37.608	16.526
600	14.350	17.841	17.217	45.100	36.311	13.226
700	14.700	18.107	17.485	44.716	34.875	10.889
800	14.920	18.274	17.650	44.325	33.497	9.151
900	15.050	18.360	17.736	43.930	32.167	7.811
1000	15.150	18.413	17.790	43.540	30.881	6.740
1100	15.190	18.443	17.820	43.155	29.634	5.888
1200	15.220	18.461	17.837	42.770	28.422	5.176
1300	15.240	18.470	17.843	42.411	27.240	4.579
1400	15.250	18.475	17.846	42.066	26.095	4.056
1500	15.250	18.475	17.846	41.734	24.981	3.587

COPPER MONOFLUORIDE (CuF)

(CRYSTAL)

GFW = 82.5384

ΔH_{f,0}^o = UnknownS_{298,15}^o = [15.5 ± 0.5] gibbs/molT_m = UnknownΔH_{f,0}^o = UnknownΔH_{f,298,15}^o = [-46 ± 10] kcal/molΔH_{f,298,15}^o = [58] kcal/mol

Heat of Formation.

The heat of formation (ΔH_{f,298,15}^o) for CuF(c) is not available from literature at the present time. The lattice energy (U_o) for CuF(c) has been calculated to be 209, 213 and 232 kcal/mol, based on the assumption of ionic bonding in CuF(c), by Pauling, Zachariasen and Ebert and Kottinek, respectively (see T. C. Haddington, Trans. Faraday Soc. 55, 1531 (1959) for details). The corresponding enthalpy change for the reaction CuF(c) = Cu⁺(g) + F⁻(g) was evaluated as 210.18, 214.18 and 235.18 kcal/mol. Using ΔH_{f,298,15}^o = 280.67 kcal/mol for Cu⁺(g) and -62.2 kcal/mol for F⁻(g), the values of ΔH_{f,298,15}^o (CuF, c) were calculated to be -11.7, -15.7 and -34.7 kcal/mol. However, based on ΔH_{f,298,15}^o(CuF, g) = 12 ± 9 kcal/mol which was measured, the values of ΔH_{f,298,15}^o would be 23.7, 27.7 and 46.7 kcal/mol which seem to be too small. By comparison with those for KF(c) and HgF(c), the value of ΔH_{f,298,15}^o was estimated as 58 kcal/mol. From this ΔH_{f,298,15}^o value and ΔH_{f,298,15}^o (CuF, g), the heat of formation for CuF(c) was derived.

Heat Capacity and Entropy.

The heat capacities, 298.15-1000°K, and S_{298,15}^o were estimated by comparison with those for CuCl(c), NaCl(c) and NaF(c). The Cp values above 1000°K were obtained by graphical extrapolation.

Heat of Sublimation.

The value of ΔH_{f,298,15}^o was estimated by comparison with those for KF(c) and HgF(c).

COPPER MONOFLUORIDE (CuF)

(IDEAL GAS)

OFW = 82.5384

Ground State Configuration $1\Sigma^+$

$\Delta H_f^\circ = 12 \pm 9 \text{ kcal/mol}$

$S_{298.15}^\circ = 54.11 \text{ gibbs/mol}$

$\Delta H_f^\circ_{298.15} = 12 \pm 9 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$$\frac{\epsilon_f, \text{cm}^{-1}}{0} = \frac{g_f}{1}$$

$$\omega_e x_e = 3.941 \text{ cm}^{-1}$$

$$\alpha_e = 0.004596 \text{ cm}^{-1}$$

$$B_e = 0.3794 \text{ cm}^{-1}$$

$$r_e = 1.743 \text{ \AA}$$

Heat of Formation

Based on spectroscopic data, the dissociation energy (D_0°) of CuF (g) was selected as $3.0 \pm 1.0 \text{ eV}$ by A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953. Using $\Delta H_f^\circ_{298.15} = 18.36$ and 80.71 kcal/mol for F(g) and Cu(g), respectively, the value of $\Delta H_f^\circ_{298.15}$ for CuF (g) was calculated to be $30 \pm 23 \text{ kcal/mol}$.

Values of the dissociation energy for CuF(g) have been derived by R. A. Kent, J. D. McDonald, and J. L. Margrave, J. Phys. Chem. **70**, 874 (1966), as 3.63 ± 0.2 to $4.1 \pm 0.5 \text{ eV}$, based on mass spectrometric studies of CuF₂ sublimation from a Knudsen cell, the appearance potential of CuF⁺ ion from CuF₂ in both reducing and nonreducing systems, and a theoretical calculation assuming an ionic model like that used by E. S. Rittner, J. Chem. Phys. **19**, 1030 (1951). Until further data are available, a value $D(\text{CuF}) = 3.8 \pm 0.5 \text{ eV}$ was recommended. Using this dissociation energy for CuF (g), the heat of formation (298.15°K) for CuF(g) was evaluated to be $12 \pm 9 \text{ kcal/mol}$ which is adopted here.

Heat Capacity and Entropy

The values of ground state configuration, ω_e , $\omega_e x_e$, B_e , α_e and r_e were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950, and corrected to the average isotopic species.

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	6.000	INFINITE	INFINITE	-	12.079	12.079	INFINITE
100	6.980	6.070	6.070	2.171	12.079	12.079	21.710
200	7.446	6.1030	6.1030	7.859	12.079	12.079	6.343
298	7.983	6.1109	6.1109	8.000	12.000	5.449	3.694
300	7.992	6.1158	6.1158	8.015	11.997	5.408	3.940
400	8.342	6.1509	6.1509	8.853	11.853	5.237	1.768
500	8.553	6.1836	6.1836	9.508	11.658	5.107	-
600	8.693	6.2106	6.2106	9.968	11.473	-	0.985
700	8.786	6.2316	6.2316	10.277	11.277	-	3.046
800	8.855	6.2494	6.2494	10.458	11.069	-	1.951
900	8.907	6.2640	6.2640	10.598	10.852	-	1.388
1000	8.948	6.2761	6.2761	10.700	10.624	-	1.081
1100	8.983	6.2861	6.2861	10.777	10.489	-	0.891
1200	9.013	6.2941	6.2941	10.825	10.344	-	0.722
1300	9.039	6.3001	6.3001	10.855	10.189	-	0.572
1400	9.063	6.3041	6.3041	10.878	10.024	-	0.437
1500	9.084	6.3071	6.3071	10.894	9.849	-	0.312
1600	9.105	6.3091	6.3091	10.904	9.664	-	0.197
1700	9.124	6.3101	6.3101	10.909	9.469	-	0.092
1800	9.143	6.3111	6.3111	10.910	9.264	-	0.000
1900	9.161	6.3121	6.3121	10.906	9.049	-	-0.092
2000	9.178	6.3131	6.3131	10.899	8.824	-	-0.187
2100	9.197	6.3141	6.3141	10.888	8.589	-	-0.282
2200	9.216	6.3151	6.3151	10.873	8.344	-	-0.377
2300	9.235	6.3161	6.3161	10.854	8.089	-	-0.472
2400	9.254	6.3171	6.3171	10.831	7.824	-	-0.567
2500	9.273	6.3181	6.3181	10.804	7.549	-	-0.662
2600	9.303	6.3187	6.3187	10.773	7.264	-	-0.757
2700	9.330	6.3193	6.3193	10.738	6.969	-	-0.852
2800	9.359	6.3199	6.3199	10.699	6.664	-	-0.947
2900	9.388	6.3205	6.3205	10.655	6.349	-	-1.042
3000	9.420	6.3211	6.3211	10.606	6.024	-	-1.137
3100	9.465	6.3217	6.3217	10.552	5.689	-	-1.232
3200	9.507	6.3223	6.3223	10.493	5.344	-	-1.327
3300	9.552	6.3230	6.3230	10.429	4.989	-	-1.422
3400	9.602	6.3236	6.3236	10.360	4.624	-	-1.517
3500	9.653	6.3243	6.3243	10.286	4.249	-	-1.612
3600	9.712	6.3250	6.3250	10.207	3.864	-	-1.707
3700	9.773	6.3257	6.3257	10.123	3.469	-	-1.802
3800	9.837	6.3264	6.3264	10.034	3.064	-	-1.897
3900	9.905	6.3271	6.3271	9.939	2.649	-	-1.992
4000	9.976	6.3278	6.3278	9.839	2.224	-	-2.087
4100	10.050	6.3285	6.3285	9.734	1.789	-	-2.182
4200	10.128	6.3292	6.3292	9.614	1.344	-	-2.277
4300	10.207	6.3300	6.3300	9.479	0.889	-	-2.372
4400	10.289	6.3307	6.3307	9.339	0.424	-	-2.467
4500	10.374	6.3315	6.3315	9.194	-0.049	-	-2.562
4600	10.460	6.3323	6.3323	9.044	-0.514	-	-2.657
4700	10.547	6.3331	6.3331	8.889	-0.979	-	-2.752
4800	10.636	6.3340	6.3340	8.729	-1.444	-	-2.847
4900	10.726	6.3349	6.3349	8.564	-1.909	-	-2.942
5000	10.816	6.3358	6.3358	8.394	-2.374	-	-3.037
5100	10.906	6.3367	6.3367	8.219	-2.839	-	-3.132
5200	10.997	6.3376	6.3376	8.039	-3.304	-	-3.227
5300	11.087	6.3385	6.3385	7.854	-3.769	-	-3.322
5400	11.177	6.3394	6.3394	7.664	-4.234	-	-3.417
5500	11.266	6.3403	6.3403	7.469	-4.699	-	-3.512
5600	11.354	6.3412	6.3412	7.269	-5.164	-	-3.607
5700	11.440	6.3421	6.3421	7.064	-5.629	-	-3.702
5800	11.525	6.3430	6.3430	6.854	-6.094	-	-3.797
5900	11.609	6.3439	6.3439	6.639	-6.559	-	-3.892
6000	11.690	6.3448	6.3448	6.419	-7.024	-	-3.987

June 30, 1966

Copper Difluoride (CuF₂)

(Crystal)

FW = 101.5368

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100	16.770	16.400	16.400	0.000	-131.200	-119.286	87.439
200	16.780	16.504	16.400	1.031	-131.194	-119.213	86.846
300	17.460	21.424	17.067	1.743	-130.849	-115.270	82.980
400	18.140	25.394	18.447	3.923	-130.492	-111.416	78.700
500	18.800	28.760	19.809	5.371	-130.109	-107.636	74.207
600	19.410	31.704	21.302	7.281	-129.695	-103.922	69.446
700	19.980	34.334	22.770	9.251	-129.248	-100.272	64.393
800	20.480	36.718	24.189	11.275	-128.767	-96.679	59.077
900	20.940	38.890	25.553	13.346	-128.257	-93.140	53.556
1000	21.300	40.914	26.859	15.460	-127.723	-89.655	47.813
1100	21.580	42.780	28.109	17.605	-127.171	-86.218	41.702
1200	21.750	44.514	29.305	19.772	-126.611	-82.827	35.394
1300	21.860	46.130	30.450	21.953	-126.035	-79.478	28.961
1400	21.918	47.651	31.546	24.142	-125.442	-76.166	22.509
1500	21.990	49.057	32.597	26.336	-124.830	-72.890	16.049
1600	21.987	50.369	33.604	28.534	-124.198	-69.648	9.582
1700	21.908	51.666	34.572	30.733	-123.542	-66.432	3.111
1800	22.000	52.855	35.502	32.933	-122.862	-63.242	-3.361
1900	22.000	53.904	36.397	35.133	-122.157	-60.077	-6.845
2000	22.000	54.904					

CuF₂COPPER DIFLUORIDE (CuF₂) (CRYSTAL)

OFW = 101.5368

$\Delta H_f^\circ = \text{Unknown}$
 $\Delta H_f^\circ_{298.15} = -131.2 \pm 0.8 \text{ kcal/mol}$
 $\Delta H_m^\circ = [9.4] \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = 82.5 \pm 0.6 \text{ kcal/mol}$
 $T_m = 1043^\circ\text{K}$

Heat of Formation.

The chemical equilibrium for the reaction (1) $\text{CuF}_2(\text{c}) + \text{H}_2(\text{g}) = \text{Cu}(\text{c}) + 2\text{HF}(\text{g})$ has been studied by K. Jellinek and A. Rudet, Z. anorg. allgem. Chem. 175, 281 (1928). The equilibrium gas phase composition was found to be HF 4.3% and H₂ 95.7%, at 423°K. From this data the enthalpy change ($\Delta H^\circ_{298.15}$) of the reaction was evaluated. The equilibrium for the reaction (2) $\text{CuF}_2(\text{c}) + \text{H}_2\text{O}(\text{g}) = \text{CuO}(\text{c}) + 2\text{HF}(\text{g})$ was investigated by L. Donange, Compt. rend. 200, 239 (1935). Based on the equilibrium data reported, the $\Delta H^\circ_{298.15}$ value for the reaction was derived. The results obtained are presented as follows.

Reaction	Temperature, °K	Second Law Value	Third Law Value	Drift	$\Delta H^\circ_{298.15}$ kcal/mol
(1)	423	22.38	22.15	-	-132.0
(2)	473.15-723.15	23.06 ± 1.33	22.15	-1.67 ± 1.96	-131.2

Using the third law values for $\Delta H^\circ_{298.15}$, the corresponding $\Delta H^\circ_{298.15}$ (CuF₂, c) values were calculated. The adopted heat of formation for CuF₂(c) is $-131.2 \pm 0.8 \text{ kcal/mol}$.

Heat Capacity and Entropy.

The heat capacities, 298.15-1000°K, and $S^\circ_{298.15}$ were estimated by comparison with those for CuCl₂(c), CuF₂(c) and CaCl₂(c), respectively. The Cp values above 1000°K were obtained by graphical extrapolation.

Melting Data.

T_m was reported by H. M. Haendler, L. H. Towle, E. P. Bennett and W. L. Patterson, Jr., J. Am. Chem. Soc. 76, 2178 (1954). T_m for CuF₂(c) in HF(g) or H₂(g) was found to be $950 \pm 5^\circ\text{C}$ or $785 \pm 10^\circ\text{C}$, respectively, by H. von Wartenberg, Z. anorg. allgem. Chem. 241, 381 (1959). Heat of melting was estimated by comparison with those for other related compounds.

Heat of Sublimation.

See CuF₂(g) table for details.

T, °K	C _p ^o	gibbs/mol S ^o - (C ^o - H ^o)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	22.500	20.584	0.000	- 124.300	- 113.633	89.295
300	22.500	20.723	2.082	- 124.283	- 113.568	82.734
400	22.500	21.216	2.467	- 124.150	- 110.530	60.172
500	22.500	21.617	4.582	- 122.539	- 106.909	40.130
600	22.500	21.939	6.762	- 121.788	- 103.851	37.828
700	22.500	22.187	9.042	- 121.034	- 100.920	31.500
800	22.500	22.462	11.262	- 120.307	- 98.009	26.790
900	22.500	22.762	13.436	- 119.600	- 95.369	23.136
1000	22.500	23.087	15.562	- 118.900	- 92.900	20.000
1100	22.500	23.436	17.642	- 118.241	- 90.121	17.905
1200	22.500	23.807	19.676	- 117.584	- 87.594	15.953
1300	22.500	24.196	21.662	- 116.941	- 85.120	14.310
1400	22.500	24.603	23.600	- 116.300	- 82.699	12.853
1500	22.500	25.026	25.492	- 115.667	- 80.329	11.653
1600	22.500	25.464	27.338	- 115.037	- 78.009	10.573
1700	22.500	25.915	29.138	- 114.407	- 75.739	9.624
1800	22.500	26.379	30.892	- 113.779	- 73.519	8.786
1900	22.500	26.854	32.600	- 113.152	- 71.349	8.069
2000	22.500	27.339	34.262	- 112.526	- 69.229	7.469

OPW = 101.5368

(LIQUID)

COPPER DIFLUORIDE (CuF₂)

S_{298.15}^o = [20.584] gibbs/mol

ΔH_{298.15}^o = [-124.30] kcal/mol

ΔH_m^o = [9.4] kcal/mol

ΔH_v^o = [43.98] kcal/mol

T_m = 1043°K

T_b = [1722]°K

Heat of Formation.

The heat of formation (ΔH_{298.15}^o) was obtained from ΔH_{298.15}^o (CuF₂, c) by adding ΔH_m^o and the difference between H₁₀₄₃^o-H_{298.15}^o for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated based on an assumption that the average heat capacity for CuF₂(l) is 7.5 gibbs/atom. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See CuF₂(c) table for details.

Vaporization Data.

T_b is the temperature at which the free energy change for the reaction CuF₂(l) = CuF₂(g) becomes zero. The difference between ΔH_f^o for liquid and gas at T_b is ΔH_v^o.

Copper Difluoride (CuF₂)CuF₂

GFW = 101.5368

(Ideal Gas)

T, °K	C _p gibbs/mol	S° -(C°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔH _f ⁰	ΔG ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.999	49.386	2.160	-68.315	-68.315	INFINITE
200	11.016	56.302	62.056	-68.400	-68.400	150.884
298	12.340	60.966	∞	-68.581	-69.600	76.055
300	12.360	61.062	∞	-68.700	-70.073	51.365
400	13.260	68.064	∞	-68.702	-70.082	51.055
500	13.709	71.723	62.424	-68.788	-70.522	38.955
600	14.029	73.524	4.040	-68.940	-71.365	25.995
700	14.250	74.437	5.456	-69.022	-71.753	22.405
800	14.386	75.066	6.113	-69.113	-72.523	19.410
900	14.488	75.489	6.794	-69.213	-73.141	16.810
1000	14.564	77.579	9.782	-69.323	-72.885	15.929
1100	14.624	78.970	68.751	-69.441	-73.235	14.550
1200	14.673	80.245	99.656	-69.569	-73.575	13.400
1300	14.714	81.412	127.716	-69.696	-73.906	12.440
1400	14.758	82.513	151.650	-69.820	-74.228	11.670
1500	14.801	83.553	171.428	-69.941	-74.541	11.069
1600	14.846	84.540	18.610	-70.058	-74.846	10.527
1700	14.892	85.481	20.087	-70.173	-75.143	10.051
1800	14.939	86.384	21.087	-70.285	-75.433	9.631
1900	15.008	87.034	74.903	-70.394	-75.716	9.263
2000	15.072	87.825	75.550	-70.501	-76.000	8.947
2100	15.131	88.562	76.133	-70.602	-76.284	8.671
2200	15.213	89.268	76.714	-70.698	-76.568	8.436
2300	15.297	90.000	77.281	-70.788	-76.852	8.241
2400	15.367	90.599	77.816	-70.872	-77.136	8.086
2500	15.447	91.227	78.340	-70.954	-77.420	7.969
2600	15.528	91.835	78.848	-71.032	-77.704	7.880
2700	15.610	92.422	79.340	-71.106	-77.988	7.813
2800	15.693	93.000	79.816	-71.176	-78.272	7.766
2900	15.772	93.564	80.281	-71.242	-78.556	7.736
3000	15.852	94.080	80.732	-71.304	-78.840	7.716
3100	15.929	94.601	81.177	-71.362	-79.124	7.703
3200	16.008	95.108	81.599	-71.416	-79.408	7.696
3300	16.088	95.600	82.000	-71.466	-79.692	7.696
3400	16.168	96.082	82.422	-71.512	-79.976	7.703
3500	16.215	96.551	82.819	-71.554	-80.260	7.716
3600	16.280	97.009	83.207	-71.592	-80.544	7.736
3700	16.356	97.456	83.586	-71.626	-80.828	7.766
3800	16.438	97.896	83.956	-71.656	-81.112	7.800
3900	16.503	98.319	84.320	-71.682	-81.396	7.840
4000	16.563	98.736	84.675	-71.704	-81.680	7.884
4100	16.621	99.145	85.023	-71.722	-81.964	7.932
4200	16.678	99.544	85.364	-71.736	-82.248	7.984
4300	16.733	99.936	85.696	-71.746	-82.532	8.040
4400	16.788	100.318	86.026	-71.752	-82.816	8.100
4500	16.843	100.693	86.354	-71.756	-83.100	8.164
4600	16.898	101.060	86.684	-71.756	-83.384	8.232
4700	16.953	101.424	86.996	-71.752	-83.668	8.304
4800	17.008	101.784	87.300	-71.746	-83.952	8.380
4900	17.063	102.140	87.596	-71.736	-84.236	8.460
5000	17.118	102.496	87.884	-71.722	-84.520	8.544
5100	17.173	102.848	88.162	-71.704	-84.804	8.632
5200	17.228	103.196	88.436	-71.682	-85.088	8.724
5300	17.283	103.544	88.706	-71.656	-85.372	8.820
5400	17.338	103.892	88.972	-71.626	-85.656	8.920
5500	17.393	104.240	89.236	-71.592	-85.940	9.024
5600	17.448	104.588	89.500	-71.556	-86.224	9.132
5700	17.503	104.936	89.760	-71.516	-86.508	9.244
5800	17.558	105.284	90.016	-71.472	-86.792	9.360
5900	17.613	105.632	90.268	-71.424	-87.076	9.480
6000	17.668	105.980	90.516	-71.372	-87.360	9.604

June 30, 1966

COPPER DIFLUORIDE (CuF₂)

(IDEAL GAS)

GFW = 101.5368

Point Group D_{∞h}ΔH_f⁰ = -68.3 ± 1.0 kcal/molΔH_f⁰298.15 = -68.7 ± 1.0 kcal/mol

S°298.15 = [60.97] gibbs/mol

Electronic Levels and Quantum Weights

ε _i , cm ⁻¹	g _i
0	2
[9000] [4]	
[18000] [4]	

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[608] (1)
[205] (2)
768 (1)

Bond Distance: Cu-F = [1.72] Å

Bond Angle: F-Cu-F = [180]°

Rotational Constant: B₀ = [0.14996] cm⁻¹

σ = 2

Heat of Formation.

The vapor pressures of CuF₂(c), at temperatures from 897 to 1026°K, have been determined by R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966). Based on these data, the heat of sublimation (ΔH_{sub}298.15) of CuF₂(c) was derived to be 62.45 ± 0.5 and 62.50 kcal/mol by the second and third law method, respectively. From the values of ΔH_{sub}298.15 and ΔH_f298.15 for CuF₂(c), the heat of formation (ΔH_f298.15) for CuF₂(g) was evaluated.

Heat Capacity and Entropy.

The molecular structure, bond distance and angle were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The ground state electronic configuration, Σ_g⁺, was obtained from A. Böhler, J. L. Stauffer and W. Klemperer, Intern. Tech. Rept. No. 6, Apr. 30, 1964, Arthur D. Little, Inc., Cambridge, Mass. The other electronic levels and quantum weights were assumed from those for CuCl₂(g) reported by J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. 33, 1670 (1961). The vibrational frequency, ν₂, was determined by P. H. Kasai, E. B. Whipple and W. Weltner, Jr., J. Chem. Phys. 44, 2581 (1966). The other two frequencies, ν₁ and ν₃, were calculated by Valence Force Treatment described by G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, 1945, using appropriate force constants. The principal moment of inertia is I = 1.66649 × 10⁻³⁸ g cm².

CuF₂

Copper Dihydroxide (Cu(OH)₂)

(Crystal) GFW = 97.55474

T, °K	Cp	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
0						
100						
200						
298	22.750	25.900	4.000	-107.640	-89.088	65.303
300	22.760	26.041	4.042	-107.635	-88.973	64.817
400	23.780	32.728	26.805	-107.310	-82.800	43.240
500	24.800	38.144	28.568	-106.927	-76.715	33.532
600	25.820	42.756	30.541	-106.484	-70.713	25.757
700	26.840	46.617	32.581	-105.976	-64.790	20.728
800	27.860	50.478	34.596	-105.414	-58.945	16.686
900	28.880	53.735	36.538	-104.815	-53.172	12.592
1000	28.600	56.729	38.610	-104.197	-47.468	10.374
1100	28.860	59.467	40.202	-103.574	-41.824	8.310
1200	29.130	61.917	41.916	-102.956	-36.239	6.600
1300	29.410	64.315	43.689	-102.343	-30.723	5.240
1400	29.170	66.475	45.912	-101.693	-25.111	3.920
1500	29.200	68.489	48.602	-101.022	-19.427	2.631

COPPER DIHYDROXIDE (Cu(OH)₂)

(CRYSTAL)

OPW = 97.55474

CuH₂O₂

ΔHf° = Unknown

ΔHf°_{298.15} = -107.64 ± 2.0 kcal/molS°_{298.15} = [25.9] gibbs/molT₀ = 433°K

Heat of Formation.

The enthalpy change (ΔH°₄₃₃) for the reaction Cu(OH)₂(c) = CuO(c) + H₂O(g) has been determined by L. V. My, Bull. soc. chim. France, No. 3, 545 (1964). Based on the reported value, ΔH°₄₃₃ = 12 kcal/mol, the heat of formation (ΔHf°_{298.15}) for Cu(OH)₂(c) was derived as -107.64 kcal/mol, using ΔHf°_{298.15} = -37.250 and -57.798 kcal/mol for CuO(c) and H₂O(g), respectively, which was adopted here.

The free energy change (ΔG°_{298.15}) of the reaction Cu(OH)₂(c) = Cu⁺⁺(aq) + 2 OH⁻(aq) was evaluated to be 26.36 and 26.26 kcal/mol, based on the solubility product for Cu(OH)₂(c) reported by (1) E. S. Daniel, Zh. prikl. Khim. 37, 1358 (1964) and (2) N. P. Zhuk, Zh. Fiz. Khim. 28, 1523 (1954), respectively. Using values of S°_{298.15} and ΔHf°_{298.15} for Cu⁺⁺(aq) and OH⁻(aq) from "Selective Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952, and NBS Technical Note 270-1, 1955, by D. D. Wagman and co-workers, the corresponding enthalpy change ΔH°_{298.15} and heat of formation (ΔHf°_{298.15}) for Cu(OH)₂(c) were derived. The results obtained are presented as follows.

Chemical Reaction	ΔHf° _{298.15} kcal/mol	ΔHf° _{298.15} kcal/mol	Reference
Cu(OH) ₂ (c) = Cu ⁺⁺ (aq) + 2 OH ⁻ (aq)	10.06	-104.61	(1)
Cu(OH) ₂ (c) = Cu ⁺⁺ (aq) + 2 OH ⁻ (aq)	9.97	-104.52	(2)
CuO(c) + H ₂ O(l) = Cu(OH) ₂ (c)	-1.9	-107.5	(3)
CuO(c) + H ₂ O(l) = Cu(OH) ₂ (c)	0.3	-105.3	(4)

The heats of solution of CuO(c) and Cu(OH)₂(c) in HNO₃(aq.) have been determined by (3) de Forcrand, Compt. rend. 157, 441 (1913) to be -16.38 and -14.46 kcal/mol, respectively. From these data the enthalpy change for the reaction CuO(c) + H₂O(l) = Cu(OH)₂(c) was derived as -1.9 kcal/mol. For the same reaction, the enthalpy change was reported to be 0.3 kcal/mol by (4) P. Sabatier, Compt. rend. 125, 301 (1897). Based on ΔHf°_{298.15} = -37.25 and -68.315 kcal/mol for CuO(c) and H₂O(l), respectively, the heat of formation for Cu(OH)₂(c) was evaluated. The results obtained are presented in the above table.

Heat Capacity and Entropy.

The heat capacities, 298.15-700°K, were estimated by comparison with those for CuO(c), CaO(c) and Ca(OH)₂(c). The Cp values above 700°K were obtained by graphical extrapolation. S°_{298.15} was estimated such that the derived ΔGf° (Cu(OH)₂, c) = ΔGf° (CuO, c) + ΔGf° (H₂O, g) at 433°K.

Decomposition Temperature.

Td is the temperature at which the Gibbs energy change for the reaction Cu(OH)₂(c) = CuO(c) + H₂O(g) equals zero.

June 30, 1965

CuH₂O₂

T, °K	Cp*	$\frac{g\text{ cal}}{\text{mol}} \cdot \frac{1}{^\circ\text{K}}$	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-1.495	-36.713	-36.713	INFINITE
100	3.945	2.335	17.732	-1.840	-37.043	-37.043	INFINITE
200	8.321	6.440	11.038	-2.920	-37.272	-37.272	INFINITE
298	10.066	10.183	10.183	0.000	-37.250	-30.622	22.446
300	10.094	10.245	10.183	0.019	-37.249	-30.581	22.278
400	11.460	10.505	10.505	1.091	-37.129	-28.374	15.503
500	11.960	10.614	11.406	2.254	-36.948	-26.704	11.434
600	12.500	10.648	12.348	3.478	-36.734	-24.076	8.770
700	12.980	10.690	13.319	4.752	-36.494	-21.084	6.864
800	13.430	10.730	14.280	6.073	-36.229	-18.930	5.445
900	13.840	10.768	15.218	7.444	-35.948	-16.544	4.349
1000	14.310	10.802	16.115	8.847	-35.621	-13.923	3.400
1100	14.750	10.837	16.983	10.300	-35.273	-11.070	2.776
1200	15.190	10.872	17.818	11.797	-34.896	-8.050	2.195
1300	15.630	10.907	18.622	13.338	-34.488	-4.961	1.708
1400	16.070	10.942	19.397	14.923	-34.053	-1.806	1.281
1500	16.510	10.976	20.146	16.552	-33.589	1.417	0.896
1600	16.950	11.010	20.869	18.225	-33.105	4.121	0.563
1700	17.390	11.044	21.570	19.942	-32.599	6.779	0.273
1800	17.830	11.078	22.250	21.703	-32.072	9.380	0.019
1900	18.270	11.112	22.913	23.506	-31.525	11.924	-0.204
2000	18.710	11.146	23.553	25.357	-30.958	14.406	-0.401

June 30, 1956

COPPER MONOXIDE (CuO)

(CRYSTAL)

OPW = 79.5394

CuO

$$\Delta H_f^\circ = -36.71 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -37.25 \pm 0.5 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 10.18 \pm 0.1 \text{ e.u.}$$

$$T_d = 1395^\circ\text{K}$$

Heat of Formation.

The more consistent data relative to the heat of formation are reviewed below. The selected value of -37.25 kcal/mol was derived from $\Delta H_{298}^\circ = -40.7$ kcal/mol for $\text{Cu}_2\text{O}(c)$ and $\Delta H_{298}^\circ = 33.80$ kcal/mol for $2\text{CuO}(c) = \text{Cu}_2\text{O}(c) + \text{O}_2(g)$. Four different sets of oxygen dissociation pressure measurements yield heats of reaction in close agreement with each other and with the aqueous calorimetry of Thomsen. Thomsen's data may be reduced to the heat of reduction of $\text{CuO}(c)$ with H_2 by combining heats of reaction for $\text{CuO} + \text{H}_2\text{SO}_4$, $\text{Fe} + \text{H}_2\text{SO}_4$, and $\text{Fe} + \text{CuSO}_4(aq)$. Direct calorimetric measurement of the heat of reduction by von Wartenberg and Werth yields $\Delta H_{298}^\circ = -36.04 \pm 0.2$ when corrected for incomplete condensation of water. Direct measurement is difficult and this value may correspond to incomplete reduction. The value of -35.02 reported by Wöhler and Jochum, *Z. physik. Chem.* **167A**, 169 (1933), is unreasonable. Equilibrium constants derived from Balesdent and Chiche yield -37.6 kcal/mol by third law analysis, but a serious entropy error is present. This is no doubt due to uncertainties in the activity of Cu in Cu-Au alloys. Other data have been reviewed by Randall, Nielsen and West, *Ind. Eng. Chem.* **23**, 388 (1931).

Author	Method	Reaction**	Temp.	No. of Points	ΔH_{298}° (kcal/mol)	Drift (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-31.15	-37.16
2. Wartenberg et al. (1932)	Calorimetry	A	295	—	-30.27 \pm 0.2	-36.04
3. Balesdent (1955)	Equilibrium Data	B	1011-1156	32	60.2 \pm 0.7	75.18
4. Assayag (1955)	Kp	C	1047-1342	11	33.28 \pm 0.15	33.81
5. Becker (1927)	Kp	C	1195-1293	6	33.84 \pm 0.27	33.80
6. Roberts et al. (1921)	Kp	C	1189-1358	20	33.95 \pm 0.07	33.76
7. Foote et al. (1908)	Kp	C	1223-1323	7	33.19 \pm 0.17	33.74
8. Combined 4, 5, 6, 7	Kp	C	1047-1358	45	33.70 \pm 0.10	33.77

*Based on third law where possible.

**Reaction A: $\text{CuO}(c) + \text{H}_2 = \text{Cu}(c) + \text{H}_2\text{O}(l)$ B: $2\text{CuO}(c) = 2\text{Cu}(c) + \text{O}_2$ C: $2\text{CuO}(c) = \text{Cu}_2\text{O}(c) + 0.5 \text{O}_2$

1. J. Thomsen, "Thermochemische Untersuchungen," vol. I, III, Barth, Leipzig, 1883.
2. H. von Wartenberg and H. Werth, *Z. elektrochem.* **38**, 51 (1932).
3. D. Balesdent, *Compt. rend.* **240**, 760 (1955); **168A** (1955); *P. Chiche, Ann. chim.* **7**, 361 (1952).
4. P. Assayag, *Ann. chim. (Paris)* **12**, 837 (1955).
5. P. Becker, Dissertation, Darmstadt, 1927; cf. Wöhler and Jochum, *Z. physik. Chem.* **167A**, 169 (1933).
6. H. S. Roberts and P. H. Smyth, *J. Am. Chem. Soc.* **43**, 1061 (1921); **42**, 2582 (1920).
7. H. W. Foote and E. K. Smith, *J. Am. Chem. Soc.* **30**, 1344 (1908).

Heat Capacity and Entropy.

Low temperature values are based on data (15-297°K) from J. Fu and H. I. Johnston, *J. Am. Chem. Soc.* **75**, 2471 (1953). Earlier data from R. W. Miller (71-302°K), *J. Am. Chem. Soc.* **51**, 215 (1929), are in satisfactory agreement, while those of K. Clusius and P. Harteck (30-200°K), *Z. physik. Chem.* **134**, 243 (1929), are higher by several percent. A small anomaly in the heat capacity is observed in the region 210-230°K. Magnetic measurements of M. O'Keefe and F. S. Stone, *Phys. Chem. Solids* **23**, 261 (1952), and neutron diffraction studies of B. N. Brockhouse, *Phys. Rev.* **95**, 781 (1954), suggest that this is a Néel point associated with antiferromagnetism. The entropy was obtained from the heat capacities based on $S_{15}^\circ = 0.016$ e.u.

High temperature values are based on specific heats (373-1273°K) obtained from a dynamic method by D. M. Chishikov and A. S. Khirik, *Tr. Inst. Met. im. A. A. Baikova, Akad. Nauk SSSR*, No. 12, 79 (1963); cf. *Chem. Abn.* **59**, 5800 b (1963). Enthalpy data (523-1263°K) of Wöhler and Jochum, *loc. cit.*, lead to a value for S_{1200} lower by about 0.25 e.u., but this is inconsistent with the equilibrium data for $2\text{CuO} = \text{Cu}_2\text{O} + 0.5 \text{O}_2$.

Temperature of Decomposition.

T_d is calculated as the temperature at which ΔF equals zero for $2\text{CuO}(c) = \text{Cu}_2\text{O}(c) + 0.5 \text{O}_2(g)$.

CuO

Copper Monoxide (CuO)

GFW = 79.5394

(Ideal Gas)

Symmetry Number = 1

 $S_{298.15}^{\circ} = 56.07 \pm 0.1$ gibbs/mol $\Delta H_f^{\circ} = 58.8 \pm 8$ kcal/mol $\Delta H_f^{\circ}{}_{298.15} = 58.9 \pm 8$ kcal/mol

T, °K	Cp*	S° gibbs/mol	$-(G^{\circ}-H^{\circ})/T$ cal/mol	$H^{\circ}-H_{298}^{\circ}$ kcal/mol	ΔH_f° kcal/mol	ΔG_f°	Log Kp
0	7.090	47.000	INFINITE	-2.333	58.800	INFINITE	INFINITE
100	7.222	47.320	1.622	-1.622	58.005	58.592	191.681
200	7.345	47.643	3.245	-3.245	57.208	57.792	11.004
298	7.468	47.966	4.868	-4.868	56.413	56.987	3.005
300	7.478	48.000	5.000	-5.000	56.400	56.900	3.734
400	7.591	48.323	6.623	-6.623	55.605	56.195	27.396
500	7.704	48.646	8.246	-8.246	54.810	55.400	16.376
600	7.817	48.969	9.869	-9.869	54.015	54.605	11.004
700	7.930	49.292	11.492	-11.492	53.220	53.810	7.330
800	8.043	49.615	13.115	-13.115	52.425	53.015	5.005
900	8.156	49.938	14.738	-14.738	51.630	52.220	3.676
1000	8.269	50.261	16.361	-16.361	50.835	51.425	2.734
1100	8.382	50.584	17.984	-17.984	50.040	50.630	2.110
1200	8.495	50.907	19.607	-19.607	49.245	49.835	1.681
1300	8.608	51.230	21.230	-21.230	48.450	49.040	1.352
1400	8.721	51.553	22.853	-22.853	47.655	48.245	1.096
1500	8.834	51.876	24.476	-24.476	46.860	47.450	0.896
1600	8.947	52.199	26.099	-26.099	46.065	46.655	0.734
1700	9.060	52.522	27.722	-27.722	45.270	45.860	0.600
1800	9.173	52.845	29.345	-29.345	44.475	45.065	0.496
1900	9.286	53.168	30.968	-30.968	43.680	44.270	0.416
2000	9.399	53.491	32.591	-32.591	42.885	43.475	0.352
2100	9.512	53.814	34.214	-34.214	42.090	42.680	0.300
2200	9.625	54.137	35.837	-35.837	41.295	41.885	0.258
2300	9.738	54.460	37.460	-37.460	40.500	41.090	0.224
2400	9.851	54.783	39.083	-39.083	39.705	40.295	0.196
2500	9.964	55.106	40.706	-40.706	38.910	39.500	0.172
2600	10.077	55.429	42.329	-42.329	38.115	38.705	0.150
2700	10.190	55.752	43.952	-43.952	37.320	37.910	0.128
2800	10.303	56.075	45.575	-45.575	36.525	37.115	0.106
2900	10.416	56.398	47.198	-47.198	35.730	36.320	0.084
3000	10.529	56.721	48.821	-48.821	34.935	35.525	0.062
3100	10.642	57.044	50.444	-50.444	34.140	34.730	0.040
3200	10.755	57.367	52.067	-52.067	33.345	33.935	0.018
3300	10.868	57.690	53.690	-53.690	32.550	33.140	0.006
3400	10.981	58.013	55.313	-55.313	31.755	32.345	0.004
3500	11.094	58.336	56.936	-56.936	30.960	31.550	0.002
3600	11.207	58.659	58.559	-58.559	30.165	30.755	0.001
3700	11.320	58.982	60.182	-60.182	29.370	29.960	0.000
3800	11.433	59.305	61.805	-61.805	28.575	29.165	0.000
3900	11.546	59.628	63.428	-63.428	27.780	28.370	0.000
4000	11.659	59.951	65.051	-65.051	26.985	27.575	0.000
4100	11.772	60.274	66.674	-66.674	26.190	26.780	0.000
4200	11.885	60.597	68.297	-68.297	25.395	25.985	0.000
4300	11.998	60.920	69.920	-69.920	24.600	25.190	0.000
4400	12.111	61.243	71.543	-71.543	23.805	24.395	0.000
4500	12.224	61.566	73.166	-73.166	23.010	23.600	0.000
4600	12.337	61.889	74.789	-74.789	22.215	22.805	0.000
4700	12.450	62.212	76.412	-76.412	21.420	22.010	0.000
4800	12.563	62.535	78.035	-78.035	20.625	21.215	0.000
4900	12.676	62.858	79.658	-79.658	19.830	20.420	0.000
5000	12.789	63.181	81.281	-81.281	19.035	19.625	0.000
5100	12.902	63.504	82.904	-82.904	18.240	18.830	0.000
5200	13.015	63.827	84.527	-84.527	17.445	18.035	0.000
5300	13.128	64.150	86.150	-86.150	16.650	17.240	0.000
5400	13.241	64.473	87.773	-87.773	15.855	16.445	0.000
5500	13.354	64.796	89.396	-89.396	15.060	15.650	0.000
5600	13.467	65.119	91.019	-91.019	14.265	14.855	0.000
5700	13.580	65.442	92.642	-92.642	13.470	14.060	0.000
5800	13.693	65.765	94.265	-94.265	12.675	13.265	0.000
5900	13.806	66.088	95.888	-95.888	11.880	12.470	0.000
6000	13.919	66.411	97.511	-97.511	11.085	11.675	0.000

Sept. 30, 1966; June 30, 1970

Electronic Levels and Molecular Constants

State	E_e , cm ⁻¹	F_2 , A	B_e , cm ⁻¹	ω_e , cm ⁻¹	$\omega_e x_e$, cm ⁻¹
X ² Π	0	2	1.726	0.4446	632
A ² Π	269	2	[0.4420]	[0.0040]	633
B ² Σ	4460	2	[0.4426]	[0.0052]	637
C ² Π	4735	2	[0.4213]	[0.0046]	[610]

Heat of Formation

The heat of formation is calculated from that of the crystal, $\Delta H_{298}^{\circ} = 36.1$ kcal/mol, which was obtained by 3rd law analysis of the sublimation pressure at 1273°K reported by Mack et al. (1). They employed a transpiration method and analysed for copper (in minute amounts) by its catalytic effect on the oxidation rate of sodium sulfite. The resulting pressure is only 100 times the predicted pressure of Cu(g) over CuO(c). Three pressures were reported but not used in the range 873-1173°K, since these yield a much smaller value for the heat of vaporization and imply a high dissociation energy.

Some estimates of D_0° CuO obtained by different methods are given below. These estimates along with a correlation of D_0° values for MnO, FeO, NiO and ZnO favor $D_0^{\circ} = 82 \pm 10$, close to the value adopted.

Method

Method	D_0°	ΔH_{298}°
Mack et al. (1) Transpiration	80.6	58.9
Arithmetic mean of D_0° for O ₂ and Cu ₂	82	57.7
Geometric mean of D_0° for O ₂ and Cu ₂	73	66.7
Linear Birge-Sponer extrapolation of A ² Π state	76.12	63.7212

Heat Capacity and Entropy

The visible spectrum of CuO has been extensively investigated, but only very recently has significant progress been made in its analysis. Antic-Jovanovic et al. (2) were able to obtain a vibrational analysis of the major band system by use of ⁶⁴Ni isotope studies. Shirk and Bass (3) recently reported absorption and fluorescence spectra in inert-gas matrices which allows assignment of the ground state and the first two excited states. They have strong evidence for the lower state of the blue system being the ground state and also for the second system, which corresponds to the red-orange system, originating in the upper state of the blue system. Thus, it is probable that the B state is ² Σ and the X and A states are both ² Π with very similar molecular constants, which serves to confuse the analysis of the spectra. It also appears likely that the 4187Å band analysed by Lagerqvist and Uhler (4) is a ² Π -² Π transition terminating in the ground state; thus we adopt their rotational constants for the X and C states. The vibrational frequencies and anharmonicities for the A and B states were from Antic-Jovanovic (2), as well as the vibrational interval for the ground state. The anharmonicity for the ground state was chosen so as to provide a reasonable Birge-Sponer extrapolation of the dissociation energy. The values of the ω_e were estimated from the Morse potential function relations. The rotational constants were assumed to be nearly constant. The values of the splitting in the electronic levels in the X and A states are from Antic-Jovanovic (2), and are roughly confirmed by Shirk and Bass (3).

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states.

References

1. E. Mack, G. O. Osterhof and H. M. Kramer, J. Amer. Chem. Soc. **45**, 617 (1923).

2. A. Antic-Jovanovic, D. S. Peacic and A. G. Gaydon, Proc. Roy. Soc. (London) **307A**, 399 (1968).

3. J. S. Shirk and A. M. Bass, J. Chem. Phys. **52**, 1894 (1970).

4. A. Lagerqvist and U. Uhler, Z. Naturforsch. **22B**, 551 (1967).

Copper Sulfate (CuSO₄)

(Crystal) GFW = 159.6016

CuO₄S

T, °K	Cp	S	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-4.030	-181.662	-181.662	INFINITE
100	10.449	7.808	43.361	-3.555	-182.698	-174.864	382.166
200	18.405	17.726	28.119	-2.078	-183.687	-166.489	181.931
298	23.630	26.112	26.112	0.000	-184.030	-157.960	115.788
300	23.730	26.259	26.113	-0.044	-184.033	-157.708	114.954
400	27.470	33.617	27.691	2.611	-184.584	-149.023	81.422
500	30.400	40.076	29.055	5.510	-184.701	-140.113	61.243
600	32.580	45.820	31.479	8.664	-184.547	-131.205	47.792
700	34.400	50.806	33.616	12.005	-184.207	-122.315	36.188
800	35.900	55.050	35.443	15.548	-183.687	-113.445	24.393
900	36.100	58.811	36.843	19.052	-182.971	-104.569	12.597
1000	36.750	63.649	40.954	22.695	-181.101	-94.458	20.644
1100	37.300	67.178	43.180	26.398	-179.205	-84.439	16.776
1200	37.750	70.485	45.316	30.152	-177.286	-74.500	13.508
1300	38.100	73.485	47.347	33.957	-175.347	-64.640	10.567
1400	38.330	76.336	49.337	37.798	-173.377	-54.749	8.567
1500	39.010	79.014	51.227	41.680	-171.355	-44.796	6.527
1600	39.370	81.543	53.044	45.599	-169.268	-34.903	4.768
1700	39.600	83.920	54.791	49.553	-167.117	-25.072	3.223
1800	40.050	86.122	56.487	53.542	-164.906	-15.286	1.943
1900	40.370	88.394	58.098	57.542	-162.636	-5.586	1.043
2000	40.690	90.472	59.665	61.615	-160.304	4.072	0.445

COPPER SULFATE (CuSO₄)

(CRYSTAL)

QFW = 159.6016

$$\Delta H_f^\circ = -181.66 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_f^{298.15} = -184.03 \pm 0.2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 26.11 \pm 0.1 \text{ gibbs/mol}$$

$$T_d = 1078^\circ\text{K}$$

Heat of Formation.

The heat of solution ($\Delta H_{298.15}^\circ$) of CuO(c) in sulfuric acid to form CuSO₄(c) has been measured by L. H. Adams and E. O. King, U. S. Bur. Mines RI 6617, 1965. From the reported value, $\Delta H_f^\circ = -5.61 \pm 0.09 \text{ kcal/mol}$ for the reaction CuO(c) + H₂SO₄(7.068 H₂O) = CuSO₄(c) + H₂O(l), the heat of formation ($\Delta H_f^{298.15}$) for CuSO₄(c) was evaluated as -184.03 kcal/mol, using $\Delta H_f^{298.15} = -37.25$, -209.49 and -68.315 kcal/mol for CuO(c), H₂SO₄(7.068 H₂O) and H₂O(l), respectively. See Fe₂(SO₄)₃(c) table for the sources of the last two $\Delta H_f^{298.15}$ values.

The equilibrium pressures for the following chemical reactions: (A) 2CuSO₄(c) = CuO·CuSO₄(c) + SO₃(g), (B) 3Cu(c) + CuSO₄(c) = 2Cu₂O(c) + SO₂(g), and (C) 4CuSO₄(c) + Cu₂O(c) = 3Cu₂O·CuSO₄(c) + SO₂(g), were determined by several investigators. For reaction (A), the partial pressures of SO₃(g) at different temperatures were calculated from the measured total pressures exerted by SO₃(g), SO₂(g) and O₂(g) produced by the reaction SO₃(g) = SO₂(g) + 1/2 O₂(g). From these vapor pressure data, the corresponding enthalpy changes ($\Delta H_{298.15}^\circ$) for the three reactions were evaluated by the second and third law methods. The results obtained are presented in the following table. The value of $\Delta H_f^{298.15}$ (CuSO₄, c) adopted was -184.03 ± 0.2 kcal/mol.

Investigator	Reaction	Temperature, °K	Second Law Value	Third Law Value	Drift	$\Delta H_f^{298.15}$ kcal/mol
Wöhler, et al. (1)	(A)	819.15-1004.15	25.90±3.60	47.45	22±4	-181.87
Reinders and Goudrian (2)	(A)	953.15-1053.15	56.54±0.77	51.96	-4.55±0.79	-184.13
	(C)	825.15- 921.15	42.84±1.38	42.34	-0.55±1.57	-184.42
Ingraham (3)	(A)	880.15-1071.75	51.59±0.41	51.75	0.07±0.43	-184.02
Randall et al. (4)	(B)	525.1 - 608.1	31.71±0.76	32.27	0.84±1.30	-184.62

(1) L. Wöhler, W. Plüddemann and P. Wöhler, Ber. Deut. Chem. Gesell. 41, 703 (1908).

(2) W. Reinders and F. Goudrian, Z. anorg. allgem. Chem. 126, 85 (1923).

(3) T. R. Ingraham, Trans. Met. Soc. AIME, 233, 259 (1965).

(4) M. Randall, R. F. Nielsen and G. H. West, Ind. Eng. Chem. 23, 388 (1931). In this report, the high temperature equilibrium reactions of copper were critically reviewed.

Heat Capacity and Entropy.

The low temperature heat capacities, 52.67-296.29°K, were obtained from W. W. Weller, U. S. Bur. Mines RI 6659, 1965. The high temperature heat capacities were measured by H. Schottky, Z. phys. Chem. 54, 415 (1908), 282°K; R. Ewald, Ann. Physik., 44, 1213 (1914), 275-373°K; A. N. Krestovnikov and E. J. Peigins, J. Gen. Chem. USSR, 6, 1481 (1935), 288-873°K; and D. M. Chizhikov and A. S. Khirlik, Tr. Inst. Met. Im. A. A. Baikova, Akad. Nauk SSSR, No. 12 79-84 (1963), 373-1273°K. The heat capacities below 51°K were obtained from J. W. Stout, J. Chem. Phys. 9, 285 (1941). In that paper, the Cp values, 15-58°K, were plotted as function of temperature and the Cp curve shows a maximum at 34.8°K. In an attempt to evaluate the entropy due to the anomalous portion of the curve, a "normal" heat capacity curve was drawn. The entropy above the normal Cp curve is reported to be 0.48 eu, rather than a magnetic entropy of Rln2 = 1.377 eu. Apparently the magnetic entropy increases gradually above 40°K so that it is not feasible to separate the heat capacity due to magnetic effects from that of the crystal lattice.

The Cp values above 298.15°K were extrapolated smoothly by comparison with those for MnSO₄(c) (see FeSO₄(c) table for details). The adopted Cp values are close to the average of the reported Cp values.

The value of $S_{298.15}^\circ$ was derived using the low temperature Cp data reported by W. W. Weller, loc. cit., based on $S_{51}^\circ = 2.851 \text{ eu}$ evaluated from Cp data determined by J. W. Stout, loc. cit.

Decomposition Temperature.

T_d is the temperature at which the total pressure of the gaseous decomposition products equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for CuSO₄(c), determined by T. R. Ingraham, loc. cit.

June 30, 1966

CuO₄S

Copper, Diatomic (Cu_2)
(Ideal Gas)

GF_W = 127.080

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	7.640	48.700	65.302	-2.973	116.017	116.017	INFINITE
200	8.471	54.304	59.538	-1.660	116.412	116.412	-24.020
298	8.744	57.745	57.745	-0.000	116.263	107.667	-117.653
300	8.747	57.799	57.745	0.016	115.996	103.502	-175.869
400	8.608	60.334	59.080	0.868	115.682	94.260	-75.344
500	8.495	62.321	58.745	1.788	115.340	95.220	-41.620
600	8.391	63.954	59.481	2.684	114.970	91.229	-33.230
700	8.294	65.257	60.535	3.547	114.580	87.234	-27.628
800	8.204	66.287	61.414	4.287	114.169	83.236	-23.709
900	8.099	67.114	62.022	5.392	113.740	79.618	-19.334
1000	8.002	68.570	62.270	6.301	113.293	75.851	-16.577
1100	7.913	69.438	62.883	7.211	112.831	72.129	-14.331
1200	7.834	70.463	63.463	8.125	112.351	68.448	-12.466
1300	7.761	71.568	64.098	9.043	111.851	64.761	-10.887
1400	7.693	72.743	64.733	9.954	111.331	61.074	-9.487
1500	7.629	73.978	65.368	10.872	110.796	57.382	-8.249
1600	7.569	75.263	66.003	11.792	110.246	53.693	-7.149
1700	7.512	76.598	66.628	12.714	109.686	50.006	-6.149
1800	7.457	77.983	67.253	13.638	109.116	46.322	-5.228
1900	7.404	79.418	67.878	14.566	108.536	42.639	-4.376
2000	7.352	80.903	68.503	15.491	107.946	38.956	-3.584
2100	7.301	82.438	69.128	16.420	107.346	35.273	-2.842
2200	7.250	84.023	69.753	17.351	106.736	31.590	-2.140
2300	7.200	85.658	70.378	18.282	106.116	27.907	-1.478
2400	7.150	87.343	71.003	19.219	105.486	24.224	-0.856
2500	7.100	89.078	71.628	20.156	104.846	20.541	-0.274
2600	7.050	90.863	72.253	21.094	104.196	16.858	0.268
2700	7.000	92.698	72.878	22.031	103.536	13.175	0.792
2800	6.950	94.583	73.503	22.968	102.866	9.492	1.296
2900	6.900	96.518	74.128	23.905	102.186	5.809	1.780
3000	6.850	98.503	74.753	24.842	101.496	2.126	2.244
3100	6.800	100.538	75.378	25.817	100.796	-1.557	2.688
3200	6.750	102.623	76.003	26.792	100.086	-3.240	3.112
3300	6.700	104.758	76.628	27.767	99.366	-4.923	3.516
3400	6.650	106.943	77.253	28.742	98.636	-6.606	3.890
3500	6.600	109.178	77.878	29.717	97.896	-8.289	4.234
3600	6.550	111.463	78.503	30.692	97.146	-9.972	4.548
3700	6.500	113.798	79.128	31.667	96.386	-11.655	4.832
3800	6.450	116.183	79.753	32.642	95.616	-13.338	5.086
3900	6.400	118.618	80.378	33.617	94.836	-15.021	5.310
4000	6.350	121.103	81.003	34.592	94.046	-16.704	5.504
4100	6.300	123.638	81.628	35.567	93.246	-18.387	5.668
4200	6.250	126.223	82.253	36.542	92.436	-20.070	5.802
4300	6.200	128.858	82.878	37.517	91.616	-21.753	5.906
4400	6.150	131.543	83.503	38.492	90.786	-23.436	5.980
4500	6.100	134.278	84.128	39.467	89.946	-25.119	6.024
4600	6.050	137.013	84.753	40.442	89.096	-26.802	6.048
4700	6.000	139.748	85.378	41.417	88.236	-28.485	6.052
4800	5.950	142.583	86.003	42.392	87.366	-30.168	6.036
4900	5.900	145.418	86.628	43.367	86.486	-31.851	6.000
5000	5.850	148.253	87.253	44.342	85.596	-33.534	5.934
5100	5.800	151.088	87.878	45.317	84.696	-35.217	5.838
5200	5.750	153.923	88.503	46.292	83.786	-36.900	5.712
5300	5.700	156.758	89.128	47.267	82.866	-38.583	5.556
5400	5.650	159.593	89.753	48.242	81.936	-40.266	5.370
5500	5.600	162.428	90.378	49.217	80.996	-41.949	5.154
5600	5.550	165.263	91.003	50.192	80.046	-43.632	4.908
5700	5.500	168.098	91.628	51.167	79.086	-45.315	4.632
5800	5.450	170.933	92.253	52.142	78.116	-46.998	4.326
5900	5.400	173.768	92.878	53.117	77.136	-48.681	3.990
6000	5.350	176.603	93.503	54.092	76.146	-50.364	3.624

Sept. 30, 1966

COPPER, DIATOMIC (Cu_2)

(IDEAL GAS)

GF_W = 127.080

Cu_2

Ground State Configuration [$1^1\Sigma$]

$S_{298.15} = 57.74$ gibbs/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0 \pm 3$ kcal/mol

$\Delta H_f^\circ = 116.0 \pm 3$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$

ϵ_i

$\omega_e x_e = 1.015 \text{ cm}^{-1}$

$\sigma = 2$

$\omega_e = 265.34 \text{ cm}^{-1}$

$B_e = 0.10776 \text{ cm}^{-1}$

$\alpha_e = 0.000608 \text{ cm}^{-1}$

$r_e = 2.219 \text{ \AA}$

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

$\Delta H_f^\circ = 116.0$ kcal/mol

Copper Monoxide (Cu₂O)

GFW = 143.0794

(Crystal)

Cu₂O

GFW = 143.0794

(CRYSTAL)

DICOPPER MONOXIDE (Cu₂O)

T, °K	Cp°, gbmol/mol	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°, kcal/mol	ΔG°	Log Kp
0	0.000	INFINITE	3.037	40.308	40.308	INFINITE
100	9.506	34.082	2.518	40.455	38.798	84.792
200	12.493	16.598	2.537	40.635	37.068	84.507
298	15.199	22.213	0.000	40.700	35.299	23.875
300	15.230	22.307	0.028	40.700	35.266	25.691
400	16.560	26.893	1.626	40.652	33.859	18.281
500	17.410	30.687	2.032	40.548	31.671	13.843
600	18.640	33.919	25.417	40.418	29.909	10.894
700	19.620	36.743	6.934	40.264	28.167	8.794
800	19.220	39.269	8.826	40.085	26.454	7.227
900	19.850	41.568	29.592	39.873	24.760	6.013
1000	20.520	43.694	10.687	39.624	23.094	5.047
1100	21.220	45.683	32.152	39.320	21.448	4.263
1200	21.920	47.559	33.358	38.968	19.846	3.614
1300	22.620	49.341	34.520	38.597	18.295	3.071
1400	23.320	51.043	35.640	38.205	16.714	2.578
1500	24.020	52.676	36.721	37.792	15.129	2.117
1600	24.720	54.242	37.762	37.358	13.540	1.689
1700	25.420	55.768	38.782	36.902	11.948	1.284
1800	26.120	57.241	39.767	36.425	10.354	0.894
1900	26.820	58.672	40.725	35.930	8.758	0.528
2000	27.520	60.066	41.657	35.417	7.160	0.184
2100	28.220	61.425	42.566	34.886	5.559	-0.157
2200	28.920	62.754	43.454	34.338	3.955	-0.499
2300	29.620	64.055	44.321	33.782	2.349	-0.846
2400	30.320	65.331	45.170	33.212	0.741	-1.197
2500	31.020	66.582	46.002	32.630	-0.870	-1.552

Summarized below are the more consistent results for the heat of formation. The selected value of -40.7 kcal/mol is based on data from Thomsen and from Iwahara and Kimura. More recent equilibrium data yield essentially the same average for ΔHf but the separate values scatter by about ±0.7 kcal/mol and significant entropy errors are apparent.

Thomsen obtained values of -40.80, -40.87 and -41.51 from aqueous calorimetry using three different paths. He favored the first path which may be recalculated by combination of the heats of reaction of Cu₂O + H₂SO₄, Fe + H₂SO₄ and Fe + CuSO₄(aq) to yield the heat of reduction of Cu₂O with H₂. Direct measurements of the heat of reduction reported by L. Wöhler and N. Jochum, Z. physik. Chem. 157A, 169 (1933), appear to be unreliable since they lead to -43.0 for the heat of formation. The cell data of Iwahara and Kimura show very little drift and are in excellent agreement with Thomsen.

Author	Method	Reaction**	Temp., °K	No. of Points	ΔHf° ₂₉₈ (kcal/mol)	Drift (eu)	ΔHf° ₂₉₈ (kcal/mol)
1. Thomsen (1883)	Aqueous Calorimetry	A	291	—	-27.61	—	-40.70
2. Hill et al. (1958)	Fused salt Emf	B	987	1	-41.38	—	-41.38
3. Kluckholz et al. (1957)	Emf vs. Fe/Fe ₂ O ₃	B	1073-1323	4	-43.03±0.56	2.1±0.5	-40.42
	Emf vs. Fe ₂ O ₃ /Fe ₃ O ₄	B	1073-1323	4	-44.14±0.10	3.1±0.1	-40.36
4. Balendran (1955)	Equilibrium data	C	1011-1156	28	36.03±1.1	41.20	4.7±1.0
5. Mskolkin (1942)	Aqueous Emf	D	288-308	3	29.46±0.7	28.30	-4.0±2.5
6. Maier (1929)	Aqueous Emf	D	298-318	7	29.94±0.4	28.07	-6.2±1.3
7. Iwahara et al. (1927)	Aqueous Emf	D	273-318	5	27.42±0.04	27.63	0.7±0.1

*Based on 3rd law values wherever possible.

**Reaction A: Cu₂O(c) + H₂ = 2Cu + H₂O(l), B: 2Cu + 0.5 O₂ = Cu₂O(c)

C: Cu₂O(c) = 2Cu + 0.5 O₂, D: 2Cu + H₂O(l) = Cu₂O(c) + H₂

- J. Thomsen, "Thermochemische Untersuchungen," vol. III, Barth, Leipzig, 1883.
- D. O. Hill, B. Porter and A. S. Gillespie, Jr., J. Electrochem. Soc. 105, 408 (1958).
- K. Kluckholz, C. Wagner, J. Electrochem. Soc. 104, 379 (1957).
- D. Balendran, Compt. rend. 240, 760 (1955); 1884 (1955).
- I. A. Mskolkin, J. Phys. Chem. (U.S.S.R.) 16, 13 (1942); cf. Chem. Abs. 37, 2641 (1943).
- C. O. Maier, J. Am. Chem. Soc. 51, 194 (1929).
- F. Iwahara and G. Kimura, "Seisgint, Yikichi Oseki," pp. 255-69, Chem. Inst. Kyoto Imp. Univ., Kyoto, Japan, 1927; cf. Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931).

Heat Capacity and Entropy.

Low temperature values are based on data from L. V. Oregor (2.8-21°K), J. Phys. Chem. 56, 1845 (1952) and from J. Hu and H. L. Johnston (15-300°K), J. Am. Chem. Soc. 73, 4550 (1951). Earlier data by R. W. Miller (76-291°K), J. Am. Chem. Soc. 52, 215 (1929) are in satisfactory agreement. The entropy was obtained from the heat capacities based on S°₂₉₈ = 0.0015 eu.

High temperature values were obtained from specific heats (373-1273°K) determined with a dynamic method by D. M. Chisholm and A. S. Knirk, Tr. Inst. Met. in A. A. Baikova, Akad. Nauk SSSR, No. 12, 79 (1963); cf. Chem. Abs. 59, 79 (1963). Entropy data (545-1223°K) from Wöhler and Jochum, loc. cit., yield for S°₁₀₀₀ a value about 0.4 eu higher, but this is inconsistent with extensive equilibrium data for 2CuO(c) = Cu₂O(c) + 0.5 O₂ [see CuO(c)].

Melting Data.

For details see Cu₂O(l).

Cu₂O

T, K Cp^o $\frac{\text{gibbs/mol}}{S^o} - \frac{-(G^o - H^o_{298})}{T}$ H^o - H^o₂₉₈ $\frac{\text{kcal/mol}}{\Delta H^o}$ ΔG^o Log Kp

0						
100						
200						
298	24.000	22.901	22.901	4.000	- 32.029	- 26.893
300	24.000	23.049	22.901	4.044	- 32.013	- 26.801
400	24.000	29.954	23.843	2.444	- 31.163	- 25.194
500	24.000	35.309	25.620	4.844	- 30.360	- 23.794
600	24.000	39.685	27.611	7.244	- 29.604	- 22.554
700	24.000	43.385	29.607	12.644	- 28.893	- 21.435
800	24.000	46.416	31.367	16.444	- 27.537	- 19.487
900	24.000	48.416	33.167	16.844	- 26.906	- 18.627
1000	24.000	51.945	35.100			4.071
1100	24.000	54.232	36.737	10.244	- 26.298	- 17.828
1200	24.000	56.321	38.284	21.644	- 25.714	- 17.086
1300	24.000	58.140	39.740	26.444	- 25.150	- 16.425
1400	24.000	60.620	41.131	26.444	- 30.978	- 15.531
1500	24.000	61.676	42.446	28.844	- 30.514	- 14.446
1600	24.000	63.225	43.697	31.244	- 30.052	- 13.390
1700	24.000	64.680	44.889	33.644	- 29.593	- 12.361
1800	24.000	65.940	46.015	36.044	- 29.135	- 11.360
1900	24.000	67.140	47.076	38.444	- 28.689	- 10.389
2000	24.000	68.280	48.156	40.844	- 28.235	- 9.433
2100	24.000	69.751	49.159	43.244	- 27.788	- 8.503
2200	24.000	70.868	50.120	45.644	- 27.344	- 7.596
2300	24.000	71.956	51.048	48.044	- 26.902	- 6.715
2400	24.000	72.956	51.938	50.444	- 26.463	- 5.842
2500	24.000	73.936	52.798	52.844	- 26.027	- 4.989
2600	24.000	74.877	53.629	55.244	- 25.593	- 4.156
2700	24.000	75.783	54.433	57.644	- 25.162	- 3.340
2800	24.000	76.656	55.206	60.044	- 24.735	- 2.540
2900	24.000	77.498	55.945	62.444	- 149.623	- 1.894
3000	24.000	78.312	56.697	64.844	- 168.890	- 6.762

June 30, 1966

$$\Delta H^o_{298,15} = -32.029 \text{ kcal/mol}$$

$$\Delta H_m^o = 13.58 \pm 2 \text{ kcal/mol}$$

$$S^o_{298,15} = 22.901 \text{ gibbs/mol}$$

$$T_m = 1509^\circ\text{K}$$

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding ΔH_m^o and the difference between ($H^o_{1509} - H^o_{298}$) for the crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated on the basis of 8 gibbs per g atom, giving a value of 24 gibbs/mol which is essentially the same as that of the crystal at the melting point. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

T_m is the value recommended by S. J. Schneider, NBS Monograph 68, U. S. Govt. Printing Office, Washington, D.C., October, 1963, based on pressure-temperature-composition studies of H. S. Roberts and P. H. Smyth, J. Am. Chem. Soc. 43, 1061 (1921). The heat of melting was selected as 13.58 kcal/mol, corresponding to $\Delta H_m^o = 5 \text{ eu per g atom}$. A value of 13.4 kcal/mol has been derived from the Cu₂O-CuCl phase diagram by K. K. Kelley, USNM Bulletin 395, U. S. Govt. Printing Office, Washington, 1936. Another value may be obtained from oxygen dissociation pressures for the system Cu₂O(l)-CuO(c) determined by Roberts and Smyth, loc. cit. Equilibrium constants may be obtained for the reaction $2\text{CuO}(c) = \text{Cu}_2\text{O}(l) + 0.5 \text{ O}_2$ by assuming the activity of Cu₂O in the melt to be equal to its mole fraction. Based on the mole fractions given by Randall, Nielsen and West, Ind. Eng. Chem. 23, 388 (1931), the equilibrium data yield $\Delta H_m^o = 15.8 \pm 0.8 \text{ kcal/mol}$ by second law analysis of all points or 12.9 ± 1.6 by omission of 4 points at high pressure and low mole fraction. These results appear to be consistent with the selected value within the approximations involved.

Copper Oxide Sulfate ($\text{CuO} \cdot \text{CuSO}_4$)

(Crystal) $\Delta H_f^\circ = 233.141$

T, K	C_p	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0						
100						
200						
298	33.710	37.600	6000	-221.700	-189.990	138.82*
300						
325	37.820	37.651	652	-221.752	-189.991	127.825
400	38.800	38.051	9705	-221.752	-189.991	127.825
500	42.300	41.769	1768	-221.665	-189.990	73.166
600	44.890	45.034	12,433	-221.710	-189.995	57.000
800	48.500	48.627	26,721	-221.757	-189.991	45.668
900	49.600	49.440	31,378	-221.757	-189.991	37.153
1000	50.800	50.728	36,530	-221.757	-189.991	24.462
1100	51.900	51.813	41,132	-221.757	-189.991	15.959
1200	52.900	52.825	45,372	-221.757	-189.991	10.110
1300	53.900	53.837	49,352	-221.757	-189.991	10.975
1400	54.900	54.849	53,168	-221.757	-189.991	10.975
1500	55.000	54.859	56,840	-221.757	-189.991	7.748

COPPER OXIDE SULFATE ($\text{CuO} \cdot \text{CuSO}_4$) (CRYSTAL)

$\Delta H_f^\circ = 233.141$

ΔH_f° = Unknown

$\Delta H_{298.15}^\circ = -221.7 \pm 0.3 \text{ kcal/mol}$

$S_{298.15}^\circ = [37.6 \pm 2] \text{ gibbs/mol}$

$T_d = 1136.4^\circ\text{K}$

Heat of Formation.

The equilibrium pressures for the following reactions: (A) $\text{CuO} \cdot \text{CuSO}_4(c) = 2\text{CuO}(c) + \text{SO}_2(g)$ and $\text{SO}_3(g) = \text{SO}_2(g) + 0.5 \text{ O}_2(g)$, and (B) $\text{CuO} \cdot \text{CuSO}_4(c) + \text{Cu}_2\text{O}(c) = 4\text{CuO}(c) + \text{SO}_2(g)$, were determined by (1) W. Reinhardt and P. Goudrian, Z. anorg. allgem. Chem. **156**, 85 (1923), and (2) T. R. Ingraham, Trans. Met. Soc. AIME, **233**, 359 (1968). Using the reported vapor pressures, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Reference	Reaction	Temperature, °K	Second Law Value	Third Law Value	Drift, kcal/mol	$\Delta H_{298.15}^\circ$, kcal/mol
(1)	A	1013 - 1083	53.03 ± 2.53	52.43	-0.7 ± 2.4	-221.5
(2)	B	517 - 1027	41.72 ± 1.42	42.43	0.5 ± 1.4	-221.7
	A**	569 - 1136	50.92 ± 0.16	52.67	1.5 ± 0.2	-221.7

* Based on the third law value for $\Delta H_{298.15}^\circ$.

** Partial pressures were calculated from JANAF values for the $\text{SO}_3 - \text{SO}_2$ equilibrium. The value of $\Delta H_{298.15}^\circ$ ($\text{CuO} \cdot \text{CuSO}_4, c$) adopted is $-221.7 \pm 0.3 \text{ kcal/mol}$.

Heat Capacity and Entropy.

The heat capacities were calculated as the sum of those for $\text{CuO}(c)$ and $\text{CuSO}_4(c)$. The value of $S_{298.15}^\circ$ was estimated by comparison with those for $\text{CuO}(c)$ and $\text{CuSO}_4(c)$, and adjusted so that, using the derived free energy functions, the second and third law values for $\Delta H_{298.15}^\circ$ agree reasonably.

Decomposition Temperature.

T_d is the temperature at which the total pressure of the gaseous decomposition products of reaction (A) equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for $\text{CuO} \cdot \text{CuSO}_4(c)$, determined by T. R. Ingraham, loc. cit.

Fluorine, Monatomic (F)

(Ideal Gas) Mol. Wt. = 18.9984

T, °K.	C _p ^o	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	∞.000	∞.000	∞.000	18.357	18.357	∞.000
100	5.068	32.116	42.710	-1.059	18.508	17.331	-37.875
200	5.403	35.746	38.615	-5.34	18.684	16.089	-17.580
298	5.437	37.017	37.017	∞.000	18.860	14.777	-10.832
300	5.436	37.051	37.051	∞.000	18.863	14.752	-10.766
400	5.361	39.505	38.129	-5.50	19.018	13.358	-7.208
500	5.282	40.693	38.528	-1.082	19.147	11.927	-5.213
600	5.218	41.650	38.871	-1.657	19.256	10.472	-3.814
700	5.163	42.430	39.132	-2.241	19.341	9.007	-2.953
800	5.113	43.038	39.317	-2.821	19.405	7.527	-2.405
900	5.069	43.514	40.237	-3.401	19.450	6.035	-1.862
1000	5.033	43.877	40.615	-3.963	19.472	4.522	-1.328
1100	5.006	44.161	40.970	-4.510	19.483	3.001	-0.795
1200	4.984	44.395	41.305	-5.045	19.486	1.466	-0.262
1300	4.966	44.588	41.618	-5.568	19.481	0.000	∞.000
1400	4.952	44.745	41.902	-6.080	19.470	-1.488	-0.262
1500	4.940	44.882	42.161	-6.584	19.455	-2.980	-0.795
1600	4.928	45.000	42.400	-7.080	19.438	-4.472	-1.328
1700	4.916	45.100	42.618	-7.568	19.418	-5.965	-1.862
1800	4.904	45.190	42.817	-8.048	19.395	-7.458	-2.405
1900	4.892	45.268	42.990	-8.519	19.369	-8.951	-2.953
2000	4.880	45.334	43.140	-8.982	19.341	-10.444	-3.500
2100	4.869	45.388	43.268	-9.438	19.309	-11.937	-4.047
2200	4.858	45.433	43.375	-9.887	19.273	-13.430	-4.594
2300	4.848	45.470	43.463	-10.328	19.234	-14.922	-5.141
2400	4.838	45.500	43.533	-10.760	19.192	-16.414	-5.688
2500	4.828	45.525	43.588	-11.185	19.147	-17.906	-6.235
2600	4.818	45.546	43.630	-11.605	19.100	-19.398	-6.782
2700	4.808	45.563	43.659	-12.018	19.051	-20.890	-7.329
2800	4.798	45.577	43.677	-12.425	19.000	-22.382	-7.876
2900	4.788	45.588	43.684	-12.827	18.947	-23.874	-8.423
3000	4.778	45.595	43.688	-13.225	18.892	-25.366	-8.970
3100	4.768	45.599	43.688	-13.618	18.835	-26.858	-9.517
3200	4.758	45.599	43.684	-14.008	18.776	-28.350	-10.064
3300	4.748	45.595	43.677	-14.393	18.715	-29.842	-10.611
3400	4.738	45.588	43.663	-14.775	18.652	-31.334	-11.158
3500	4.728	45.577	43.645	-15.153	18.588	-32.826	-11.705
3600	4.718	45.563	43.615	-15.528	18.523	-34.318	-12.252
3700	4.708	45.546	43.575	-15.900	18.457	-35.810	-12.799
3800	4.698	45.525	43.525	-16.268	18.390	-37.302	-13.346
3900	4.688	45.500	43.463	-16.633	18.321	-38.794	-13.893
4000	4.678	45.470	43.388	-17.000	18.250	-40.286	-14.440
4100	4.668	45.433	43.300	-17.368	18.177	-41.778	-14.987
4200	4.658	45.395	43.200	-17.733	18.102	-43.270	-15.534
4300	4.648	45.357	43.088	-18.095	18.025	-44.762	-16.081
4400	4.638	45.317	42.963	-18.453	17.947	-46.254	-16.628
4500	4.628	45.275	42.825	-18.808	17.867	-47.746	-17.175
4600	4.618	45.230	42.675	-19.160	17.785	-49.238	-17.722
4700	4.608	45.183	42.513	-19.508	17.700	-50.730	-18.269
4800	4.598	45.133	42.340	-19.853	17.612	-52.222	-18.816
4900	4.588	45.080	42.155	-20.195	17.522	-53.714	-19.363
5000	4.578	45.025	41.958	-20.533	17.430	-55.206	-19.910
5100	4.568	44.968	41.750	-20.868	17.335	-56.698	-20.457
5200	4.558	44.908	41.530	-21.200	17.238	-58.190	-21.004
5300	4.548	44.845	41.298	-21.528	17.138	-59.682	-21.551
5400	4.538	44.778	41.055	-21.853	17.035	-61.174	-22.098
5500	4.528	44.708	40.800	-22.175	16.928	-62.666	-22.645
5600	4.518	44.635	40.533	-22.495	16.818	-64.158	-23.192
5700	4.508	44.558	40.255	-22.812	16.705	-65.650	-23.739
5800	4.498	44.478	39.968	-23.128	16.588	-67.142	-24.286
5900	4.488	44.395	39.670	-23.442	16.468	-68.634	-24.833
6000	4.478	44.308	39.363	-23.755	16.345	-70.126	-25.380

Dec. 31, 1960; June 30, 1961; Sept. 30, 1965

Heat of Formation.

The dissociation energy (D_0) of fluorine has been discussed by numerous investigators for many years. Until about fifteen years ago, high values of $D_0(F_2)$, about 65 kcal. mole⁻¹, were widely accepted. These values were obtained from extrapolations of the spectroscopic data for the halogens, e.g. $D_0 = 63.3$ kcal. mole⁻¹ was reported by H. V. Martenbergs, O. Sprenger and J. Taylor, Z. Physik. Chem., Bodenstein-Festband, 61 (1931). However, mean-while many indirect determinations as well as estimation have been carried out, which yield appreciably lower values. In 1950 the available data were examined critically by M. G. Evans, E. Warhurst and E. Whittle, J. Chem. Soc. 1952 (1950) and shown to support a value, $D_0(F_2) = 37 \pm 8$ kcal. mole⁻¹. The indirect determinations include (1) the thermal conductivity measurements by E. U. Franck and E. Wicke, Z. Elektrochem. 55, 643 (1951); (2) the explosion method by H. Fritz, Disert., Göttingen, 1952; (3) estimation by use of the relations between D_0 and the vibrational frequencies by A. Bucken and E. Wicke, Naturwiss., 37, 235 (1950); and (4) spectroscopic data on the dissociation energy of diatomic fluorides. Recently more direct methods have been used to determine $D_0(F_2)$. They gave similar values. The D_0 values reported by the previous investigators have been reviewed by L. Harter and C. W. Beckett, National Bureau of Standards Report 1435 (1952), and E. Wicke and H. Fritz, Z. Elektrochem. 57, 9 (1953).

The low bond dissociation energy of $F_2(g)$ has been attributed to the repulsion between the unshared electrons on the bound fluorine atoms by K. S. Pitzer, J. Am. Chem. Soc. 70, 2140 (1948), or to the absence in fluorine of strengthening of the bond by hybridization of the p- or d- orbitals as may take place in the higher halogens by R. S. Mulliken, J. Am. Chem. Soc. 77, 884 (1955). M. G. Brown, Trans. Faraday Soc. 55, 9 (1959) suggests that the observed low D_0 value results from the large energy required to promote the p atoms to the valence state from which the bond may be formed.

The equilibrium pressures for the reaction $F_2(g) \rightarrow 2F(g)$ have been measured by several investigators. Using the reported equilibrium constants, the dissociation energy, $D_{98.15}$, was evaluated by both the second and third law methods. The results obtained are presented as follows.

Temperature, °K.	2nd Law Value	3rd Law Value	Reference
759 - 1115	36.91 ± 0.41	37.76	1
810 - 950	36.7 ± 18.2	38.1	2
723 - 820	41.8 ± 0.2	36.0	4

1. R. N. Dorschner, J. Chem. Phys. 20, 330 (1952).

2. F. M. Ollies and J. L. Margrave, J. Chem. Phys. 21, 381 (1953).

3. H. Wise, J. Phys. Chem. 59, 389 (1954).

4. M. Farber, et al., "Study of Rocket Engine Exhaust Products", Thirteenth Quarterly Report, June 1 - Oct. 31, 1964, Westmont Corporation, Pasadena, California.

By use of H_2-F_2 mixture explosion method, $D_0(F_2)$ was reported as 37 ± 2 kcal. mole⁻¹ by E. Wicke and H. Fritz, loc. cit. K. L. Wray and D. F. Hornig, J. Chem. Phys. 23, 1271 (1956), using shock wave method, obtained $D_0 = 31.0 \pm 4.5$ kcal. mole⁻¹. The continuous absorption electronic spectrum of $F_2(g)$ and the Raman displacement for the $0 \rightarrow 1$ vibrational transition have been used by A. L. G. Rees, J. Chem. Phys. 26, 1567 (1957) to compute the potential energy curve for the repulsive Π_u state dissociating to two normal $F(g)$. This curve is consistent with the value, $D_0 = 37.1 \pm 0.85$ kcal. mole⁻¹. The absorption spectrum of $F_2(g)$ has been observed in the vacuum UV region by R. F. Izckowski and J. L. Margrave, J. Chem. Phys. 30, 403 (1959). From a progression of bands at 8744, the value, $D_0 = 37.5 \pm 2$ kcal. mole⁻¹ is deduced.

The F_2 dissociation energy is selected as 37.72 ± 0.80 kcal. mole⁻¹, yielding $\Delta H_f^\circ 298.15^\circ(P, g) = 18.86 \pm 0.40$ kcal. mole⁻¹.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weights were taken from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949.

Fluorine Uninegative Ion (F⁻)
(Ideal Gas) Mol. wt. = 18.99895

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0						
100	4.968	34.768	.000	-62.200	-63.857	46.806
200	4.968	34.768	.000	-62.207	-63.867	46.525
298	4.968	34.768	.000	-62.207	-63.867	46.525
300	4.968	34.768	.000	-62.207	-63.867	46.525
400	4.968	34.768	.000	-62.207	-63.867	46.525
500	4.968	34.768	.000	-62.207	-63.867	46.525
600	4.968	34.768	.000	-62.207	-63.867	46.525
700	4.968	34.768	.000	-62.207	-63.867	46.525
800	4.968	34.768	.000	-62.207	-63.867	46.525
900	4.968	34.768	.000	-62.207	-63.867	46.525
1000	4.968	34.768	.000	-62.207	-63.867	46.525
1100	4.968	34.768	.000	-62.207	-63.867	46.525
1200	4.968	34.768	.000	-62.207	-63.867	46.525
1300	4.968	34.768	.000	-62.207	-63.867	46.525
1400	4.968	34.768	.000	-62.207	-63.867	46.525
1500	4.968	34.768	.000	-62.207	-63.867	46.525
1600	4.968	34.768	.000	-62.207	-63.867	46.525
1700	4.968	34.768	.000	-62.207	-63.867	46.525
1800	4.968	34.768	.000	-62.207	-63.867	46.525
1900	4.968	34.768	.000	-62.207	-63.867	46.525
2000	4.968	34.768	.000	-62.207	-63.867	46.525
2100	4.968	34.768	.000	-62.207	-63.867	46.525
2200	4.968	34.768	.000	-62.207	-63.867	46.525
2300	4.968	34.768	.000	-62.207	-63.867	46.525
2400	4.968	34.768	.000	-62.207	-63.867	46.525
2500	4.968	34.768	.000	-62.207	-63.867	46.525
2600	4.968	34.768	.000	-62.207	-63.867	46.525
2700	4.968	34.768	.000	-62.207	-63.867	46.525
2800	4.968	34.768	.000	-62.207	-63.867	46.525
2900	4.968	34.768	.000	-62.207	-63.867	46.525
3000	4.968	34.768	.000	-62.207	-63.867	46.525
3100	4.968	34.768	.000	-62.207	-63.867	46.525
3200	4.968	34.768	.000	-62.207	-63.867	46.525
3300	4.968	34.768	.000	-62.207	-63.867	46.525
3400	4.968	34.768	.000	-62.207	-63.867	46.525
3500	4.968	34.768	.000	-62.207	-63.867	46.525
3600	4.968	34.768	.000	-62.207	-63.867	46.525
3700	4.968	34.768	.000	-62.207	-63.867	46.525
3800	4.968	34.768	.000	-62.207	-63.867	46.525
3900	4.968	34.768	.000	-62.207	-63.867	46.525
4000	4.968	34.768	.000	-62.207	-63.867	46.525
4100	4.968	34.768	.000	-62.207	-63.867	46.525
4200	4.968	34.768	.000	-62.207	-63.867	46.525
4300	4.968	34.768	.000	-62.207	-63.867	46.525
4400	4.968	34.768	.000	-62.207	-63.867	46.525
4500	4.968	34.768	.000	-62.207	-63.867	46.525
4600	4.968	34.768	.000	-62.207	-63.867	46.525
4700	4.968	34.768	.000	-62.207	-63.867	46.525
4800	4.968	34.768	.000	-62.207	-63.867	46.525
4900	4.968	34.768	.000	-62.207	-63.867	46.525
5000	4.968	34.768	.000	-62.207	-63.867	46.525
5100	4.968	34.768	.000	-62.207	-63.867	46.525
5200	4.968	34.768	.000	-62.207	-63.867	46.525
5300	4.968	34.768	.000	-62.207	-63.867	46.525
5400	4.968	34.768	.000	-62.207	-63.867	46.525
5500	4.968	34.768	.000	-62.207	-63.867	46.525
5600	4.968	34.768	.000	-62.207	-63.867	46.525
5700	4.968	34.768	.000	-62.207	-63.867	46.525
5800	4.968	34.768	.000	-62.207	-63.867	46.525
5900	4.968	34.768	.000	-62.207	-63.867	46.525
6000	4.968	34.768	.000	-62.207	-63.867	46.525

June 30, 1965

FLUORINE UNINEGATIVE ION (F⁻) (IDEAL GAS)

MOL. WT. = 18.99895

Ground State Configuration 1S₀
S_{298.15}° = 34.768 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = -61.1 ± .5 kcal/mole
ΔH_f⁰ 298.15 = -62.2 ± .5 kcal/mole

Electronic Levels and Quantum Weight
C₁, cm.⁻¹ g₁
0.00 1

Heat of Formation.

The heat of formation was calculated from the equation: P(g) + e⁻ → F⁻(g) with the JANAP auxiliary value for P(g) using the measured electron affinity = 3.448 e.v. (79.511 kcal/mole) obtained from R. S. Berry and C. W. Reimann, J. Chem. Phys. 39, 1540 (1963). Other calculated values for the electron affinity are: 3.37 reported by E. Clementi and A. D. McLean, Phys. Rev. 135, A419 (1964); 3.08 e.v. E. Clementi, A. D. McLean, D. L. Raymond, and M. Yoshimine, 135, A1274 (1964); 3.50 e.v. B. Edlen, J. Chem. Phys. 33, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Neon. The electronic levels above 1 X 10⁵ cm.⁻¹ were omitted because their contribution is negligible below 6000°K. The h⁰-h₂₉₈ value at 0°K. is -1.481 kcal/mole.

IRON MONOFLUORIDE (FeF) (IDEAL GAS) MOL. WT. = 74.8454

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	-	11.363	11.363	INFINITE
100	6.978	49.406	2.467	11.363	11.363	-19.337
200	7.421	58.129	1.572	11.363	11.363	-6.662
298	7.850	65.129	0.000	11.363	11.363	-2.559
300	7.859	65.141	0.015	11.397	11.397	-2.477
400	8.306	74.735	0.829	11.200	11.200	-
500	8.518	81.686	1.672	10.964	10.964	-
600	8.652	87.252	2.531	10.677	10.677	-
700	8.753	91.535	3.401	10.333	10.333	-
800	8.827	94.765	4.278	9.909	9.909	-
900	8.854	96.805	5.161	9.378	9.378	-
1000	8.891	97.740	6.049	8.666	8.666	-
1100	8.921	98.589	6.930	7.736	7.736	-
1200	8.946	99.366	7.833	6.639	6.639	-
1300	8.967	100.083	8.728	5.369	5.369	-
1400	8.985	100.748	9.626	4.042	4.042	-
1500	9.002	101.369	10.525	2.653	2.653	-
1600	9.017	101.950	11.426	1.209	1.209	-
1700	9.030	102.490	12.323	-0.184	-0.184	-
1800	9.043	103.004	13.217	-1.613	-1.613	-
1900	9.055	103.493	14.107	-3.025	-3.025	-
2000	9.067	103.958	15.003	-4.428	-4.428	-
2100	9.078	104.400	15.896	-5.821	-5.821	-
2200	9.089	104.821	16.786	-7.205	-7.205	-
2300	9.099	105.223	17.672	-8.580	-8.580	-
2400	9.108	105.604	18.554	-9.946	-9.946	-
2500	9.118	105.966	19.432	-11.303	-11.303	-
2600	9.128	106.318	20.307	-12.651	-12.651	-
2700	9.136	106.661	21.179	-13.991	-13.991	-
2800	9.144	106.995	22.048	-15.323	-15.323	-
2900	9.152	107.321	22.914	-16.648	-16.648	-
3000	9.160	107.639	23.777	-17.966	-17.966	-
3100	9.167	107.949	24.637	-19.277	-19.277	-
3200	9.174	108.251	25.494	-20.581	-20.581	-
3300	9.180	108.545	26.348	-21.878	-21.878	-
3400	9.186	108.832	27.199	-23.168	-23.168	-
3500	9.192	109.112	28.047	-24.451	-24.451	-
3600	9.198	109.385	28.892	-25.727	-25.727	-
3700	9.203	109.651	29.734	-27.000	-27.000	-
3800	9.208	109.910	30.573	-28.269	-28.269	-
3900	9.213	110.162	31.409	-29.534	-29.534	-
4000	9.218	110.407	32.242	-30.795	-30.795	-
4100	9.223	110.645	33.072	-32.052	-32.052	-
4200	9.228	110.877	33.896	-33.305	-33.305	-
4300	9.232	111.103	34.717	-34.554	-34.554	-
4400	9.236	111.323	35.535	-35.800	-35.800	-
4500	9.240	111.538	36.350	-37.042	-37.042	-
4600	9.244	111.748	37.162	-38.281	-38.281	-
4700	9.248	111.953	37.971	-39.517	-39.517	-
4800	9.252	112.153	38.777	-40.750	-40.750	-
4900	9.256	112.348	39.580	-41.980	-41.980	-
5000	9.260	112.539	40.380	-43.207	-43.207	-
5100	9.264	112.725	41.177	-44.431	-44.431	-
5200	9.268	112.907	41.971	-45.652	-45.652	-
5300	9.271	113.085	42.762	-46.870	-46.870	-
5400	9.275	113.259	43.549	-48.085	-48.085	-
5500	9.278	113.429	44.333	-49.297	-49.297	-
5600	9.281	113.595	45.114	-50.506	-50.506	-
5700	9.284	113.758	45.891	-51.712	-51.712	-
5800	9.287	113.918	46.665	-52.915	-52.915	-
5900	9.290	114.075	47.436	-54.115	-54.115	-
6000	9.293	114.229	48.204	-55.312	-55.312	-

Sept. 30, 1965

Ground State Configuration [6Σ⁺]S_{298.15} = [57.4] cal. deg⁻¹ mole⁻¹ΔH_f⁰ = [11.4 ± 5.0] kcal. mole⁻¹ΔF_f⁰ 298.15 = [11.4 ± 5.0] kcal. mole

Electronic Levels and Quantum Weight

E, cm ⁻¹	g _i
0	1

ω_ex_e = [2.7] cm⁻¹σ⁻ = 1r_e = [1.8] Åα_e = [0.0017] cm⁻¹B_e = [0.3870] cm⁻¹

Heat of Formation.

The dissociation energy (D₀) of FeF(g) was estimated as 4.64 ± 0.22 e.v. or 107 ± 5 kcal. mole⁻¹ by J. L. Margrave, "Optical Spectra and Molecular Parameters of Light Element Molecules", Progress Report No. 8, Jan. 1 to Mar. 31, 1965, William Marsh Rice University, Houston, Texas. From the value of D⁰ (Fe-F) the heat of formation (ΔH_f⁰ 298.15) for FeF(g) was derived to be 11.4 ± 5.0 kcal. mole⁻¹.

Heat Capacity and Entropy.

The ground state configuration and bond distance (r_e) were estimated by comparison with those for FeCl(g). The value of B_e was calculated using the relationship $B_e = \frac{2.7989 \times 10^{-39}}{I}$ where I = moment of inertia of FeF(g), and α_e was estimated by comparison with those for AlF(g), AlCl(g) and FeCl(g). The value of ω_e was derived from the bond distance, reduced mass and number of valence electrons according to the method given by K. M. Guggenheimer, Proc. Phys. Soc. (London) 59, 456 (1946), and the ω_ex_e was estimated from those for AlF(g), AlCl(g) and FeCl(g). The moment of inertia is 7.6259 × 10⁻³⁹ g. cm.²

HYDROGEN FLUORIDE (HF)

(IDEAL GAS)

GFW = 20.00637

Hydrogen Fluoride (HF)

(Ideal Gas) GFW = 20.00637

Ground State Configuration $1s^2$ $\Delta H_f^\circ = -65.13 \pm 0.2 \text{ kcal/mol}$ $S_{298.15} = 41.508 \text{ gibbs/mol}$ $\Delta H_f^\circ = -65.14 \pm 0.2 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	1

$$\omega_e x_e = 4138.37 \text{ cm}^{-1} \quad \sigma = 1$$

$$\omega_e = 20.9557 \text{ cm}^{-1} \quad \alpha_e = 0.798^{-1} \quad r_e = 0.9168 \text{ \AA}$$

Heat of Formation

The selected value is obtained from a least squares, simultaneous solution (1) for the heats of formation of HF(g), HF(50 H₂O) and five closely related fluorides. Other results, based on 23 selected observations relating the 7 variables, are as follows in kcal/mol: HF(50 H₂O), -76.78 \pm 0.1; NaF(c), -137.52 \pm 0.2; BF₃(g), -271.42 \pm 0.4; CH₄(g), -223.04 \pm 0.3; NF₃(g), -31.43 \pm 0.3; and C₂F₄ (polymer), -198.2 \pm 0.7. The \pm values are approximate estimates of the overall uncertainty including systematic error. Further details of the simultaneous solution are given in (1).

The values given above require the use of certain auxiliary data; e.g., the value for NaF(c) presumes $\Delta H_f^\circ(\text{moln}) = 0.23 \pm 0.01$ and $\Delta H_f^\circ(\text{Na}^+(\infty \text{H}_2\text{O})) = -57.47 \pm 0.04 \text{ kcal/mol}$. Use of these auxiliary data leads to $\Delta H_f^\circ(298.15) = -79.82 \text{ kcal/mol}$ for HF($\infty \text{H}_2\text{O}$) and $F^-(\infty \text{H}_2\text{O})$; however, values for HF(n H₂O) should be obtained from that of HF(50 H₂O) by use of $[\phi_L(n) - \phi_L(50)]$ taken from the tables of Parker (2). This procedure should be reliable except in dilute solutions ($n > 1000$) where the equilibria $\text{HF} + \text{H}^+ + \text{F}^- + \text{HF} \rightleftharpoons \text{HF}_2^-$ yield an overall ΔH of about 3 kcal/mol. Parker (2) used thermodynamic data for these equilibria in order to calculate ϕ_L for the dilute solutions, but recent data (3-5) suggest that minor changes in the calculations may be desirable. For this reason the simultaneous solution includes $\phi_L(50) = 3184 \pm 300 \text{ cal/mol}$ (2) as an "observation" rather than as a fixed value. The result of the simultaneous solution is smaller by only 150 cal/mol, suggesting that $\phi_L(50)$ does not contain a major inconsistency.

Heat Capacity and Entropy

The ground state configuration is that deduced from UV spectra by Johns and Barrow (6). The excited state near 85000 cm^{-1} is omitted since its contribution to the thermodynamic functions is negligible. High-resolution studies of the vibration-rotation spectrum were reported by Mann et al. (7) and subsequently confirmed by others (8, 9). The analysis of Webb and Rao (9) is adopted for this table.

References

1. Quarterly Technical Report No. 4 under Contract T04611-67-C-0009, Dow Chemical Co. Report No. T-0009-4Q-68, Jan. 1969.
2. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965. Heat of Dilution.
3. A. J. Ellis, J. Chem. Soc. 1963, 4300 (1963). Aqueous ionic equilibria.
4. L. G. Sillen and A. E. Martell, "Stability Constants," Special Publication No. 17, pp. 256-7, The Chemical Society, London, 1964; H. N. Farnham and F. J. C. Rossotti, J. Inorg. Nucl. Chem. 28, 1959 (1964). Aqueous ionic equilibria.
5. J. D. Cox and D. Harrop, Trans. Faraday Soc. 61, 1328 (1965). Heat of dilution.
6. J. W. C. Johns and R. F. Barrow, Proc. Roy. Soc. A251, 504 (1959). UV spectra.
7. D. E. Mann, B. A. Thrush, D. R. Lide, J. J. Ball and N. Acquista, J. Chem. Phys. 38, 470 (1961). Vibration-rotation spectra.
8. A. A. Mason and A. H. Nielsen, J. Opt. Soc. Amer. 57, 1484 (1957); W. G. Rothschild, ibid. 54, 20 (1964). Rotation spectra.
9. D. U. Webb and K. N. Rao, J. Mol. Spectrosc. 28, 121 (1968); E. S. Fishburne and K. N. Rao, ibid. 19, 290 (1966); V. E. Nevich and S. A. Stankevich, Dokl. Akad. Nauk SSSR 170 (6), 1376 (1966). Vibration-rotation spectra.

T, K	Cp*	gibbs/mol $S^\circ - (G^\circ - H^\circ_{298})/T$	H* - H* ₂₉₈	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	+0.00	INFINITE	2.055	-65.128	-65.128	INFINITE
100	6.962	33.902	1.380	-65.130	-65.131	142.747
200	6.962	41.508	+0.683	-65.135	-65.136	46.116
298	6.964	41.508	+0.00	-65.140	-65.141	46.116
300	6.964	41.508	+0.13	-65.141	-65.142	46.116
400	6.967	43.555	1.709	-65.176	-65.180	35.955
500	6.972	45.110	1.406	-65.232	-65.232	28.431
600	6.986	46.382	2.104	-65.300	-65.300	24.076
700	7.015	47.461	2.804	-65.377	-65.377	20.676
800	7.063	48.400	3.508	-65.459	-65.459	18.124
900	7.129	49.236	4.217	-65.544	-65.544	16.135
1000	7.210	49.991	4.934	-65.628	-65.628	14.552
1100	7.303	50.683	5.640	-65.712	-65.712	13.238
1200	7.402	51.322	6.395	-65.799	-65.799	12.149
1300	7.504	51.919	7.140	-65.870	-65.870	11.227
1400	7.606	52.479	7.896	-65.945	-65.945	10.436
1500	7.705	53.007	8.661	-66.018	-66.018	9.749
1600	7.801	53.507	9.437	-66.089	-66.089	9.147
1700	7.891	53.983	10.221	-66.157	-66.157	8.616
1800	7.977	54.436	11.015	-66.223	-66.223	8.143
1900	8.058	54.870	11.816	-66.287	-66.287	7.720
2000	8.133	55.285	12.626	-66.348	-66.348	7.339
2100	8.204	55.683	13.443	-66.408	-66.408	6.993
2200	8.270	56.067	14.267	-66.467	-66.467	6.679
2300	8.331	56.436	15.097	-66.524	-66.524	6.392
2400	8.389	56.791	15.933	-66.580	-66.580	6.128
2500	8.442	57.135	16.774	-66.637	-66.637	5.886
2600	8.493	57.467	17.621	-66.691	-66.691	5.661
2700	8.540	57.789	18.473	-66.746	-66.746	5.454
2800	8.584	58.100	19.329	-66.800	-66.800	5.264
2900	8.625	58.402	20.189	-66.853	-66.853	5.081
3000	8.664	58.695	21.054	-66.907	-66.907	4.913
3100	8.701	58.980	21.922	-66.960	-66.960	4.754
3200	8.736	59.256	22.784	-67.014	-67.014	4.600
3300	8.768	59.526	23.649	-67.067	-67.067	4.469
3400	8.800	59.788	24.518	-67.121	-67.121	4.339
3500	8.829	60.043	25.382	-67.176	-67.176	4.215
3600	8.857	60.293	26.241	-67.231	-67.231	4.099
3700	8.884	60.536	27.100	-67.287	-67.287	3.988
3800	8.910	60.773	27.959	-67.343	-67.343	3.884
3900	8.934	61.005	28.818	-67.400	-67.400	3.784
4000	8.958	61.231	29.677	-67.456	-67.456	3.690
4100	8.981	61.453	30.537	-67.512	-67.512	3.600
4200	9.002	61.669	31.396	-67.568	-67.568	3.514
4300	9.023	61.881	32.254	-67.624	-67.624	3.432
4400	9.043	62.089	33.113	-67.680	-67.680	3.354
4500	9.063	62.292	33.972	-67.736	-67.736	3.279
4600	9.082	62.492	34.831	-67.792	-67.792	3.208
4700	9.100	62.687	35.690	-67.848	-67.848	3.139
4800	9.118	62.879	36.549	-67.904	-67.904	3.073
4900	9.135	63.067	37.408	-67.960	-67.960	3.010
5000	9.152	63.252	38.267	-68.017	-68.017	2.950
5100	9.168	63.433	39.126	-68.073	-68.073	2.891
5200	9.184	63.612	39.985	-68.129	-68.129	2.835
5300	9.200	63.787	40.844	-68.185	-68.185	2.781
5400	9.215	63.959	41.703	-68.241	-68.241	2.729
5500	9.230	64.128	42.562	-68.297	-68.297	2.678
5600	9.244	64.295	43.421	-68.353	-68.353	2.630
5700	9.259	64.458	44.280	-68.409	-68.409	2.583
5800	9.272	64.619	45.139	-68.465	-68.465	2.537
5900	9.286	64.778	45.998	-68.521	-68.521	2.493
6000	9.300	64.934	46.857	-68.577	-68.577	2.451

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1963; Dec. 31, 1968

MOL. WT. = 36.00577

(IDEAL GAS)

HYPOFLUOROUS ACID (HF0)

Point Group C_{2v}
 $S^{\circ}_{298.15} = [53.954] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_f 0 = [-30 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = [-31 \pm 10] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\lambda, \text{ cm.}^{-1}$
 [1500] (1)
 [1065] (1)
 [3645] (1)

Bond Distances: H-O = [0.96] Å O-F = [1.41] Å
 Bond Angle: H-O-F = [104]°
 Product of the Moments of Inertia: $I_A I_B I_C = [1.2826 \times 10^{-117}] \text{ g.}^3 \text{ cm.}^6$
 $\sigma = 1$

Heat of Formation.

The value of $\Delta H^{\circ}_f 298.15$ for HF0(g) was calculated based on an estimated value for the heat of atomization 1.e. $\Delta H^{\circ}_f = 161.6 \text{ kcal. mole}^{-1}$ for the reaction $\text{HF0(g)} = \text{H(g)} + \text{F(g)} + \text{O(g)}$. The ΔH°_f value was assumed to be the sum of the F-O and H-O bond energies which were obtained from the corresponding bond energies in F₂O(g) and H₂O(g) molecules.

Heat Capacity and Entropy.

The H-O and F-O bond distances were assumed to be the same as those in the H₂O(g) and F₂O(g) molecules. The vibrational frequencies and H-O-F bond angle were estimated by comparison with the corresponding values for H₂O(g), F₂O(g) and Cl₂O(g). The three principal moments of inertia are $I_A = 0.1332 \times 10^{-39}$, $I_B = 3.0366 \times 10^{-39}$ and $I_C = 3.1699 \times 10^{-39} \text{ g. cm.}^2$

T, °K.	C_p°	$S^{\circ} - (F^{\circ} - H^{\circ}_{298})/T$	ΔH°_f	ΔF°_f	Log K _p
0	4.000	INFINITE	-2.391	-30.287	INFINITE
100	7.949	45.187	-1.596	-30.375	65.045
200	8.006	50.705	-0.800	-30.375	65.045
298	8.335	53.954	-0.000	-31.000	20.435
300	8.344	54.006	0.015	-31.005	20.315
400	8.876	56.477	1.876	-31.232	14.650
500	9.421	58.517	3.495	-31.435	11.227
600	9.904	60.278	5.082	-31.612	8.930
700	10.315	61.837	6.642	-31.766	7.281
800	10.668	63.238	8.191	-31.901	6.040
900	10.975	64.512	9.755	-32.020	5.066
1000	11.248	65.693	11.340	-32.123	4.291
1100	11.490	66.766	12.950	-32.215	3.651
1200	11.708	67.776	14.601	-32.294	3.117
1300	11.902	68.721	16.300	-32.366	2.665
1400	12.076	69.609	18.040	-32.429	2.275
1500	12.232	70.448	19.820	-32.487	1.938
1600	12.372	71.242	21.640	-32.542	1.642
1700	12.497	71.996	23.500	-32.592	1.380
1800	12.610	72.713	25.400	-32.640	1.147
1900	12.711	73.398	27.340	-32.687	0.938
2000	12.801	74.052	29.320	-32.732	0.750
2100	12.883	74.679	31.340	-32.777	0.580
2200	12.956	75.280	33.400	-32.824	0.425
2300	13.023	75.857	35.500	-32.870	0.283
2400	13.083	76.413	37.640	-32.918	0.153
2500	13.138	76.948	39.820	-32.969	0.033
2600	13.188	77.466	42.040	-33.020	0.000
2700	13.233	77.963	44.300	-33.074	0.000
2800	13.275	78.445	46.600	-33.130	0.000
2900	13.313	78.911	48.940	-33.189	0.000
3000	13.347	79.363	51.320	-33.251	0.000
3100	13.379	79.801	53.740	-33.314	0.000
3200	13.409	80.227	56.200	-33.381	0.000
3300	13.436	80.640	58.700	-33.451	0.000
3400	13.461	81.041	61.240	-33.523	0.000
3500	13.484	81.432	63.820	-33.599	0.000
3600	13.506	81.812	66.440	-33.678	0.000
3700	13.525	82.182	69.100	-33.761	0.000
3800	13.544	82.543	71.800	-33.846	0.000
3900	13.561	82.895	74.540	-33.935	0.000
4000	13.577	83.239	77.320	-34.027	0.000
4100	13.592	83.574	80.140	-34.123	0.000
4200	13.606	83.902	83.000	-34.223	0.000
4300	13.620	84.222	85.900	-34.322	0.000
4400	13.632	84.535	88.840	-34.428	0.000
4500	13.644	84.842	91.820	-34.536	0.000
4600	13.655	85.142	94.840	-34.647	0.000
4700	13.665	85.436	97.900	-34.762	0.000
4800	13.674	85.723	101.000	-34.883	0.000
4900	13.684	86.006	104.140	-35.009	0.000
5000	13.692	86.282	107.320	-35.142	0.000
5100	13.700	86.553	110.540	-35.281	0.000
5200	13.708	86.819	113.800	-35.426	0.000
5300	13.715	87.081	117.100	-35.576	0.000
5400	13.722	87.337	120.440	-35.731	0.000
5500	13.729	87.589	123.820	-35.891	0.000
5600	13.735	87.836	127.240	-36.056	0.000
5700	13.741	88.079	130.700	-36.226	0.000
5800	13.746	88.318	134.200	-36.401	0.000
5900	13.752	88.553	137.740	-36.581	0.000
6000	13.757	88.785	141.320	-36.766	0.000

Dec. 31, 1960; Sept. 30, 1965

Fluorosilane (H₃SiF)

(Ideal Gas) Mol. Wt. = 50.114

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	6.071	51.030	5.092	1.822	102.770	102.770	INFINITE
200	6.971	51.030	5.092	1.822	102.770	102.770	INFINITE
298	11.333	57.035	5.092	1.822	102.770	102.770	INFINITE
300	11.379	57.105	57.035	1.822	102.770	102.770	INFINITE
400	13.730	60.711	57.511	1.280	105.691	97.517	53.278
500	15.651	63.988	58.484	2.752	106.219	95.411	41.702
600	17.213	66.985	59.655	4.398	106.612	93.210	33.950
700	18.501	69.791	60.981	6.161	106.881	91.041	28.225
800	19.563	72.340	62.467	8.091	107.042	88.961	24.225
900	20.444	74.637	64.023	10.092	107.201	86.950	20.968
1000	21.173	76.629	65.655	12.174	107.263	84.930	18.364
1100	21.776	78.377	67.356	14.323	107.282	82.706	16.233
1200	22.245	80.094	69.025	16.527	107.268	80.381	14.566
1300	22.608	81.781	70.666	18.777	107.224	77.959	12.956
1400	22.865	83.441	72.280	21.066	107.166	75.439	11.667
1500	23.037	85.073	73.873	23.398	107.097	72.825	10.552
1600	23.125	86.684	75.444	25.738	107.023	70.119	9.577
1700	23.140	88.269	77.000	28.076	106.936	67.323	8.713
1800	23.077	89.821	78.543	30.506	106.838	64.469	7.953
1900	22.937	91.342	80.066	32.919	106.730	61.579	7.294
2000	22.727	92.837	81.600	35.346	106.605	58.675	6.741
2100	22.474	94.298	83.125	37.788	106.467	55.760	6.284
2200	22.193	95.731	84.644	40.244	106.317	52.834	5.924
2300	21.890	97.137	86.156	42.714	106.157	49.900	5.655
2400	21.572	98.519	87.664	45.177	105.988	46.975	5.475
2500	21.245	99.879	89.166	47.658	105.812	44.050	5.285
2600	20.900	101.218	90.664	50.147	105.630	41.125	5.088
2700	20.540	102.537	92.156	52.643	105.443	38.200	4.885
2800	20.160	103.837	93.644	55.143	105.250	35.275	4.678
2900	19.760	105.118	95.131	57.643	105.050	32.350	4.465
3000	19.340	106.380	96.616	60.142	104.845	29.425	4.248
3100	18.900	107.623	98.096	62.642	104.635	26.500	4.028
3200	18.440	108.847	99.571	65.142	104.420	23.575	3.805
3300	17.960	109.951	100.944	67.642	104.200	20.650	3.578
3400	17.460	110.936	102.313	70.142	103.975	17.725	3.348
3500	16.940	111.801	103.678	72.642	103.745	14.800	3.115
3600	16.400	112.547	105.031	75.142	103.510	11.875	2.880
3700	15.840	113.174	106.374	77.642	103.270	8.950	2.645
3800	15.260	113.691	107.707	80.142	103.025	6.025	2.410
3900	14.660	114.198	108.931	82.642	102.775	3.100	2.175
4000	14.040	114.696	110.146	85.142	102.520	0.175	1.940
4100	13.400	115.184	111.351	87.642	102.260	-2.750	1.705
4200	12.740	115.661	112.546	90.142	102.000	-5.675	1.470
4300	12.060	116.128	113.731	92.642	101.735	-8.600	1.235
4400	11.360	116.584	114.906	95.142	101.465	-11.525	1.000
4500	10.640	117.031	116.066	97.642	101.190	-14.450	0.765
4600	9.900	117.468	117.221	100.142	100.910	-17.375	0.530
4700	9.140	117.895	118.396	102.642	100.625	-20.300	0.295
4800	8.360	118.312	119.551	105.142	100.335	-23.225	0.060
4900	7.560	118.719	120.696	107.642	100.040	-26.150	-0.175
5000	6.740	119.116	121.831	110.142	99.740	-29.075	-0.410
5100	5.900	119.503	122.956	112.642	99.435	-32.000	-0.645
5200	5.040	119.880	124.071	115.142	99.125	-34.925	-0.880
5300	4.160	120.247	125.176	117.642	98.810	-37.850	-1.115
5400	3.260	120.604	126.271	120.142	98.490	-40.775	-1.350
5500	2.340	120.951	127.356	122.642	98.165	-43.700	-1.585
5600	1.400	121.288	128.431	125.142	97.835	-46.625	-1.820
5700	0.440	121.615	129.496	127.642	97.500	-49.550	-2.055
5800	-0.520	121.932	130.551	130.142	97.165	-52.475	-2.290
5900	-1.480	122.239	131.596	132.642	96.830	-55.400	-2.525
6000	-2.440	122.536	132.631	135.142	96.495	-58.325	-2.760

December 31, 1980.

FH₃Si

Fluorosilane (H₃SiF) (Ideal Gas)

Mol. Wt. = 50.114
 $\Delta H_f^\circ 298.15 = [-105 \pm 15] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = 57.04 \pm 2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Point group C_{3v}
 Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω_{cm}^{-1}	Deg.
2206 (1)	990 (1)
872 (1)	2196 (2)
943.4(2)	728.1(2)

Moments of Inertia: $I_A = 0.9784 \times 10^{-39} \text{ g. cm}^2$
 $I_B = 5.8578 \times 10^{-39} \text{ g. cm}^2$ $I_C = 5.8578 \times 10^{-39} \text{ g. cm}^2$
 $\sigma = 3$

Heat of Formation. $\Delta H_f^\circ 298.15$ was estimated in C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were found in Henderson and Scheffee, op. cit. Moments of Inertia were calculated using the constants found in C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, J. Chem. Phys. 25, 855 (1956).

FH₃Si

INTERIM TABLE

MOL. WT. = 219.61

(IDEAL GAS)

MERCUROUS FLUORIDE (HgF)

MOL. WT. = 219.61

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	0.000	∞	INFINITE	2.226	1.762	-	INFINITE
100	7.725	51.13	1.762	1.762	1.762	-	1.762
200	7.725	51.13	1.762	1.762	1.762	-	1.762
298	0.242	59.138	59.138	0.000	1.700	-	3.190
300	0.249	59.139	59.139	0.015	1.696	-	3.193
400	0.570	61.416	61.416	0.667	1.485	-	3.302
500	0.731	63.747	63.747	1.125	1.305	-	3.347
600	0.834	65.349	65.349	2.604	1.119	-	3.363
700	0.905	66.716	66.716	3.491	1.085	-	3.363
800	0.958	67.909	67.909	4.364	1.055	-	3.363
900	0.991	68.967	68.967	5.282	1.026	-	3.363
1000	0.936	69.917	69.917	6.164	1.000	-	3.363
1100	0.967	70.780	70.780	7.090	0.976	-	3.363
1200	0.995	71.570	71.570	7.998	0.958	-	3.363
1300	1.021	72.299	72.299	8.890	0.939	-	3.363
1400	1.045	72.976	72.976	9.766	0.922	-	3.363
1500	1.066	73.607	73.607	10.636	0.908	-	3.363
1600	1.084	74.200	74.200	11.505	0.895	-	3.363
1700	1.100	74.758	74.758	12.375	0.882	-	3.363
1800	1.115	75.285	75.285	13.245	0.870	-	3.363
1900	1.129	75.784	75.784	14.115	0.858	-	3.363
2000	1.142	76.254	76.254	15.000	0.846	-	3.363
2100	1.154	76.712	76.712	15.890	0.835	-	3.363
2200	1.165	77.145	77.145	16.785	0.825	-	3.363
2300	1.175	77.559	77.559	17.685	0.815	-	3.363
2400	1.184	77.956	77.956	18.590	0.805	-	3.363
2500	1.192	78.335	78.335	19.500	0.795	-	3.363
2600	1.199	78.706	78.706	20.415	0.785	-	3.363
2700	1.205	79.060	79.060	21.335	0.775	-	3.363
2800	1.210	79.402	79.402	22.260	0.765	-	3.363
2900	1.214	79.733	79.733	23.190	0.755	-	3.363
3000	1.217	80.054	80.054	24.125	0.745	-	3.363
3100	1.219	80.364	80.364	25.065	0.735	-	3.363
3200	1.220	80.665	80.665	26.010	0.725	-	3.363
3300	1.221	80.957	80.957	26.960	0.715	-	3.363
3400	1.221	81.241	81.241	27.915	0.705	-	3.363
3500	1.221	81.516	81.516	28.875	0.695	-	3.363
3600	1.220	81.787	81.787	29.840	0.685	-	3.363
3700	1.219	82.049	82.049	30.810	0.675	-	3.363
3800	1.217	82.305	82.305	31.785	0.665	-	3.363
3900	1.214	82.555	82.555	32.765	0.655	-	3.363
4000	1.210	82.798	82.798	33.750	0.645	-	3.363
4100	1.205	83.036	83.036	34.740	0.635	-	3.363
4200	1.200	83.269	83.269	35.735	0.625	-	3.363
4300	1.194	83.497	83.497	36.735	0.615	-	3.363
4400	1.187	83.720	83.720	37.740	0.605	-	3.363
4500	1.179	83.938	83.938	38.750	0.595	-	3.363
4600	1.170	84.152	84.152	39.765	0.585	-	3.363
4700	1.160	84.362	84.362	40.785	0.575	-	3.363
4800	1.149	84.567	84.567	41.810	0.565	-	3.363
4900	1.137	84.769	84.769	42.840	0.555	-	3.363
5000	1.124	84.967	84.967	43.875	0.545	-	3.363
5100	1.110	85.161	85.161	44.915	0.535	-	3.363
5200	1.095	85.352	85.352	45.960	0.525	-	3.363
5300	1.080	85.540	85.540	47.010	0.515	-	3.363
5400	1.064	85.725	85.725	48.065	0.505	-	3.363
5500	1.047	85.906	85.906	49.135	0.495	-	3.363
5600	1.030	86.084	86.084	50.210	0.485	-	3.363
5700	1.012	86.260	86.260	51.290	0.475	-	3.363
5800	0.994	86.433	86.433	52.375	0.465	-	3.363
5900	0.975	86.603	86.603	53.465	0.455	-	3.363
6000	0.955	86.771	86.771	54.560	0.445	-	3.363

December 31, 1961

Iodine Monofluoride (IF)

(Ideal Gas) Mol. wt. = 145.9028

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	(F ^o - H ₂₉₈ ^o)/T	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	INFINITE	2.176	- 22.192	- 22.192	INFINITE
100	6.983	48.396	1.481	- 22.209	- 24.285	53.071
200	7.473	53.359	.762	- 22.429	- 26.277	28.713
298	8.021	56.451	.400	- 22.648	- 28.611	20.611
300	8.030	56.451	.405	- 22.652	- 28.153	20.508
400	8.384	58.864	.837	- 24.801	- 29.885	16.328
500	8.601	60.760	1.687	- 30.116	- 30.650	13.397
600	8.763	62.341	2.555	- 30.113	- 30.757	11.203
700	8.841	63.696	3.434	- 30.108	- 30.865	9.648
800	8.915	64.882	4.322	- 30.104	- 30.973	8.461
900	8.973	65.936	5.217	- 30.099	- 31.083	7.548
1000	9.020	66.883	6.116	- 30.095	- 31.192	6.817
1100	9.061	67.745	7.020	- 30.090	- 31.292	6.219
1200	9.097	68.535	7.928	- 30.085	- 31.382	5.721
1300	9.130	69.265	8.840	- 30.080	- 31.473	5.299
1400	9.160	69.942	9.754	- 30.075	- 31.564	4.938
1500	9.188	70.575	10.672	- 30.069	- 31.655	4.625
1600	9.215	71.169	11.592	- 30.064	- 31.747	4.351
1700	9.241	71.729	12.515	- 30.058	- 31.840	4.110
1800	9.266	72.258	13.440	- 30.052	- 31.934	3.895
1900	9.290	72.759	14.368	- 30.046	- 32.028	3.703
2000	9.313	73.236	15.298	- 30.039	- 32.123	3.530
2100	9.336	73.691	16.231	- 30.032	- 32.218	3.374
2200	9.359	74.126	17.165	- 30.025	- 32.313	3.231
2300	9.381	74.543	18.102	- 30.018	- 32.408	3.103
2400	9.403	74.942	19.042	- 30.010	- 32.503	2.984
2500	9.425	75.327	19.983	- 30.003	- 32.598	2.874
2600	9.447	75.697	20.927	- 29.994	- 32.693	2.774
2700	9.468	76.054	21.872	- 29.986	- 32.788	2.680
2800	9.490	76.398	22.820	- 29.977	- 32.883	2.593
2900	9.511	76.732	23.770	- 29.968	- 32.978	2.513
3000	9.532	77.055	24.722	- 29.960	- 33.073	2.438
3100	9.553	77.367	25.677	- 29.950	- 33.168	2.367
3200	9.574	77.671	26.633	- 29.940	- 33.263	2.301
3300	9.595	77.966	27.591	- 29.930	- 33.358	2.239
3400	9.616	78.253	28.552	- 29.920	- 33.453	2.181
3500	9.636	78.532	29.515	- 29.909	- 33.548	2.126
3600	9.657	78.804	30.479	- 29.898	- 33.643	2.074
3700	9.678	79.068	31.446	- 29.887	- 33.738	2.024
3800	9.698	79.327	32.415	- 29.875	- 33.833	1.979
3900	9.719	79.579	33.386	- 29.863	- 33.928	1.935
4000	9.739	79.825	34.359	- 29.851	- 34.023	1.893
4100	9.760	80.066	35.333	- 29.839	- 34.118	1.853
4200	9.780	80.301	36.311	- 29.826	- 34.213	1.815
4300	9.801	80.532	37.290	- 29.812	- 34.308	1.779
4400	9.821	80.757	38.271	- 29.800	- 34.403	1.745
4500	9.842	80.978	39.254	- 29.786	- 34.498	1.712
4600	9.862	81.195	40.239	- 29.772	- 34.593	1.680
4700	9.882	81.407	41.226	- 29.758	- 34.688	1.650
4800	9.903	81.615	42.215	- 29.743	- 34.783	1.621
4900	9.923	81.820	43.207	- 29.728	- 34.878	1.594
5000	9.943	82.021	44.200	- 29.713	- 34.973	1.567
5100	9.964	82.218	45.195	- 29.698	- 35.068	1.542
5200	9.984	82.411	46.193	- 29.682	- 35.163	1.517
5300	10.004	82.602	47.192	- 29.666	- 35.258	1.494
5400	10.025	82.789	48.194	- 29.650	- 35.353	1.471
5500	10.045	82.973	49.197	- 29.633	- 35.448	1.449
5600	10.065	83.154	50.203	- 29.616	- 35.543	1.428
5700	10.085	83.332	51.210	- 29.599	- 35.638	1.408
5800	10.106	83.508	52.220	- 29.581	- 35.733	1.388
5900	10.126	83.681	53.231	- 29.563	- 35.828	1.370
6000	10.146	83.851	54.245	- 29.545	- 35.923	1.351

Mar. 31, 1962; Dec. 31, 1965

IODINE MONOFLUORIDE (IF)

MOL. WT. = 145.9028

(IDEAL GAS)

Ground State Configuration $[1 \Sigma^+]$
 $\Delta H_f^o = 56.451$ cal. deg.⁻¹ mole.⁻¹
 $\Delta H_f^o = -22.648 \pm 0.9$ kcal. mole.⁻¹

Electronic Levels and Quantum Weight

$$\frac{E_j}{\text{cm.}^{-1}} \quad \frac{g_j}{1}$$

$$\omega_e x_e = 4 \text{ cm.}^{-1}$$

$$\omega_e = 612 \text{ cm.}^{-1}$$

$$B_e = 0.2799 \text{ cm.}^{-1}$$

$$\alpha_e = 0.00763 \text{ cm.}^{-1}$$

$$r_e = 1.906 \text{ \AA}$$

$$\sigma^- = 1$$

Heat of Formation.

R. A. Durie and A. G. Gaydon, J. Phys. Chem. 56, 316 (1952), have obtained the dissociation limit (from the spectra) of IF as 23570 cm.⁻¹. The first excited states of F and I are 404 and 7599 cm.⁻¹ above the ground state respectively. There are two sets of dissociation products possible: $I(^2P_{1/2}) + F(^2P_{3/2})$ or $I(^2P_{3/2}) + F(^2P_{1/2})$. When corrected to the normal atoms, the observed limit gives $D_0(\text{IF}(g))$ 2.87 ± 0.04 e.v. or 66.18 ± 0.9 kcal. mole.⁻¹ and 1.96 ± 0.04 e.v. or 45.66 ± 0.9 kcal. mole.⁻¹ for dissociation energy respectively. Durie and Gaydon, loc. cit., favored the lower value. However L. Slutsky and S. H. Bauer, J. Am. Chem. Soc. 76, 270 (1954) have pointed out a numerical error in their calculations, which removes the chief support for the lower value and presented additional evidence favoring the higher value. More weight was given to the higher value which gives ΔH_f^o 59.15 = -22.648 ± 0.9 kcal. mole.⁻¹ for the reaction $1/2 I_2(c) + 1/2 F_2(g) = \text{IF}(g)$.

Heat Capacity and Entropy.

All molecular constants were obtained from W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. of Standards 55, 147 (1955) except $r_e = 1.906$ \AA was obtained from L. G. Cole and G. W. Elverum Jr., J. Chem. Phys. 20, 1543 (1952) and ground state configuration was estimated by comparison with that for IFr and ICl from G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., New York, 1950.

POTASSIUM FLUORIDE (KF)

GFW = 58.1004

(CRYSTAL)

Potassium Fluoride (KF)
(Crystal)

GFW = 58.1004

 $\Delta H_f^\circ = 16.905 \pm 0.05 \text{ gibbs/mol}$
 $T_m = 1131^\circ\text{K}$
 $\Delta H_f^\circ = -135.5 \pm 0.1 \text{ kcal/mol}$
 $\Delta H_f^\circ = -135.9 \pm 0.1 \text{ kcal/mol}$
 $\Delta H_m^\circ = 6.50 \text{ kcal/mol}$
 $\Delta H_m^\circ = 57.8 \text{ kcal/mol (to monomer)}$

Heat of Formation

The heat of solution of KF(c) in water has been measured by several investigators. Their results have been converted to ΔH_m° by Farker (5) and listed in the table below. Using $\Delta H_f^\circ = -4.24$, $\Delta H_f^\circ(\text{K}^+ \in \text{H}_2\text{O}) = -60.32$ (6), and $\Delta H_f^\circ(\text{F}^- \in \text{H}_2\text{O}) = -79.82 \text{ kcal/mol (7)}$, we obtain $\Delta H_f^\circ = -135.9 \pm 0.1 \text{ kcal/mol}$ which is adopted.

Investigator	Temperature, °K	Concentration, molality	No. of Determinations	ΔH_m° , kcal/mol
1. Guntz (1884)	291	0.28	1	-3.95
2. Forcrand (1911)	286	0.50	1	-4.54
3. Lange and Eichler (1927)	298	3.16 - 0.21	8	-4.24 ± 0.4
4. Lange and Martin (1937)	298	0.31	1	-4.01

Heat Capacity and Entropy

The low temperature heat capacities, 16-323°K, were measured by Westrum and Pitzer (8). The high temperature enthalpies, 298-530°K and 291-1187°K, were determined by Westrum and Pitzer (8), and Lyashenko (9), respectively. However, the high temperature Cp values derived from both sets appear to be inconsistent with the low temperature Cp values. The heat capacities derived from the enthalpy data of Westrum and Pitzer are too high (3% at 530°K and less at lower temperatures) to be joined smoothly with their low temperature Cp's. The adopted enthalpy at 530°K is about 1.4% lower than the reported value. The heat capacity derived from the enthalpy data of Lyashenko is 2.5% lower than the adopted one at 900°K. The differences are smaller at lower temperatures. At 900°K, the adopted enthalpy is 1.3% higher than the reported value. The adopted heat capacities in the temperature range, 323-2000°K, are estimated by graphical comparison with other alkali fluorides and chlorides, and joined smoothly with the low temperature data at 298°K.

S₂₉₈ is derived based on the adopted low temperature heat capacities.

Melting Data

See the KF(4) table.

Heat of Sublimation

The value of ΔH_{298}° is obtained as the difference between ΔH_f° for KF(c) and KF(g).

References

1. A. Guntz, Ann. Chim. et Phys. [6] 3, 5 (1884).
2. R. de Forcrand, Compt. Rend. 152, 1073 (1911).
3. E. Lange and A. Eichler, Z. Physik. Chem. 123, 285 (1927).
4. E. Lange and W. Martin, Z. Physik. Chem. 180, 233 (1937).
5. V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
6. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
7. JANAF table for HF(g) 12-31-68.
8. E. F. Westrum, Jr. and K. S. Pitzer, J. Am. Chem. Soc. 71, 1040 (1949).
9. V. S. Lyashenko, Metallurg (USSR) 10, 85 (1935).

Potassium Fluoride (KF)

(Liquid)

GFW = 58.1004

POTASSIUM FLUORIDE (KF)

(LIQUID)

GFW = 58.1004

$$S_{298.15}^{\circ} = 16.167 \text{ gibbs/mol}$$

$$\Delta H_f^{\circ}{}_{298.15} = -132.519 \text{ kcal/mol}$$

$$T_m = 1131^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 6.50 \text{ kcal/mol}$$

$$T_b = 1790^{\circ}\text{K}$$

$$\Delta H_v^{\circ}(\text{to mixture}) = 33.9 \text{ kcal/mol of liquid}$$

Heat of Formation

The $\Delta H_f^{\circ}{}_{298}(t)$ is obtained from $\Delta H_f^{\circ}{}_{298}(c)$ by adding ΔH_m° and the difference between H_{1131}° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those of the alkali fluorides and chlorides, and is assumed to be constant in the temperature range, 298-3000°K. The Cp value, 16 gibbs/mol, derived from the enthalpy data of Lyashenko (12) appears low and is not adopted.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Tm has been reported as 1119 (1, 2), 1129 (3, 4), 1131 (5, 6), and 1153°K (7). The value 1131°K is adopted. Kelley (8) evaluated the following freezing-point data of binary systems: KF-AlF₃ (9), KF-K₂SO₄ (10), KF-KCl (11), KF-K₂CO₃ (13), and KF-K₂PO₄ (14), and derived the values of ΔH_m° (in kcal/mol) as 5.5, 5.55, 6.51, 7.1, and 7.1 respectively. The best value is recommended as 6.50 kcal/mol. Other reported ΔH_m° values are 6.70 (7) and 6.75 ± 0.1 kcal/mol (12). The value of heat of melting is tentatively adopted as 6.50 kcal/mol.

Vaporization Data

The boiling point (Tb) is calculated to be the temperature at which the partial pressures of KF(g) and K₂F₂(g) equal one atmosphere. The composition of the gaseous mixture in equilibrium with KF(l) at Tb is calculated as K₂F₂ 21.1% and KF 78.9%. The heat required to vaporize one mole of liquid at Tb is evaluated to be 33.9 kcal. The experimental values for the boiling point are 1778°K (1) and 1771°K (15).

References

1. H. von Wartenberg and H. Schulz, Z. Elektrochem. **27**, 568 (1921).
2. B. S. Zakharova, L. P. Reshetnikova, and A. V. Novoselova, Vestn. Mosk. Univ., Ser. II **22**, 102 (1967).
3. O. Schmitz-Dumont and E. Schmitz, Z. Anorg. Chem. **252**, 329 (1944).
4. E. P. Dergunov and A. G. Bergman, Zh. Fiz. Khim. **22**, 625 (1948).
5. J. W. Johnson and H. A. Bradig, J. Phys. Chem. **62**, 604 (1958).
6. B. Porter and E. A. Brown, J. Am. Ceram. Soc. **45**, 49 (1962).
7. G. Petit and A. Crémieu, Compt. Rend. **243**, 360 (1956).
8. K. K. Kelley, U. S. Bur. Mines Bull. **393**, 1936.
9. N. A. Puchin and A. B. Baskov, J. Russ. Phys. Chem. Soc. **45**, 82 (1913); Z. Anorg. Chem. **81**, 347 (1913).
10. B. Karandeuff, Zentr. Min. Geol. **728**, 1909.
11. M. Plato, Z. Physik. Chem. **55**, 721 (1906).
12. V. S. Lyashenko, Metallurg (USSR) **10**, 85 (1935).
13. M. Amadori, Atti Accad. Lincei, Ser. 5, **22**, 366 (1913).
14. M. Amadori, Atti Accad. Lincei, Ser. 5, **21**, 688 (1912).
15. O. Ruff, G. Schmidt, and S. Hugdan, Z. Anorg. Allg. Chem. **123**, 83 (1922).

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	17.200	16.167	16.167	.000	-132.519	-125.508	92.000
300	17.200	16.273	16.167	-.032	-132.507	-125.465	91.401
400	17.200	21.222	16.882	1.752	-132.486	-123.101	67.259
500	17.200	25.060	16.116	3.472	-131.913	-120.821	52.611
600	17.200	28.196	19.542	5.192	-131.335	-116.656	43.221
700	17.200	30.687	20.973	6.432	-130.786	-112.409	36.109
800	17.200	32.544	22.344	7.612	-130.264	-108.105	30.309
900	17.200	35.170	23.668	10.352	-129.611	-112.692	27.345
1000	17.200	36.982	24.910	12.072	-129.055	-110.843	24.225
1100	17.200	38.621	26.003	13.792	-128.414	-108.024	21.402
1200	17.200	40.118	27.151	15.512	-127.693	-105.196	18.479
1300	17.200	41.583	28.264	17.192	-126.906	-102.366	15.459
1400	17.200	42.749	29.232	18.952	-126.052	-99.570	12.375
1500	17.200	43.956	30.175	20.672	-125.135	-96.201	9.241
1600	17.200	45.066	31.071	22.392	-124.159	-92.884	6.061
1700	17.200	46.109	31.925	24.112	-123.126	-89.516	2.841
1800	17.200	47.104	32.741	25.832	-122.036	-86.100	-0.421
1900	17.200	48.052	33.521	27.552	-120.887	-82.639	-3.641
2000	17.200	48.964	34.268	29.272	-119.681	-79.131	-6.861
2100	17.200	49.743	34.985	30.992	-118.418	-75.581	-10.081
2200	17.200	50.508	35.677	32.712	-117.100	-72.000	-13.301
2300	17.200	51.260	36.344	34.432	-115.728	-68.396	-16.521
2400	17.200	52.040	36.977	36.152	-114.303	-64.771	-19.741
2500	17.200	52.742	37.593	37.872	-112.826	-61.126	-22.961
2600	17.200	53.417	38.189	39.592	-111.297	-57.461	-26.181
2700	17.200	54.061	38.765	41.312	-109.716	-53.776	-29.401
2800	17.200	54.681	39.321	43.032	-108.084	-50.071	-32.621
2900	17.200	55.295	39.863	44.752	-106.400	-46.346	-35.841
3000	17.200	55.878	40.387	46.472	-104.665	-42.601	-39.061

Potassium Fluoride (KF) (Ideal Gas)

Ground State Configuration $1s^2$

$$\Delta H_f^\circ = -77.6 \pm 0.5 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 54.135 \pm 0.01 \text{ gibbs/mol}$$

$$\Delta H_{f298}^\circ = -78.1 \pm 0.5 \text{ kcal/mol}$$

GFW = 58.1004

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	$\frac{g_1}{0}$	$\frac{g_1}{1}$
$\omega_e = 426.04 \text{ cm}^{-1}$	$\omega_e x_e = 2.43 \text{ cm}^{-1}$	$\sigma = 1$
$B_e = 0.27994 \text{ cm}^{-1}$	$\alpha_e = 0.002335 \text{ cm}^{-1}$	$r_e = 2.17155 \text{ \AA}$

Heat of Formation

The total vapor pressures of KF(g) and $K_2F_2(g)$ over KF(s, l) have been determined by many investigators using the boiling point (1, 2, 5), Knudsen-effusion (3), transpiration (4), and torsion-effusion (5) methods. A method of trial and error is employed to select the appropriate values for $\Delta H_{f298}^\circ(\text{KF}, \text{c})$ and $\Delta H_{f298}^\circ(\text{KF}, \text{g})$ such that by use of these two values and $\Delta H_{f298}^\circ = 50 \text{ kcal/mol}$ for the reaction $K_2F_2(g) = 2\text{KF}(g)$ and the Gibbs energy functions for KF(c), KF(l), KF(g), and $K_2F_2(g)$, the calculated total pressures of KF(g) and $K_2F_2(g)$ are consistent with the measured ones. Adopting $\Delta H_{f298}^\circ = 37.8$ and $\Delta H_{f298}^\circ = 54.42 \text{ kcal/mol}$, we evaluate the partial pressures of KF(g) and $K_2F_2(g)$ from the reported total pressure measurements. Based on the derived partial pressures for KF(g), the enthalpy changes for the processes: A. KF(c) = KF(g), and B. KF(l) = KF(g) are calculated by the second and third law methods. Using the third law ΔH_{f298}° and $\Delta H_{f298}^\circ = -135.90$ and $-132.519 \text{ kcal/mol}$ for KF(c) and KF(l), respectively, we obtain the ΔH_{f298}° for KF(g). The results are presented in the table below.

The dissociation energy (D_0) of KF(g) has been determined as $117 \pm 8 \text{ kcal/mol}$ by flame photometry by Page and Sugden (2), and Bulewicz, Phillips, and Sugden (5), yielding $\Delta H_{f298}^\circ(\text{KF}, \text{g}) = -77.6 \pm 8 \text{ kcal/mol}$. Barrow and Caunt (3) measured the fluctuation bands in the ultraviolet absorption spectra of KF and reported the upper limit for the $D_0(\text{KF}, \text{g})$ value to be 121.8 kcal/mol which leads to $\Delta H_{f298}^\circ(\text{KF}, \text{g}) = -81.4 \text{ kcal/mol}$ as the lower limit. Gaydon (10) reported $D_0 = 116.9 \pm 4.6 \text{ kcal/mol}$ for KF(g). The corresponding value of ΔH_{f298}° is calculated as $-77.5 \pm 4.6 \text{ kcal/mol}$.

The heat of formation for KF(g) at 298°K is adopted as $-78.1 \pm 0.5 \text{ kcal/mol}$.

Investigator	Method	Temperature, °K	No. of Points	Process	ΔH° , kcal/mol	Drift	ΔH_{f298}° , kcal/mol
1. Wartenberg (1921)	boiling point	1624-1776	5	B	54.4 ± 0.9	54.16	-78.36
2. Ruff (1922)	boiling point	1551-1773	6	B	58.1 ± 2.5	54.14	-78.38
3. Nix (1938)	Knudsen-effusion	913-973	2	A	56.2 ± 0.3	55.67	-80.23
4. Maryshkin (1938)	transpiration	1023-1108	2	A	—	57.23	-78.67
5. Cantor (1958)	boiling point	1188-1233	2**	B	—	54.60	-77.92
6. Pugh (1958)	torsion-effusion	1200-1500	7*	B	54.4	54.38	-78.14
		910-1020	6*	A	57.7	58.12	-77.78

* Data points calculated from the given vapor pressure equation.

** The data point at 1233°K is adopted for evaluation.

Heat Capacity and Entropy

The rotational transition spectrum of KF(g) has been measured in the millimeter- and submillimeter-wave region with a high resolution molecular-beam absorption spectrometer by Veasey and Gordy (13). From the derived potential constants the vibrational constants were calculated. The reported values for ω_e , $\omega_e x_e$, B_e , α_e , and r_e are adopted.

Other values of ω_e reported are (in cm^{-1}): 390 ± 39 (11), 408 ± 28 (9), 429 ± 3 (12), and 426 ± 4 (13). The value of $\omega_e x_e$ has been determined as 1.45 cm^{-1} by Barrow and Caunt (3), and 2.4 cm^{-1} by Ritchie and Lew (12) and Baikov and Vasilevskii (13). Using the molecular beam electric resonance method, Green and Lew (14) measured the rotational transitions between the $J = 0$ and $J = 1$ states of K_2F_2 and reported the following values: $B_e = 0.27994 \text{ cm}^{-1}$, $\alpha_e = 0.002335 \text{ cm}^{-1}$, and $r_e = 2.17144 \pm 0.00005 \text{ \AA}$ which are in excellent agreement with the adopted values. By use of the same method, Grabner and Hughes (11) investigated the rotational Stark spectrum of K_2F_2 and reported the K-F bond distance for the zeroth vibrational state as $2.55 \pm 0.06 \text{ \AA}$.

References

1. H. von Wartenberg and H. Schulz, Z. Electrochem. 27, 568 (1921).
2. O. Ruff, G. Schmidt, and S. Hugdan, Z. Anorg. Allg. Chem. 123, 83 (1922).
3. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) A133, 270 (1931).
4. I. N. Maryshkin, Zh. Fiz. Khim. 12, 153 (1938).
5. S. Cantor and F. Blankenship, paper presented at the annual meeting of the American Chemical Society, Chicago, Sept. 7-12, 1958.
6. A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 671 (1958).
7. F. H. Page and T. H. Sugden, Nature 163, 1872 (1949).
8. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) A133, 270 (1931).
9. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) A133, 270 (1931).
10. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1968.
11. L. K. Ritchie and V. Hughes, Phys. Rev. 79, 819 (1950).
12. R. K. Ritchie and H. Lew, Can. J. Phys. 42, 43 (1964).
13. G. I. Baikov and K. P. Vasilevskii, Opt. Spektrosk. 22, 138 (1967).
14. G. I. Green and H. Lew, Can. J. Phys. 38, 482 (1960).
15. S. E. Veasey and W. Gordy, Phys. Rev. 136, 4303 (1965).

Dec. 31, 1961; Mar. 31, 1964; June 30, 1969

LITHIUM FLUORIDE (LiF)

(CRYSTAL)

GFW = 25.9374

Lithium Fluoride (LiF)

(Crystal)

GFW = 25.9374

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log Kp
0	3.000	0.000	INFINITE	1.547	146.837	146.837	INFINITE
100	3.063	1.161	15.761	1.460	147.122	147.122	317.164
200	7.840	4.945	9.375	0.886	147.433	147.433	103.113
298	9.994	8.523	8.523	0.000	147.433	147.433	103.113
300	10.023	8.585	8.583	0.019	147.449	140.454	102.466
400	11.124	11.681	8.932	1.084	147.390	138.396	75.616
500	11.790	14.197	9.737	2.230	147.065	135.060	59.481
600	12.330	16.395	10.627	3.437	147.088	133.689	48.696
700	12.780	18.324	11.576	4.695	147.655	131.316	40.999
800	13.230	20.040	12.576	6.003	147.672	128.966	35.232
900	13.770	21.677	13.500	7.359	147.445	126.641	30.753
1000	14.240	23.153	14.392	8.760	147.176	124.343	27.175
1100	14.700	24.532	15.252	10.208	146.863	122.075	24.254
1200	15.150	25.820	16.080	11.699	146.508	119.837	21.625
1300	15.599	27.024	16.877	13.230	146.114	117.630	19.775
1400	15.881	28.128	17.646	14.800	145.683	115.454	18.023
1500	16.230	29.325	18.388	16.406	145.216	113.311	16.509
1600	16.557	30.363	19.105	18.045	144.715	111.200	15.189
1700	16.864	31.268	19.798	19.716	144.180	109.120	13.958
1800	17.154	32.068	20.470	21.417	143.607	107.079	12.800
1900	17.405	32.782	21.121	23.144	142.997	105.072	11.702
2000	17.643	33.420	21.753	24.897	142.350	103.100	10.662
2100	17.859	34.007	22.366	26.672	141.666	101.159	9.680
2200	18.052	34.552	22.953	28.466	140.946	99.247	8.759
2300	18.224	35.070	23.523	30.282	140.193	97.363	7.917
2400	18.373	35.563	24.080	32.112	139.410	95.505	7.228
2500	18.500	36.040	24.628	33.956	138.599	93.675	6.597

Heat of Formation

The heats of solution and reaction of LiF(c) in water and hydrochloric acid have been measured by many investigators. The reported ΔH_{soln} values are listed in the table below. Using ΔH₂₉₈^o(Li⁺, ∞ H₂O) = -66.56 kcal/mol (8), and ΔH₂₉₈^o(F⁻, ∞ H₂O) = -79.82 kcal/mol (9), we calculate the corresponding ΔH₂₉₈^o values for LiF(c). Based on the heat of solution of LiOH(c) in excess HF solution measured by Sinko (7), the value, ΔH₂₉₈^o(LiF(c)) = -146.65 ± 0.5 kcal/mol is derived. The value of ΔH₂₉₈^o for LiF(c) is adopted as -147.45 ± 0.2 kcal/mol.

Investigator	Solvent	Temperature, °K	Concentration (LiF·nH ₂ O)	ΔH _r , kcal/mol	ΔH _f ^a , kcal/mol*	ΔH _f ^a , kcal/mol
1. de Forcrand (1911)	H ₂ O	289.2	unavailable	1.04	---	---
2. Kolesov-Skuratov (1961)	H ₂ O	294.7	3800 H ₂ O	1.25 ± 0.02	1.13 ± 0.05	-147.50
3. Wulff (1962)	HCl	298.2	unavailable	unavailable	1.10 ± 0.10	-147.47
4. Stephenson et al. (1964)	H ₂ O	298.2	2780-5560 H ₂ O	unavailable	1.07 ± 0.05	-147.44
5. Cox and Harrop (1964)	H ₂ O	298.2	50000 H ₂ O	1.059 ± 0.028	1.014 ± 0.055	-147.38

*The heat of dilution data of Parker (5) are used to convert ΔH_r to ΔH_f.

Heat Capacity and Entropy

Clusius, Goldman, and Perlick (10) measured the low temperature heat capacities in the temperature range 19 to 272°K and Clusius and Eichenauer (11) from 10 to 111°K. Below 20°K a number of investigators have reported values of θ_p, and the average value of 729 ± 6 is used here. The high temperature enthalpies from 298°K to the melting point 1121.3°K were measured by Douglas and Dever (12), and Voskresenskaya et al. (13). All these data are taken and smoothed by computer up to 400°K. Above 400°K the Cp values are obtained graphically by drawing a smooth line through the data points.

S₂₉₈ is derived from the adopted low temperature heat capacities, based on S₂₉₈^o = 0.064 eu.

Melting Data

See the LiF(4) table for details.

Heat of Sublimation

The difference between ΔH₂₉₈^o for LiF(g) and LiF(c) is ΔH_s^o₂₉₈.

References

1. R. de Forcrand, *Compt. Rend.* **152**, 27 (1911).
2. V. P. Kolesov and S. M. Skuratov, *Russ. J. Inorg. Chem. (English Transl.)* **6**, 889 (1961).
3. C. A. Wulff, Ph.D. Thesis, Massachusetts Institute of Technology, 1962.
4. C. C. Stephenson, H. P. Hopkins and C. A. Wulff, *J. Phys. Chem.* **68**, 1427 (1964).
5. J. D. Cox and D. Harrop, *Trans. Faraday Soc.* **61**, 1328 (1965).
6. V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965.
7. G. C. Sinko, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan, private communication, February 1959.
8. S. R. Gurn and L. G. Green, *J. Am. Chem. Soc.* **80**, 4782 (1958).
9. Derived from JANAF value of ΔH₂₉₈^o(HF,g), dated Dec. 31, 1968.
10. K. Clusius, J. Goldman, and A. Perlick, *Z. Naturforsch.* **43**, 424 (1949).
11. K. Clusius and W. Eichenauer, *Z. Naturforsch.* **2a**, 715 (1956).
12. T. B. Douglas and J. L. Dever, *J. Am. Chem. Soc.* **76**, 4826 (1954).
13. N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek, and N. E. Shmidt, *Acad. Nauk SSSR, Izvest. Sect. Fiz. Khim. Anal.* **27**, 233 (1956).

Lithium Fluoride (LiF)

GFW = 25.9374

$$S_{298.15}^{\circ} = 10.269 \text{ gibbs/mol}$$

$$\Delta H_f^{\circ}{}_{298.15} = -143.081 \text{ kcal/mol}$$

$$T_m = 1121.3 \pm 1.0^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 6.474 \pm 0.005 \text{ kcal/mol}$$

$$T_b = 1990^{\circ}\text{K}$$

$$\Delta H_v^{\circ}(\text{to mixture}) = 35.08 \text{ kcal/mol}$$

Heat of Formation

The $\Delta H_f^{\circ}{}_{298}(l)$ is obtained from $\Delta H_f^{\circ}{}_{298}(c)$ by adding ΔH_m° and the difference between $H_{1121.3}^{\circ}$ and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. **76**, 4876 (1954), and N. K. Voskresenskaya, V. A. Sokolov, E. I. Banashek, and N. E. Schmidt, Akad. Nauk SSSR, Izvest. Sek. Fiz. - Khim. Anal. **27**, 233 (1956), have measured the enthalpies of LiF liquid to 1200 and 1400°K, respectively. Using the reported enthalpy data, a constant heat capacity is derived for each set. The adopted C_p for LiF(l) is the mean of the two derived heat capacities, and is extended arbitrarily to the temperatures above T_b and below T_m . The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point has been determined by many investigators. See the table below for details. The adopted value, 1121.3 \pm 1.0°K, is that reported by Douglas and Dever, loc. cit. The heat of melting is the mean of the ΔH_m° values reported by Douglas and Dever, loc. cit., and Voskresenskaya et al., loc. cit.

T_m , °K	Source
1115	H. von Wartenberg and H. Schulz, Z. Elektrochem. 27 , 568 (1921).
1115	G. Petit and A. Cramieu, Compt. Rend. 243 , 360 (1956).
1119	H. Flood, V. Fyke, and S. Urnes, Z. Elektrochem. 59 , 364 (1955).
1120	V. P. Goryachava, A. G. Bergman, and A. G. Kislova, Zh. Neorg. Khim. 4 , 2744 (1959).
1121	H. M. Haendler, P. S. Sennett, and C. M. Wheeler, J. Electrochem. Soc. 106 , 264 (1959).
1121.2	Z. A. Matsko and G. A. Bukhalova, Zh. Neorg. Khim. 4 , 1649 (1959).
1121.3	T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. 76 , 4876 (1954).
1123	G. A. Bukhalova and D. V. Semantsova, Russ. J. Inorg. Chem. (English Transl.) 10 , 1027 (1965).

Vaporization Data

T_b is the temperature at which the partial pressures of LiF(g), $\text{Li}_2\text{F}_2(\text{g})$, and $\text{Li}_3\text{F}_3(\text{g})$, in equilibrium with LiF(l), equal one atmosphere. The vapor composition at the boiling point is evaluated as LiF 68%, Li_2F_2 26.6%, and Li_3F_3 4.4%. The heat required to vaporize one mole of liquid to form 0.739 mole of vapor mixture of the above composition at T_b is calculated to be 35.08 kcal.

The value of T_b for LiF(l) has been reported to be 1943 and 1949°K by O. Ruff, G. Schmidt, and S. Mugdan, Z. Anorg. Allgem. Chem. **223**, 83 (1922), and H. von Wartenberg and H. Schulz, loc. cit., respectively, which were obtained by extrapolation of their vapor pressure data, measured by the boiling point method.

T, °K	C_p°	$\frac{\text{gibbs/mol}}{S^{\circ}}$	$-(G^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$	$\frac{\text{kcal/mol}}{\Delta H^{\circ}}$	ΔC_p°	Log Kp
100							
200							
298	15.340	10.269	10.269	0.000	143.081	136.647	100.311
300	15.340	10.343	10.269	0.028	143.071	136.609	99.665
400	15.340	10.776	10.870	1.562	142.543	134.602	73.652
500	15.340	18.200	12.007	3.096	142.630	132.846	58.047
600	15.340	20.996	13.279	4.630	142.425	130.687	47.275
700	15.340	23.161	14.555	7.189	142.008	127.165	34.740
800	15.340	25.000	15.825	9.232	141.400	123.648	27.023
900	15.340	27.216	16.958	10.766	140.601	121.952	24.230
1000	15.340	28.632	18.066				
1100	15.340	30.284	19.112	12.200	140.401	118.646	19.950
1200	15.340	31.689	20.100	13.638	139.001	117.070	16.275
1300	15.340	32.994	21.021	16.902	139.212	115.502	16.829
1400	15.340	33.994	21.921	16.902	139.212	115.502	16.829
1500	15.340	35.052	22.761	18.436	136.616	113.960	15.568
1600	15.340	36.052	23.561	19.970	136.421	107.448	13.051
1700	15.340	36.972	24.320	21.008	132.693	103.690	11.980
1800	15.340	37.818	25.048	22.572	131.922	100.325	10.963
1900	15.340	38.678	25.746	24.106	131.349	96.769	10.073
2000	15.340	39.465	26.412	26.412	130.812	89.796	9.252
2100	15.340	40.214	27.052	27.640	130.212	86.335	7.662
2200	15.340	40.927	27.666	29.174	129.548	82.698	7.247
2300	15.340	41.600	28.250	30.698	128.824	79.485	6.661
2400	15.340	42.242	28.808	32.242	128.054	76.154	6.154
2500	15.340	42.668	29.378	33.776	127.176	69.366	5.228
2600	15.340	43.490	29.909	35.310	126.197	65.033	4.810
2700	15.340	44.069	30.423	36.844	125.122		
2800	15.340	44.662	30.922	38.378	123.952		
2900	15.340	45.265	31.402	39.912	122.683		
3000	15.340	45.655	31.870	41.446	121.316		

Des. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	INFINITE	2.588	-21.390	-21.390	INFINITE
100	8.029	49.124	1.792	-21.417	-22.043	48.173
200	10.004	90.676	4.863	-21.473	-22.669	44.843
298	10.295	109.775	8.000	-22.000	-22.923	10.802
300	10.307	58.839	-0.019	-22.005	-22.929	16.703
400	11.331	61.953	1.104	-22.282	-23.104	12.672
500	12.501	64.562	2.274	-23.299	-23.315	10.191
600	12.502	66.800	3.502	-23.577	-23.291	8.483
700	12.824	68.753	4.770	-23.824	-23.225	7.251
800	13.052	70.481	6.000	-24.054	-23.124	6.317
900	13.217	72.028	7.378	-24.276	-22.994	5.583
1000	13.339	73.427	8.766	-24.494	-22.839	4.991
1100	13.433	74.703	10.065	-24.709	-22.664	4.503
1200	13.505	75.875	11.392	-24.922	-22.469	4.092
1300	13.563	76.958	12.715	-25.135	-22.255	3.741
1400	13.609	77.965	14.040	-25.346	-22.026	3.438
1500	13.646	78.905	15.467	-25.558	-21.781	3.173
1600	13.678	79.787	16.832	-25.768	-21.522	2.940
1700	13.704	80.617	18.202	-25.968	-21.258	2.741
1800	13.725	81.401	19.574	-26.157	-20.982	2.561
1900	13.744	82.144	20.947	-26.336	-20.695	2.412
2000	13.760	82.844	22.322	-26.508	-20.398	2.282
2100	13.774	83.521	23.699	-26.673	-20.092	2.173
2200	13.786	84.162	25.077	-26.832	-19.776	2.076
2300	13.796	84.775	26.456	-26.985	-19.451	1.991
2400	13.805	85.362	27.836	-27.132	-19.116	1.916
2500	13.813	85.926	29.217	-27.273	-18.772	1.851
2600	13.821	86.468	30.599	-27.408	-18.419	1.794
2700	13.827	86.990	32.000	-27.538	-18.058	1.744
2800	13.833	87.493	33.364	-27.663	-17.688	1.700
2900	13.838	87.978	34.748	-27.783	-17.308	1.662
3000	13.843	88.447	36.132	-27.898	-16.918	1.629
3100	13.847	88.901	37.517	-27.999	-16.518	1.600
3200	13.851	89.341	38.904	-28.095	-16.108	1.574
3300	13.855	89.767	40.287	-28.186	-15.688	1.551
3400	13.858	90.181	41.673	-28.272	-15.258	1.529
3500	13.861	90.583	43.058	-28.353	-14.818	1.508
3600	13.864	90.973	44.445	-28.429	-14.368	1.488
3700	13.866	91.353	45.831	-28.500	-13.908	1.468
3800	13.868	91.723	47.218	-28.566	-13.438	1.448
3900	13.871	92.083	48.605	-28.627	-12.958	1.428
4000	13.873	92.434	49.992	-28.683	-12.468	1.408
4100	13.876	92.777	51.379	-28.734	-11.968	1.388
4200	13.878	93.111	52.767	-28.780	-11.458	1.368
4300	13.878	93.438	54.155	-28.821	-10.938	1.348
4400	13.879	93.757	55.542	-28.858	-10.408	1.328
4500	13.881	94.069	56.930	-28.890	-9.868	1.308
4600	13.882	94.374	58.310	-28.917	-9.318	1.288
4700	13.883	94.673	59.707	-28.940	-8.758	1.268
4800	13.884	94.965	61.095	-28.958	-8.188	1.248
4900	13.885	95.251	62.484	-28.972	-7.608	1.228
5000	13.886	95.532	63.872	-28.982	-7.018	1.208
5100	13.887	95.807	65.261	-28.988	-6.418	1.188
5200	13.888	96.076	66.650	-28.990	-5.808	1.168
5300	13.889	96.341	68.039	-28.988	-5.188	1.148
5400	13.890	96.600	69.428	-28.982	-4.558	1.128
5500	13.891	96.855	70.817	-28.972	-3.918	1.108
5600	13.891	97.104	72.206	-28.958	-3.268	1.088
5700	13.892	97.352	73.595	-28.940	-2.608	1.068
5800	13.893	97.593	74.984	-28.917	-1.938	1.048
5900	13.893	97.831	76.373	-28.886	-1.258	1.028
6000	13.894	98.064	77.763	-28.851	-0.568	1.008

Dec. 31, 1960; Sept. 30, 1965

$\Delta H_f^\circ = [-21 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta F_f^\circ = [-22 \pm 10] \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = [58.775] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

$\omega_e, \text{cm.}^{-1}$	Deg.
[800] (1)	1
[500] (1)	1
[950] (1)	1

Bond Distances: Li-O = [1.59] Å P-O = [1.41] Å

Bond Angle: P-O-Li = [104]°

$\sigma^- = 1$

Product of the Moments of Inertia: $I_{A,B,C} = [4.21884 \times 10^{-116}] \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation ($\Delta H_f^\circ 298.15$) for LiFO(g) was calculated from $\Delta H_f^\circ 298.15 = 139 \text{ kcal. mole}^{-1}$ for the reaction $\text{LiFO(g)} = \text{Li(g)} + \text{F(g)} + \text{O(g)}$ where the value of $\Delta H_f^\circ 298.15$ was estimated to be the sum of the P-O and Li-O bond energies. The values of the P-O and Li-O bond energies were obtained from those in $\text{P}_2\text{O(g)}$ and $\text{Li}_2\text{O(g)}$ molecules, respectively.

Heat Capacity and Entropy.

The P-O and Li-O bond distances were assumed to be the same as those in $\text{P}_2\text{O(g)}$ and $\text{Li}_2\text{O(g)}$ molecules, respectively. The P-O-Li bond angle and vibrational frequencies were estimated by comparison with the corresponding values for the same oxide molecules. The three principal moments of inertia are: $I_A = 5.1543 \times 10^{-39}$, $I_B = 1.2729 \times 10^{-39}$ and $I_C = 6.4272 \times 10^{-39} \text{ g. cm.}^2$

Magnesium Monofluoride (MgF)

(Ideal Gas) GFW = 43.3104

T, K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	6.200	0.00	INF.MITE	2.143	-52.992	-52.992	INF.MITE
100	6.892	46.892	59.371	1.484	-52.798	-55.726	120.258
200	7.280	40.789	53.497	.740	-53.002	-57.293	42.613
298	7.782	52.791	52.791	.000	-53.100	-59.284	43.459
300	7.790	52.830	52.791	.041	-53.104	-59.274	43.210
400	8.168	52.136	52.132	.911	-53.103	-59.274	37.532
500	8.413	56.987	53.700	1.648	-53.519	-61.163	27.696
600	8.574	58.536	54.350	2.494	-53.754	-65.311	23.789
700	8.584	59.866	55.071	3.357	-54.009	-67.214	20.986
800	8.562	61.021	55.755	4.220	-54.295	-69.384	18.873
900	8.512	62.031	56.391	5.083	-54.603	-71.804	16.966
1000	8.466	62.959	57.006	5.991	-54.991	-74.525	15.650
1100	8.405	63.846	57.590	6.889	-55.451	-77.559	14.713
1200	8.326	64.622	58.144	7.774	-55.934	-80.945	13.759
1300	8.236	65.304	58.670	8.643	-56.433	-84.666	12.784
1400	8.136	65.896	59.167	9.494	-56.946	-88.704	11.793
1500	8.035	66.424	59.637	10.346	-57.472	-93.067	11.242
1600	7.924	67.206	60.101	11.367	-58.150	-97.761	10.430
1700	7.801	67.754	60.536	12.271	-58.202	-102.784	9.714
1800	7.678	68.211	60.931	13.155	-58.255	-107.134	9.077
1900	7.556	68.571	61.294	14.019	-58.308	-111.804	8.504
2000	7.435	68.856	61.632	14.864	-58.360	-116.784	7.992
2100	7.309	69.670	62.099	15.899	-58.413	-122.327	7.527
2200	7.111	70.094	62.453	16.800	-58.466	-128.166	7.104
2300	6.915	70.451	62.781	17.674	-58.519	-134.284	6.719
2400	6.715	70.787	63.093	18.531	-58.572	-140.684	6.363
2500	6.517	71.261	63.441	19.344	-58.625	-147.359	6.037
2600	6.319	71.620	63.749	20.111	-58.680	-154.284	5.735
2700	6.169	71.965	64.027	21.381	-58.735	-161.466	5.456
2800	6.024	72.291	64.274	22.614	-58.787	-168.896	5.196
2900	5.884	72.604	64.504	23.814	-58.840	-176.574	4.954
3000	5.750	72.933	64.848	25.135	-58.906	-184.496	4.729
3100	5.621	73.235	65.132	26.454	-58.965	-192.666	4.518
3200	5.493	73.528	65.410	27.874	-59.027	-201.084	4.319
3300	5.369	73.807	65.679	29.284	-59.089	-209.759	4.134
3400	5.253	74.087	65.929	30.684	-59.150	-218.684	3.957
3500	5.143	74.356	66.161	32.074	-59.212	-227.859	3.792
3600	5.038	74.616	66.373	33.449	-59.274	-237.284	3.635
3700	4.938	74.870	66.559	34.809	-59.335	-246.959	3.487
3800	4.842	75.119	66.724	36.154	-59.396	-256.884	3.343
3900	4.750	75.359	66.874	37.484	-59.457	-267.059	3.213
4000	4.662	75.594	67.024	38.804	-59.518	-277.484	3.086
4100	4.578	75.828	67.154	40.114	-59.579	-288.159	2.965
4200	4.498	76.058	67.274	41.414	-59.639	-299.084	2.849
4300	4.422	76.284	67.384	42.704	-59.699	-310.259	2.737
4400	4.350	76.504	67.484	44.004	-59.759	-321.684	2.629
4500	4.282	76.719	67.574	45.294	-59.819	-333.359	2.524
4600	4.218	76.929	67.659	46.574	-59.879	-345.284	2.424
4700	4.158	77.134	67.734	47.844	-59.939	-357.459	2.328
4800	4.102	77.334	67.804	49.104	-59.999	-369.884	2.236
4900	4.049	77.529	67.864	50.354	-60.059	-382.559	2.148
5000	4.000	77.719	67.914	51.604	-60.119	-395.484	2.064
5100	3.954	77.904	67.954	52.844	-60.179	-408.659	2.010
5200	3.911	78.084	67.984	54.074	-60.239	-422.084	1.954
5300	3.870	78.259	68.004	55.294	-60.299	-435.759	1.894
5400	3.831	78.429	68.014	56.504	-60.359	-449.684	1.834
5500	3.794	78.594	68.014	57.704	-60.419	-463.859	1.774
5600	3.760	78.754	68.004	58.894	-60.479	-478.284	1.714
5700	3.728	78.909	67.984	60.074	-60.539	-492.959	1.655
5800	3.698	79.059	67.954	61.244	-60.599	-507.884	1.595
5900	3.670	79.204	67.914	62.404	-60.659	-523.059	1.535
6000	3.644	79.344	67.864	63.554	-60.719	-538.484	1.475

MAGNESIUM MONOFLUORIDE (MgF) (IDEAL GAS) OPW = 43.3104 FMG

Ground State Configuration 2Σ $\Delta H_f^\circ = -53.0 \pm 1.3$ kcal/mol $\Delta H_{298.15}^\circ = -53.1 \pm 1.3$ kcal/mol

$S_{298.15}^\circ = 52.791$ gibbs/mol $\Delta H_{298.15}^\circ = -53.1 \pm 1.3$ kcal/mol

Electronic Levels and Quantum Heights

$$\frac{E_i}{\text{cm}^{-1}} - \frac{E_0}{2}$$

$w_e = 717.6 \text{ cm}^{-1}$ $\sigma = 1$

$B_e = 0.5199 \text{ cm}^{-1}$ $r_e = 1.752 \text{ \AA}$

Heat of Formation

The equilibrium constants for the decomposition of MgF(g) into Mg(g), MgF₂(c) and MgF₂(g) were determined by T. C. Ehler, Ph.D. Thesis, University of Wisconsin, 1963. Using this data, the heats of decomposition are evaluated by both the third and second law methods. The results are presented in the table below. The equilibrium constants for the reaction $\text{AlF}_3(\text{g}) + 2\text{Mg}(\text{g}) \rightarrow \text{AlF}(\text{g}) + 2\text{MgF}(\text{g})$ were also reported by T. C. Ehler, loc. cit. The heat of reaction is calculated by the third and second law methods, respectively. The dissociation energy (D_0°) of MgF(g) was reported to be 3.2 ± 0.7 and 4.2 eu by A. O. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953, and G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., 1950, respectively. The corresponding values of $\Delta H_{298.15}^\circ$ for MgF(g) are derived. The results are also listed in the table. The value of $\Delta H_{298.15}^\circ$ for MgF(g) adopted is the average of the first two $\Delta H_{298.15}^\circ$ values.

Investigator	Chemical Reaction	Third Law Value	Second Law Value	$\Delta H_{298.15}^\circ$ kcal/mol
T. C. Ehler	$2\text{MgF}(\text{g}) = \text{Mg}(\text{g}) + \text{MgF}_2(\text{g})$	-54.76 ± 0.74	-70 ± 19	$-52.8 \pm 1.3^*$
	$2\text{MgF}(\text{g}) = \text{Mg}(\text{g}) + \text{MgF}_2(\text{c})$	-126.66 ± 0.80	-92 ± 21	$-53.4 \pm 1.2^*$
G. Herzberg	$\text{AlF}_3(\text{g}) + 2\text{Mg}(\text{g}) = \text{AlF}(\text{g}) + 2\text{MgF}(\text{g})$	18.66 ± 0.40	2.7 ± 3.2	$-67.7 \pm 1.0^*$
A. O. Gaydon	$\text{MgF}(\text{g}) \rightarrow \text{Mg}(\text{g}) + \text{F}(\text{g})$	$D_0^\circ = 4.2 \text{ eV}$		-42.6 ± 16.1
	$\text{MgF}(\text{g}) \rightarrow \text{Mg}(\text{g}) + \text{F}(\text{g})$	$D_0^\circ = 3.2 \pm 0.7 \text{ eV}$		

*Based on $\Delta H_{298.15}^\circ$ value by the third law method.

Heat Capacity and Entropy

All the molecular constants are taken from G. Herzberg, loc. cit., except α_e which is estimated.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T cal. mole ⁻¹ deg. ⁻¹	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0	0.000	INFINITE	2.090	59.501	59.501	INFINITE
100	6.957	43.760	57.715	1.394	59.504	129.091
200	7.007	48.590	52.081	- .608	59.501	58.636
298	7.253	51.427	51.427	0.000	59.500	58.212
300	7.259	51.472	51.427	0.013	59.500	58.204
400	7.400	55.407	46.973	5.435	59.500	57.752
500	7.513	55.339	32.773	1.533	59.531	57.334
600	8.156	56.804	52.909	2.337	59.563	56.893
700	8.340	58.075	53.558	3.162	59.599	56.445
800	8.480	59.199	54.194	4.003	59.635	55.991
900	8.584	60.111	54.777	4.848	59.668	55.535
1000	8.674	61.113	55.393	5.720	59.704	55.072
1100	8.743	61.944	55.951	6.591	59.736	54.607
1200	8.799	62.707	56.483	7.468	59.764	54.139
1300	8.846	63.413	56.989	8.351	59.790	53.670
1400	8.885	64.064	57.467	9.231	59.814	53.200
1500	8.922	64.684	57.932	10.126	59.833	52.726
1600	8.953	65.261	58.373	11.022	59.851	52.251
1700	8.981	65.805	58.794	11.918	59.867	51.775
1800	9.006	66.316	59.198	12.818	59.881	51.298
1900	9.028	66.794	59.584	13.720	59.894	50.816
2000	9.050	67.270	59.958	14.623	59.906	50.345
2100	9.070	67.712	60.317	15.529	59.916	49.865
2200	9.088	68.134	60.663	16.437	59.924	49.387
2300	9.106	68.539	60.997	17.347	59.932	48.907
2400	9.122	68.928	61.320	18.258	59.939	48.427
2500	9.138	69.299	61.631	19.171	59.944	47.949
2600	9.154	69.658	61.933	20.086	59.949	47.469
2700	9.169	70.004	62.225	21.002	59.953	46.989
2800	9.183	70.336	62.500	21.919	59.957	46.509
2900	9.197	70.656	62.765	22.839	59.960	46.029
3000	9.211	70.972	63.052	23.759	59.961	45.547
3100	9.224	71.274	63.313	24.681	59.963	45.067
3200	9.237	71.567	63.566	25.604	59.963	44.587
3300	9.250	71.852	63.813	26.528	59.963	44.104
3400	9.262	72.129	64.054	27.453	59.963	43.623
3500	9.276	72.397	64.288	28.381	59.962	43.145
3600	9.286	72.658	64.517	29.309	59.961	42.666
3700	9.300	72.911	64.740	30.239	59.959	42.184
3800	9.312	73.161	64.959	31.169	59.957	41.705
3900	9.324	73.406	65.172	32.099	59.954	41.226
4000	9.336	73.639	65.381	33.034	59.951	40.745
4100	9.348	73.870	65.585	33.968	59.947	40.263
4200	9.359	74.095	65.785	34.904	59.943	39.785
4300	9.371	74.316	65.981	35.840	59.940	39.304
4400	9.383	74.531	66.173	36.776	59.936	38.823
4500	9.394	74.742	66.361	37.717	59.932	38.345
4600	9.405	74.949	66.545	38.657	59.924	37.865
4700	9.417	75.151	66.726	39.598	59.918	37.386
4800	9.428	75.350	66.904	40.540	59.912	36.906
4900	9.439	75.544	67.078	41.483	59.905	36.427
5000	9.450	75.735	67.250	42.428	59.898	35.946
5100	9.461	75.922	67.418	43.373	59.891	35.467
5200	9.473	76.106	67.583	44.320	59.884	34.991
5300	9.484	76.287	67.746	45.268	59.875	34.510
5400	9.495	76.464	67.906	46.217	59.867	34.031
5500	9.506	76.638	68.063	47.167	59.858	33.557
5600	9.517	76.810	68.217	48.118	59.849	33.075
5700	9.528	76.978	68.370	49.070	59.839	32.601
5800	9.539	77.144	68.519	50.024	59.829	32.122
5900	9.550	77.307	68.667	50.978	59.818	31.643
6000	9.560	77.468	68.812	51.933	59.807	31.163

Dec. 31, 1960; June 30, 1965

NITROGEN MONOFLUORIDE (NF)

(IDEAL GAS)

MOL. WT. = 33.0051

Ground State Configuration [$\frac{1}{2}^-$]
 $S_{298.15}^\circ = 51.427$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^\circ = 59.5 \pm 8$ kcal. mole⁻¹
 $\Delta H_f^\circ = 59.5 \pm 8$ kcal. mole⁻¹

Electronic Levels and Quantum Weight

$$\frac{\sum_i \epsilon_i \exp(-\epsilon_i/kT)}{0} \frac{g_1}{3}$$

$\nu_0 = 1115$ cm.⁻¹
 $B_0 = [-.923]$ cm.⁻¹
 $\nu_0 x_0 = [12.175]$
 $\Delta_0 = [-.0120]$
 $r_0 = [1.51 \text{ \AA}]$
 $\sigma = 1$

Heat of Formation.

The heat of formation was obtained by taking an average of two estimates of the dissociation energy of NF. The first estimate of 3.15 e.v. (72.4 kcal./mole) was obtained from W. C. Price, T. R. Pasmore and D. M. Roessler Discussions Faraday Soc. 55, 201 - 11 (1953). The second estimate of 70.4 kcal./mole was obtained by taking one-half the dissociation energy of NF₂ (g) calculated from JANAF values. The ΔH_f° 298.15 for NF (g) was then calculated with auxiliary JANAF data from a dissociation energy of 71.4 kcal./mole.

Heat Capacity and Entropy.

The M_e value was obtained from infrared studies of D. E. Milligan and M. E. Jacox, J. Chem. Phys. 40, 2461 (1964). The r_0 value was estimated from Guggenheimer's relation for single bonded molecules. [K. M. Guggenheimer, Proc. Phys. Soc. (London), 59, 456 (1946)] The anharmonicity constant x_0 was estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The Δ_0 value was then calculated using the Morse potential function; B was determined from the bond length. The ground state configuration was assumed to be the same as that in NBr. The principal moment of inertia is 3.05247×10^{-39} g. cm.²

Nitrosyl Fluoride (ONF)

(Ideal Gas) Mol. Wt. = 49.01

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	2.554	15.129	INFINITE	INFINITE
100	5.000	55.532	1.923	15.129	13.213	14.438
200	9.866	55.532	1.923	15.129	13.213	14.438
298	14.683	55.532	1.923	15.129	13.213	14.438
300	9.699	55.274	0.014	15.702	12.001	6.742
400	11.229	64.731	2.143	15.786	9.502	2.677
500	11.646	66.822	3.290	15.790	8.244	3.003
600	12.055	68.652	4.477	15.780	6.987	2.181
700	12.452	70.262	5.698	15.763	5.733	1.566
800	12.832	71.661	6.946	15.740	4.480	1.066
900	13.191	72.961	8.215	15.714	3.230	0.666
1000	13.534	74.184	9.501	15.687	1.983	0.394
1100	13.861	75.334	10.802	15.659	0.738	0.134
1200	14.175	76.444	12.114	15.632	0.504	0.085
1300	14.478	77.517	13.437	15.606	0.272	0.042
1400	14.771	78.556	14.767	15.581	0.043	0.000
1500	15.053	79.564	16.103	15.559	0.000	0.000
1600	15.326	80.544	17.446	15.537	0.000	0.000
1700	15.591	81.498	18.794	15.519	0.000	0.000
1800	15.848	82.431	20.145	15.500	0.000	0.000
1900	16.097	83.347	21.501	15.480	0.000	0.000
2000	16.339	84.241	22.859	15.460	0.000	0.000
2100	16.574	85.116	24.221	15.444	0.000	0.000
2200	16.802	85.974	25.583	15.428	0.000	0.000
2300	17.023	86.817	26.945	15.413	0.000	0.000
2400	17.237	87.646	28.316	15.400	0.000	0.000
2500	17.444	88.461	29.688	15.388	0.000	0.000
2600	17.644	89.264	31.059	15.377	0.000	0.000
2700	17.837	90.056	32.432	15.368	0.000	0.000
2800	18.023	90.837	33.805	15.360	0.000	0.000
2900	18.202	91.608	35.168	15.353	0.000	0.000
3000	18.374	92.369	36.556	15.348	0.000	0.000
3100	18.540	93.121	37.933	15.345	0.000	0.000
3200	18.699	93.864	39.310	15.343	0.000	0.000
3300	18.852	94.599	40.689	15.342	0.000	0.000
3400	19.000	95.326	42.066	15.342	0.000	0.000
3500	19.143	96.046	43.444	15.343	0.000	0.000
3600	19.281	96.759	44.828	15.345	0.000	0.000
3700	19.414	97.466	46.209	15.348	0.000	0.000
3800	19.542	98.167	47.586	15.352	0.000	0.000
3900	19.665	98.862	48.972	15.357	0.000	0.000
4000	19.783	99.552	50.355	15.363	0.000	0.000
4100	19.896	100.237	51.737	15.370	0.000	0.000
4200	19.999	100.917	53.121	15.378	0.000	0.000
4300	20.102	101.592	54.508	15.387	0.000	0.000
4400	20.205	102.263	55.898	15.397	0.000	0.000
4500	20.307	102.929	57.292	15.408	0.000	0.000
4600	20.409	103.591	58.688	15.420	0.000	0.000
4700	20.510	104.248	60.084	15.433	0.000	0.000
4800	20.611	104.901	61.477	15.447	0.000	0.000
4900	20.712	105.550	62.866	15.462	0.000	0.000
5000	20.813	106.195	64.251	15.478	0.000	0.000
5100	20.914	106.836	65.632	15.495	0.000	0.000
5200	21.015	107.473	67.009	15.513	0.000	0.000
5300	21.116	108.106	68.382	15.532	0.000	0.000
5400	21.217	108.735	69.751	15.552	0.000	0.000
5500	21.318	109.360	71.116	15.573	0.000	0.000
5600	21.419	110.000	72.477	15.595	0.000	0.000
5700	21.520	110.635	73.834	15.618	0.000	0.000
5800	21.621	111.266	75.187	15.642	0.000	0.000
5900	21.722	111.892	76.536	15.667	0.000	0.000
6000	21.823	112.514	77.881	15.693	0.000	0.000

(IDEAL GAS)

NITROSYL FLUORIDE (ONF)

MOL. WT. = 49.01

 $\Delta H_f^\circ = -15.1 \pm 0.4$ kcal. mole⁻¹ $\Delta H_f^\circ = -15.7 \pm 0.4$ kcal. mole⁻¹Point group C_s $S_{298.15}^\circ = 59.273$ cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

 ω , cm.⁻¹

1844.03 (1)

521 (1)

755.85 (1)

Bond lengths and angles: N-O distance = 1.13 Å N-F distance = 1.52 Å O-N-F angle = 110.2°

Moments of inertia: I_A = 9.8135 X 10⁻⁴⁰ g. cm.² I_B = 70.8354 X 10⁻⁴⁰ g. cm.² I_C = 79.8375 X 10⁻⁴⁰ g. cm.²O_r = 1

Heat of Formation

For the reaction 2NO(g) + F₂(g) → 2ONF(g), H. S. Johnston and H. J. Bertin, J. Am. Chem. Soc. 81, 8402 (1959), report ΔH_f° 298.15 = -74.8 ± 0.8 kcal., determined calorimetrically. This yields -15.7 ± 0.4 kcal. mole⁻¹ for ΔH_f° 298.15°.

Heat Capacity and Entropy

C. V. Stephenson and E. A. Jones, J. Chem. Phys. 20, 135 (1952), report the frequencies, obtained from the infrared spectrum, and moments of inertia, obtained from the microwave spectrum.

NITRYL FLUORIDE (NO₂F)

(IDEAL GAS)

MOL. WT. = 65.0039

Point Group C_{2v}

$$\Delta H_f^\circ = -24.6 \pm 5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^\circ = -26.0 \pm 5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 62.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm. ⁻¹	ω_e , cm. ⁻¹
1312 (1)	1793 (1)
822 (1)	970 (1)
460 (1)	742 (1)

Bond Distances: N-F = 1.40 Å

Bond Angles: O-N-O = 129.5°

Product of the Moments of Inertia: $I_A I_B I_C = 6.401698 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of reaction at 25°C for direct synthesis of nitryl fluoride from nitrogen dioxide with fluorine ($\text{NO}_2(\text{g}) + 1/2 \text{F}_2(\text{g}) = \text{NO}_2\text{F}(\text{g})$) has been measured calorimetrically as $-33.9 \text{ kcal. mole}^{-1}$ by J. D. Breasale and R. O. MacLaren, "Thermochemistry of Oxygen-Fluorine Bonding" (Final Tech. Summary Report, Contract No. Nonr 3433(00)), ARPA Order No. 184-62 United Technology Corporation, Sunnyvale, Calif., Mar. 1963. The heat of formation, $\Delta H_f^\circ = -28.0 \text{ kcal. mole}^{-1}$, for $\text{NO}_2\text{F}(\text{g})$ was then derived. The values of $\Delta H_f^\circ = -20 \pm 5$ and $-19 \pm 2 \text{ kcal. mole}^{-1}$ were issued in their second and third quarterly tech. reports, and have been quoted in the literature by E. Tschukow-Roux, J. Phys. Chem. 66, 1636 (1962).

G. Hetherington and P. L. Robinson, Special Publication No. 10, The Chem. Soc., London, 1957 quoted $\Delta H_f^\circ = 26 \text{ kcal. mole}^{-1}$ (presumably it has a minus sign) for $\text{NO}_2\text{F}(\text{g})$ which was derived from the heat of solution measured by Nichols and Robinson, a private communication to Hetherington and Robinson.

Heat Capacity and Entropy.

D. P. Smith and D. W. Magnuson, Phys. Rev. 87, 226 (1952), have measured the moments of inertia from microwave spectrum of $\text{NO}_2\text{F}(\text{g})$. In order to calculate the bond distances, given as N-F = 1.35 Å and N-O = 1.23 Å, the bond angle O-N-O was assumed to be 125°. The selected bond distances and angle were obtained from L. Clayton, Q. Williams and T. Wetherly, J. Chem. Phys. 30, 1328 (1959). Clayton et al. assumed the bond angle O-N-O in $\text{NO}_2\text{F}(\text{g})$ should be the same as that in $\text{NO}_2\text{Cl}(\text{g})$, and then calculated the bond distances N-F and N-O from Smith and Magnuson's data of the moments of inertia.

The selected vibrational frequencies were obtained from the infrared and Raman spectra measurements by R. Dodd, J. Rolfe and L. Woodward, Trans. Faraday Soc. 52, 145 (1956).

The three principal moments of inertia are $I_A = 6.3658 \times 10^{-39}$, $I_B = 7.3383 \times 10^{-39}$ and $I_C = 13.7041 \times 10^{-39} \text{ g. cm.}^2$

Mar. 31, 1962; Dec. 31, 1965

Fluorine Nitrate (FNO₃)
(Ideal Gas) Mol. Wt. = 81.008

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	Log K _p
0	0.000	INFINITE	INFINITE	-	3.390	4.313	INFINITE
100	12.747	56.955	12.747	-	2.922	17.322	-17.322
200	15.589	69.988	15.589	-	2.450	17.594	-12.896
300	15.638	70.085	15.638	0.029	2.466	17.687	-12.885
400	17.951	74.915	17.951	1.714	2.381	22.774	-12.443
500	19.687	79.117	19.687	3.600	2.415	27.871	-11.182
600	20.975	82.826	20.975	5.636	2.567	32.952	-12.002
700	21.933	86.135	21.933	7.784	2.738	38.005	-11.865
800	22.654	89.113	22.654	10.015	2.968	43.025	-11.753
900	23.203	91.814	23.203	12.309	3.223	48.018	-11.660
1000	23.679	94.282	23.679	14.651	3.496	52.982	-11.579
1100	23.963	96.550	23.963	17.032	3.778	57.911	-11.506
1200	24.229	98.647	24.229	19.442	4.067	62.825	-11.442
1300	24.444	100.595	24.444	21.876	4.358	67.710	-11.383
1400	24.620	102.414	24.620	24.328	4.652	72.572	-11.328
1500	24.765	104.117	24.765	26.799	4.945	77.414	-11.279
1600	24.886	105.720	24.886	29.249	5.236	82.235	-11.232
1700	24.988	107.231	24.988	31.775	5.527	87.040	-11.189
1800	25.075	108.662	25.075	34.278	5.811	91.825	-11.149
1900	25.149	110.020	25.149	36.760	6.091	96.598	-11.111
2000	25.213	111.312	25.213	39.208	6.367	101.353	-11.075
2100	25.268	112.543	25.268	41.632	6.638	106.095	-11.041
2200	25.317	113.720	25.317	44.031	6.899	110.825	-11.009
2300	25.359	114.846	25.359	46.457	7.157	115.542	-10.978
2400	25.397	115.926	25.397	48.913	7.408	120.251	-10.950
2500	25.430	116.964	25.430	51.394	7.649	124.945	-10.922
2600	25.460	117.962	25.460	53.891	7.885	129.634	-10.895
2700	25.487	118.923	25.487	56.406	8.114	134.313	-10.871
2800	25.510	119.850	25.510	58.941	8.335	138.982	-10.848
2900	25.532	120.746	25.532	61.498	8.549	143.648	-10.825
3000	25.551	121.612	25.551	64.078	8.755	148.301	-10.803
3100	25.569	122.450	25.569	66.679	8.956	152.949	-10.782
3200	25.585	123.262	25.585	69.306	9.148	157.590	-10.762
3300	25.600	124.049	25.600	71.958	9.334	162.224	-10.743
3400	25.613	124.814	25.613	74.636	9.512	166.856	-10.725
3500	25.625	125.557	25.625	77.338	9.685	171.479	-10.707
3600	25.637	126.279	25.637	80.061	9.852	176.103	-10.690
3700	25.647	126.981	25.647	82.805	10.012	180.718	-10.674
3800	25.657	127.665	25.657	85.571	10.167	185.332	-10.659
3900	25.666	128.332	25.666	88.359	10.316	189.935	-10.643
4000	25.674	128.982	25.674	91.169	10.459	194.538	-10.629
4100	25.681	129.616	25.681	94.001	10.596	199.140	-10.615
4200	25.689	130.235	25.689	96.848	10.730	203.736	-10.601
4300	25.695	130.839	25.695	99.709	10.859	208.336	-10.588
4400	25.700	131.430	25.700	102.584	10.982	212.924	-10.575
4500	25.707	132.008	25.707	105.477	11.106	217.510	-10.563
4600	25.713	132.573	25.713	108.381	11.216	222.102	-10.552
4700	25.718	133.126	25.718	111.296	11.325	226.683	-10.540
4800	25.723	133.667	25.723	114.221	11.432	231.266	-10.529
4900	25.728	134.198	25.728	117.158	11.535	235.837	-10.518
5000	25.731	134.718	25.731	120.109	11.634	240.414	-10.508
5100	25.735	135.227	25.735	123.068	11.729	244.990	-10.498
5200	25.739	135.727	25.739	126.036	11.822	249.561	-10.488
5300	25.742	136.217	25.742	129.014	11.911	254.139	-10.479
5400	25.745	136.696	25.745	132.001	12.000	258.716	-10.470
5500	25.749	137.171	25.749	135.000	12.089	263.295	-10.461
5600	25.752	137.635	25.752	138.001	12.160	267.837	-10.452
5700	25.755	138.091	25.755	141.000	12.237	272.401	-10.444
5800	25.758	138.539	25.758	144.000	12.312	276.971	-10.436
5900	25.761	138.982	25.761	147.000	12.384	281.558	-10.428
6000	25.763	139.412	25.763	150.000	12.453	286.093	-10.420

March 31, 1963

FNO₃

MOL. WT. = 81.008

(IDEAL GAS)

FLUORINE NITRATE (FNO₃)

Point Group C_{3v}
S_{298.15} = [70] cal. deg.⁻¹ mole⁻¹
Ground State Multiplicity = [1]

ΔH_f^o = [4.3 ± 0.5] kcal. mole⁻¹
ΔH_f^o 298.15 = 2.5 ± 0.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
[1300] (1)	[780] (1)
[800] (1)	[980] (1)
[680] (1)	[370] (1)
[1700] (1)	[130] (1)
[450] (1)	

Bond Distance: O-N = 1.29 ± 0.05 Å N-O' = 1.39 ± 0.05 Å O'-F = 1.42 ± 0.05 Å

Bond Angle: O-N-O = 125° ± 5° F-O'-N = 105° ± 5°

Angle between NO₂F plane and O₂NO' plane = 90°.

Product of the Moments of Inertia: I_AI_BI_C = 3.88637 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

The value, 2.5 ± 0.5 kcal. mole⁻¹, for the heat of formation of FNO₃(g) was obtained from R. Anderson, et al., "Thermochemistry of Oxygen-Fluorine Bonding," UTC 2002-Q74, United Technology Corporation, Sunnyvale, California, March 1, 1961, through February 28, 1962. The value of ΔH_f^o reported by O. G. Tsalkin, et al., Russ. J. Phys. Chem., 36, 561 (1962) was -4.2 ± 0.9 kcal. mole⁻¹ at 294°K.

Heat Capacity and Entropy.

Vibrational frequencies were estimated by comparison with those of HNO₃(g) reported by A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955). Bond distances and angles were taken from L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 59, 13 (1937). The three principal moments of inertia are 8.8598 X 10⁻³⁸, 1.8572 X 10⁻³⁸, and 2.3518 X 10⁻³⁸ g. cm.². The possible existence of restricted internal rotation in the molecule was not considered. Thus the values of C_p and S° calculated may be low.

FNO₃

Sodium Fluoride (NaF)
(Crystal)

GFW = 41.9882

$$\Delta H_f^\circ = -136.95 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_f^\circ{}_{298.15} = -137.52 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 7.97 \text{ kcal/mol}$$

$$\Delta H_f^\circ{}_{298.15} = 88.1 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 12.24 \pm 0.02 \text{ gibbs/mol}$$

$$T_m = 1269 \pm 2^\circ\text{K}$$

Heat of Formation

The heats of solution and reaction of NaF(c) have been determined by many investigators. Incorporating their reported data with auxiliary $\Delta H_f^\circ{}_{298}$ values (1, 2), we calculate the corresponding values of $\Delta H_f^\circ{}_{298}$ (NaF, c). The results are presented in the table below. The adopted $\Delta H_f^\circ{}_{298}$ (NaF, c) is $-137.52 \pm 0.2 \text{ kcal/mol}$.

Investigator	Reaction*	Temperature, °K	Concentration NaF·nH ₂ O	No. of determinations	$\Delta H_f^\circ{}_{298}$ kcal/mol	$\Delta H_f^\circ{}_{298}$ kcal/mol
1. Guntz (1884)	A	285	400	1	0.13	-137.42
2. Latimer - Jolly (1953)	A	298	1850	2	0.23 ± 0.01	-137.52
3. Hepler et al. (1953)	A	298	1540	1	0.22 ± 0.01	-137.51
4. Davies - Benson (1965)	A	298	222	1	0.24 ± 0.01	-137.53
5. Thomsen (1882)	B	291	—	2	16.24 ± 0.15	-137.38
6. Wartenberg - Fitzner (1926)	C	293	—	1	-39.3 ± 0.1	-137.62
7. Schmitz - Schumaker (1947)	C	291	—	1	-39.5	-137.82
8. Coughlin (1958)	D	298	—	6	-1.40 ± 0.06	-137.58
9. Vorob'yev - Skuratov (1960)	E	298	—	5	-325.5 ± 2.2	-137.13

*A represents NaF(c) = NaF(n H₂O) and $\Delta H_f^\circ{}_{298} = \Delta H_f^\circ$; B, NaOH(200 H₂O) + HF(401 H₂O) = NaF(401 H₂O) + H₂O(l); C, NaCl(c) + 1/2 F₂(g) = NaF(c) + 1/2 Cl₂(g); D, NaCl(c) + HF(5.716 H₂O) = NaF(c) + HCl(12.731 H₂O); E, 4Na(c) + CF₄(g) = 4NaF(c) + C (graphite).

Heat Capacity and Entropy

The low temperature heat capacities, 0.05 - 15°K and 54.01 - 295.86°K, were measured by Harrison et al. (10) and King (11), respectively. These two sets of data are joined smoothly with the high temperature heat capacities at 298°K which were derived from the enthalpy measurements, 406.1 - 1282.2°K, determined by O'Brien and Kelley (12). The Cp values above 1282.2°K are obtained by linear extrapolation. S°_{298} is calculated using the adopted low temperature heat capacities and $S^\circ_{298} = 0.555 \text{ eu}$.

Frank (13) commented that the temperature measurements of O'Brien and Kelley (12) seemed to be about 20°K high at 1000°K with a smaller error at lower temperatures. A correction for the assumed error in the temperature measurement was used in the previous JANAF table. However, Douglas and Dittmars (14) have questioned this correction, since new enthalpy data for AlF₃ yielded Cp values in better agreement with the original Cp values of O'Brien and Kelley than with the corrected values of Frank. The $\alpha + \beta$ transition of AlF₃(c) was found in the range 723 - 6°K, while O'Brien and Kelley selected 727°K based on a point at 728.1°K in the β region and a point at 724.9°K in the pretransition region. Frank's correction yields an error of 9° at 727°K, yet the true error appears to be negligible (<2°) for AlF₃(c). Based on the above reasoning and the comparison of the Cp curve of NaF(c) with those of NaCl(c), LiCl(c), and LiF(c) in the temperature range 300 - 1300°K, we adopt the high temperature enthalpy data of O'Brien and Kelley without any correction.

The low temperature heat capacities in the temperature ranges 81 - 190 and 198 - 273°K were also measured by Koref (15); and high temperature enthalpies at temperatures 288 - 1073 and 290 - 1287°K were reported by Krestovnikov and Karetnikov (16), and Lyashenko (17), respectively. They are not used for evaluation.

Melting Data

See the NaF(l) table for details.

Heat of Sublimation

ΔH_{298}° is the difference between $\Delta H_f^\circ{}_{298}$ for NaF(g) and NaF(c).

References

1. A. Guntz, Ann. Chim. Phys. [6] 3, 5 (1884).
2. W. M. Latimer and W. L. Jolly, J. Am. Chem. Soc. 75, 1548 (1953).
3. D. H. Hepler, W. L. Jolly, and G. C. Bevilacqua, J. Am. Chem. Soc. 75, 2809 (1953).
4. D. H. Hepler and G. C. Bevilacqua, Can. J. Chem. 43, 1010 (1965).
5. J. Thomsen, Thermochemische Untersuchungen, Vol. I, J. Barth Verlag, Leipzig, 1882, p. 157.
6. H. Wartenberg and O. Fitzner, Z. Anorg. Allgem. Chem. 151, 313 (1926).
7. H. Schmitz and H. J. Schumacher, Z. Naturforsch. 2A, 352 (1947).
8. J. P. Coughlin, J. Am. Chem. Soc. 80, 1802 (1958).
9. V. Vorob'yev and S. H. Skuratov, Russ. J. Inorg. Chem. (English Transl.) 5, 679 (1960).
10. E. G. King, J. Am. Chem. Soc. 79, 2056 (1957).
11. E. G. King, J. Am. Chem. Soc. 79, 2056 (1957).
12. C. J. O'Brien and K. K. Kelley, J. Am. Chem. Soc. 79, 5616 (1957).
13. W. B. Frank, J. Phys. Chem. 65, 2081 (1961).
14. T. B. Douglas and D. A. Dittmars, Natl. Bur. Std. Rept. 9389, 1966.
15. A. Koref, Ann. Physik (4) 36, 49 (1911).
16. A. Krestovnikov and S. Karetnikov, Dokl. Akad. Nauk SSSR, 129, 85 (1959).
17. V. S. Lyashenko, Metallurg (USSR) 10, 85 (1955).

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1968

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH_f°	ΔG°	Log Kp
0	5.060	2.000	INFINITE	= 7.029	= 136.953	= 136.953	INFINITE
100	5.456	21.053	21.053	= 137.432	= 137.432	= 137.432	295.246
200	6.754	6.032	13.227	= 137.567	= 137.567	= 137.567	954.980
298	11.158	12.240	12.240	= 137.520	= 130.240	= 130.240	954.980
300	11.215	12.309	12.240	= 137.518	= 130.235	= 130.235	94.876
400	11.654	15.633	12.669	= 138.090	= 127.763	= 127.763	59.676
500	12.123	18.323	13.555	= 138.024	= 125.193	= 125.193	54.722
600	12.590	20.587	14.544	= 137.923	= 122.635	= 122.635	44.670
700	12.936	22.553	15.550	= 137.779	= 120.099	= 120.099	37.487
800	13.315	24.305	16.537	= 137.595	= 117.565	= 117.565	32.123
900	13.741	25.897	17.480	= 137.370	= 115.097	= 115.097	27.949
1000	14.222	27.370	18.405	= 137.105	= 112.636	= 112.636	24.617
1100	14.760	28.750	19.283	= 136.799	= 110.205	= 110.205	21.896
1200	15.360	30.059	20.127	= 136.458	= 107.845	= 107.845	19.550
1300	16.000	31.314	20.940	= 136.086	= 105.550	= 105.550	17.317
1400	16.530	32.520	21.724	= 135.685	= 103.322	= 103.322	15.111
1500	16.880	33.674	22.483	= 135.252	= 101.165	= 101.165	13.066
1600	17.000	34.768	23.217	= 134.798	= 99.097	= 99.097	12.334
1700	17.000	35.799	23.927	= 134.317	= 97.119	= 97.119	11.076
1800	17.000	36.770	24.614	= 133.817	= 95.237	= 95.237	9.963
1900	17.000	37.689	25.278	= 133.300	= 93.456	= 93.456	8.972
2000	17.000	38.551	25.920	= 132.768	= 91.765	= 91.765	8.095
2100	17.000	39.361	26.540	= 132.220	= 90.164	= 90.164	7.285
2200	17.000	40.124	27.144	= 131.658	= 88.644	= 88.644	6.562
2300	17.000	40.937	27.728	= 131.082	= 87.200	= 87.200	5.905
2400	17.000	41.661	28.293	= 130.497	= 85.837	= 85.837	5.306
2500	17.000	42.355	28.842	= 129.902	= 84.558	= 84.558	4.757
2600	17.000	43.022	29.375	= 129.297	= 83.362	= 83.362	4.253
2700	17.000	43.663	29.892	= 128.682	= 82.247	= 82.247	3.789
2800	17.000	44.281	30.395	= 128.057	= 81.212	= 81.212	3.359
2900	17.000	44.878	30.884	= 127.422	= 80.257	= 80.257	2.961
3000	17.000	45.454	31.360	= 126.777	= 79.382	= 79.382	2.592

Sodium Fluoride (NaF)

(Liquid)

GFw = 41.9882

SODIUM FLUORIDE (NaF)

(LIQUID)

GFw = 41.9882

 $S_{298.15}^{\circ} = 17.559$ gibbs/mol $\Delta H_f^{\circ} 298.15 = -130.545$ kcal/mol $T_m = 1269 \pm 2^{\circ}\text{K}$ $\Delta H_m^{\circ} = 7.97$ kcal/mol $\Delta H_f^{\circ}(\text{to mixture}) = 42.1$ kcal/mol of NaF(l) $T_b = 2060^{\circ}\text{K}$

Heat of Formation

 $\Delta H_f^{\circ}(\text{NaF}(l))$ is obtained from $\Delta H_f^{\circ}(\text{NaF}(c))$ by adding ΔH_m° and the difference between H_{1269}° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

The heat capacities of NaF(l) are derived from the enthalpy data, 1287.6 - 1746.5°K, determined by O'Brien and Kelley (1). A glass transition temperature is assumed at 900°K, i.e. the heat capacities below 900°K are taken from those for NaF(c). The Cp values above 1746.5°K are obtained by extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data

The value of T_m has been reported as (°K): 1313 (2), 1285 (3), 1270 (3, 4, 5), 1269 (6), 1268 (7, 8, 9), 1267 (10, 11, 12), 1265 (13), 1263 (14), and 1253 (15). We select $T_m = 1269^{\circ}\text{K}$. The value 1285°K reported by O'Brien and Kelley seems unreasonably high and is not adopted. The cause of this discrepancy is still unresolved (17). The heat of melting is calculated as the difference between the adopted enthalpies for NaF(c) and NaF(l) at 1269°K. Kelley (18) derived $\Delta H_m^{\circ} 1265$ to be 5.82 - 8.43 kcal/mol, based on 13 sets of molten salts equilibrium data involving NaF. The value $\Delta H_m^{\circ} 1285 = 8.03$ kcal/mol reported by O'Brien and Kelley is not used.

Vaporization Data

T_b is the temperature at which the partial pressures of NaF(g) and Na_2F_2 (g) in equilibrium with NaF(l) equal one atmosphere. The vapor composition at T_b is evaluated as NaF 84.84 and Na_2F_2 15.24. The heat required to vaporize one mole of liquid to form 0.868 mole of vapor mixture of the above composition at T_b is calculated to be 42.1 kcal/mol. Ruff et al. (16) measured the vapor pressure of NaF(l) in the temperature range of 1699 - 1974°K and reported $T_b = 1978^{\circ}\text{K}$.

References

1. C. J. O'Brien and K. K. Kelley, J. Am. Chem. Soc. **79**, 5616 (1957).
2. N. Puschin and A. Baskow, Z. Anorg. Chem. **81**, 347 (1913).
3. N. S. Kurnakow and S. F. Zencuznyj, Z. Anorg. Chem. **52**, 186 (1907).
4. G. J. Landon and A. R. Ubbelohde, Proc. Roy. Soc. (London) **240A**, 160 (1957).
5. M. Rolin, Bull. Soc. Chim. France, **1960**, 671 (1960).
6. K. A. Sasse, C. A. Alexander, R. E. Bowman, R. W. Stone, R. B. Filbert, Jr., J. Phys. Chem. **61**, 384 (1957).
7. H. S. Booth and B. A. Starry, J. Phys. Chem. **35**, 3553 (1931).
8. M. A. Bredig, J. W. Johnson, and W. T. Smith, Jr., J. Am. Chem. Soc. **77**, 307 (1955).
9. S. Cantor, J. Phys. Chem. **65**, 2208 (1961).
10. B. Porter and E. A. Brown, J. Am. Ceram. Soc. **45**, 49 (1962).
11. N. W. F. Phillips, R. H. Singleton, and E. A. Hollingshead, J. Electrochem. Soc. **102**, 690 (1955).
12. J. Brynestad, K. Griethelm, and S. Urnes, Metallurgia Ital. **52**, NO.8, 495 (1960).
13. W. Plato, Z. Physik. Chem. **58**, 350 (1907).
14. A. G. Bergman and E. P. Dergunov, Compt. Rend. Acad. Sci. U.R.S.S. **31**, 753 (1941).
15. O. Ruff and W. Plato, Ber. **36**, 2363 (1903).
16. O. Ruff, G. Schmidt and S. Hugdan, Z. Anorg. Allgem. Chem. **123**, 83 (1922).
17. K. K. Kelley, private communication, May 31, 1963, U. S. Bureau of Mines, Berkeley, California.
18. K. K. Kelley, U. S. Bur. Mines Bull. **393**, 1936.

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0							
100							
200							
268	11.168	17.559	17.559	0.000	-130.545	-124.691	91.546
300	11.215	17.609	17.560	0.021	-130.543	-124.656	90.937
400	11.283	17.693	17.609	1.176	-131.115	-125.491	87.161
500	12.252	18.095	18.095	2.384	-131.054	-126.078	82.636
600	12.590	19.663	19.663	3.626	-130.948	-118.852	83.292
700	12.936	20.870	20.870	4.902	-130.804	-116.848	36.481
800	13.315	22.856	22.856	6.214	-130.620	-114.866	31.380
900	13.720	25.609	25.609	7.561	-130.395	-112.909	27.418
1000	14.140	29.112	29.112	8.935	-129.129	-110.083	24.260
1100	17.280	34.779	24.676	11.114	-129.122	-109.162	21.688
1200	16.960	36.269	25.581	12.826	-151.799	-109.514	19.472
1300	16.700	37.616	26.436	14.504	-151.085	-103.203	17.350
1400	16.500	38.656	27.257	16.168	-150.356	-99.340	15.590
1500	16.340	39.578	28.105	17.809	-149.667	-95.444	13.979
1600	16.210	41.029	28.681	19.437	-148.994	-92.364	12.619
1700	16.100	42.008	29.624	21.052	-148.334	-88.865	11.424
1800	16.010	42.626	30.338	22.658	-147.684	-85.367	10.387
1900	15.930	43.769	31.074	24.254	-147.040	-81.942	9.486
2000	15.860	44.604	31.602	25.844	-146.421	-78.532	8.502
2100	15.800	45.377	32.316	27.427	-145.800	-75.155	7.621
2200	15.750	46.111	32.927	29.004	-145.187	-71.805	7.133
2300	15.710	46.810	33.515	30.577	-144.576	-68.483	6.507
2400	15.670	47.477	34.088	32.146	-143.966	-65.186	5.836
2500	15.640	48.117	34.632	33.712	-143.357	-61.917	5.113
2600	15.610	48.729	35.162	35.274	-142.752	-58.669	4.932
2700	15.580	49.318	35.676	36.834	-142.207	-55.445	4.488
2800	15.560	49.884	36.173	38.391	-141.628	-52.244	4.078
2900	15.540	50.426	36.653	39.946	-141.053	-49.069	3.697
3000	15.520	50.956	37.133	41.499	-140.484	-45.904	3.334
3100	15.500	51.465	37.578	43.049	-139.921	-42.755	3.014
3200	15.480	51.957	38.020	44.599	-139.362	-39.629	2.707
3300	15.470	52.433	38.469	46.147	-138.811	-36.521	2.419
3400	15.460	52.896	38.917	47.694	-138.260	-33.430	2.146
3500	15.450	53.343	39.275	49.239	-137.727	-30.351	1.895

Ground State Configuration $1s^2$ $\Delta H_f^\circ = -69.03 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^\circ = -69.03 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^\circ = -69.03 \pm 0.5 \text{ kcal/mol}$ $\Delta H_f^\circ = -69.03 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

 $\frac{g_i}{g_0} = 1$ $\omega_e = 536.10 \pm 0.35 \text{ cm}^{-1}$ $\sigma = 1$ $\omega_e x_e = 3.83 \pm 0.14 \text{ cm}^{-1}$ $r_e = 1.9260 \text{ \AA}$

Heat of Formation

The total pressures of NaF(g) and Na₂F₂(g), in equilibrium with NaF(c, s) at temperatures 1020 - 1974°K, have been determined by many investigators, using manometric (1, 2, 3), torsion-effusion (6, 8), Knudsen-effusion (3, 7), transpiration (4), and molecular-beam velocity-selector (9, 10) methods. In order to evaluate ΔH_f° (NaF, g) we have used a trial and error variation of ΔH_f° and ΔH_v° for the monomer and dimer such that the ΔH_f° values derived by the second and third law methods are in reasonable agreement.

Incorporating ΔH_f° = 68.1 and ΔH_v° = 61.12 and 58.75 kcal/mol for NaF and Na₂F₂, respectively, with JANAF functions for NaF(c), NaF(s), NaF(g) and Na₂F₂(g), we derive the partial pressures of NaF monomer from the reported total pressures. Based on the calculated partial pressures of NaF(g), the corresponding heats of vaporization are evaluated by the second and third law methods. Using the third law ΔH_f° and ΔH_v° = -137.52 and -130.545 kcal/mol for NaF(c) and NaF(s), we obtain values of ΔH_f° for NaF(g). The results are presented in the table below. The ΔH_f° (NaF, g) value adopted is -69.42 kcal/mol.

The vapor pressure data reported by Miller and Kusch (3) and Eisenstadt et al. (10) are not consistent with the other sets and are not used for evaluation.

Gaydon (11) and Herzberg (12) reported $D_0^\circ = 114.2 \pm 6.9$ (4.95 \pm 0.3 eV) and ≤ 122.2 kcal/mol (5.3 eV), respectively. Using JANAF ΔH_f° values for NaF(c) and F(g), we obtain ΔH_f° (NaF, g) = -70.5 \pm 5.8 and -78.5 kcal/mol. Employing flame-photometric method, Bulevskii et al. (13) and Page and Sugden (14) derived $D_0^\circ = 121 \pm 7$ and 119 ± 120 kcal/mol for NaF(g), which lead to ΔH_f° (NaF, g) = -77.3 \pm 7 and -75 to -76 kcal/mol.

Investigator	Temperature, °K	Process	No. of Points	Second Law	Third Law	Drift	ΔH_f° kcal/mol
1. Wartenberg - Schulz (1921)	1659 - 1830	B	5	67.76 \pm 0.11	59.30	-4.5 \pm 0.1	-70.65
2. Ruff et al. (1922)	1659 - 1974	B	14	64.07 \pm 0.58	59.54	-2.4 \pm 0.3	-71.01
3. Niwa (1938)	1053 - 1112	A	5	63.18 \pm 1.04	66.68	3.2 \pm 1.0	-70.84
4. Sense et al. (1957)	1208 - 1285	A	7	71.26 \pm 0.63	66.25	-2.4 \pm 0.5	-69.27
5. Cantor - Blankenship (1958)	1274 - 1348	B	9	65.88 \pm 0.76	61.14	-3.6 \pm 0.6	-69.41
6. Pugh - Barrow (1958)	1023 - 1166	A	7*	66.13	60.84	-3.6	-69.71
7. Porter - Schoonmaker (1958)	1121	A	1	68.13	68.14	0.0	-65.38
8. Entner - Neckel (1967)	1016 - 1236	A	6*	68.54 \pm 0.10	67.74	-0.7 \pm 0.1	-68.78

* Data points calculated from a given total pressure equation.

** Process A: NaF(c) = NaF(g); B: NaF(s) = NaF(g).

Heat Capacity and Entropy

Veazey and Gordy (15) have measured the rotational transitions of NaF in the millimeter- and sub-millimeter-wave region with a high-resolution molecular-beam absorption spectrometer. The derived values of ω_e , $\omega_e x_e$, B_e , $B_e x_e$ and r_e are adopted here.

Using the molecular beam electric resonance method, Bauer and Lew (16) measured the transition between the $J = 0$ and $J = 1$ rotational levels of Na₂F₂ in the three lowest vibrational states. Radio-frequency transitions for Na₂F₂ have been observed by Hollowell et al. (19). Infrared spectra of NaF have been analyzed by Snellson and Pitzer (17), Ritchie and Lew (18), and Baikov and Vasilevskii (20). The molecular constants derived by the above authors are similar to the values adopted, except the value $\omega_e = 550 \text{ cm}^{-1}$ (17) which is different from the value 536.1 cm^{-1} reported by Veazey and Gordy (15).

References

- H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).
- O. Ruff, G. Schmidt, and S. Mugdan, Z. Anorg. Allgem. Chem. 123, 83 (1922).
- K. Niwa, J. Fac. Sci., Hokkaido Imp. Univ. Ser. III, 2, 201 (1938).
- S. Cantor and F. Blankenship, R. E. Bowman, R. W. Stone, and R. B. Filbert, Jr., J. Phys. Chem. 61, 384 (1957).
- A. C. P. Pugh and R. F. Barrow, Trans. Faraday Soc. 54, 577 (1958).
- R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. 23, 1070 (1958).
- P. Entner and A. Neckel, Monatsh. Chem. 98, 1083 (1967).
- K. E. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).
- A. G. Gaydon, "Infrared Spectra of Diatomic Molecules," Chapman and Hall Ltd., London, 1968.
- G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., Van Nostrand Reinhold Co., New York, 1950.
- E. M. Page and T. M. Sugden, Nature 183, 1672 (1959).
- F. M. Page and T. M. Sugden, Phys. Rev. 138, A 1303 (1965).
- S. K. Veazey and W. Gordy, J. Phys. Chem. 67, 1461 (1963).
- A. Snellson and H. L. Pitzer, J. Phys. Chem. 63, 882 (1963).
- R. K. Ritchie and H. Lew, Can. J. Phys. 41, 1921 (1963).
- C. D. Hollowell, A. J. Hebert, and K. Street, Jr., J. Chem. Phys. 41, 3540 (1964).
- V. I. Baikov and K. P. Vasilevskii, Opt. Spectry. 22 198 (1967).

Dec. 31, 1960; Dec. 31, 1963; Dec. 31, 1968

Sodium Fluoride (NaF)

(Ideal Gas) GFw = 41.9882

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔH_f°	Log Kp
100	7.016	43.787	INFINITE	2.205	69.029	69.029	INFINITE
200	7.643	48.623	52.716	1.779	72.872	72.872	154.679
298	8.178	51.993	59.030	1.420	76.925	76.925	299.104
300	8.185	52.034	59.030	1.420	76.925	76.925	300.000
400	8.494	54.435	61.961	1.170	78.516	78.516	412.600
500	8.674	56.351	62.932	1.015	79.317	79.317	531.951
600	8.789	57.943	63.536	0.866	79.992	79.992	664.009
700	8.868	59.353	63.931	0.736	80.581	80.581	809.415
800	8.916	60.617	64.157	0.621	81.097	81.097	976.915
900	8.942	61.787	64.296	0.521	81.546	81.546	1167.425
1000	8.957	62.884	64.354	0.434	81.919	81.919	1382.025
1100	8.963	63.934	64.393	0.353	82.209	82.209	1629.596
1200	8.961	64.952	64.412	0.276	82.410	82.410	1900.131
1300	8.952	65.940	64.421	0.204	82.529	82.529	2192.631
1400	8.938	66.907	64.421	0.137	82.566	82.566	2506.131
1500	8.919	67.854	64.412	0.076	82.520	82.520	2839.631
1600	8.896	68.786	64.393	0.021	82.393	82.393	3192.131
1700	8.869	69.707	64.354	0.000	82.185	82.185	3562.631
1800	8.839	70.617	64.296	0.000	81.897	81.897	3950.131
1900	8.806	71.517	64.221	0.000	81.529	81.529	4354.631
2000	8.771	72.407	64.134	0.000	81.085	81.085	4786.131
2100	8.728	73.287	64.029	0.000	80.566	80.566	5244.631
2200	8.678	74.157	63.907	0.000	79.973	79.973	5730.131
2300	8.623	75.017	63.767	0.000	79.307	79.307	6242.631
2400	8.563	75.869	63.611	0.000	78.566	78.566	6782.131
2500	8.500	76.707	63.441	0.000	77.741	77.741	7348.631
2600	8.434	77.534	63.247	0.000	76.834	76.834	7942.131
2700	8.366	78.354	63.031	0.000	75.846	75.846	8562.631
2800	8.297	79.167	62.797	0.000	74.777	74.777	9210.131
2900	8.228	79.974	62.547	0.000	73.637	73.637	9884.631
3000	8.159	80.774	62.283	0.000	72.426	72.426	10586.131
3100	8.089	81.567	62.007	0.000	71.144	71.144	11314.631
3200	8.019	82.354	61.717	0.000	69.791	69.791	12070.131
3300	7.949	83.134	61.413	0.000	68.366	68.366	12852.631
3400	7.879	83.907	61.097	0.000	66.879	66.879	13672.131
3500	7.809	84.674	60.770	0.000	65.330	65.330	14528.631
3600	7.739	85.434	60.431	0.000	63.721	63.721	15422.131
3700	7.669	86.187	60.077	0.000	62.052	62.052	16354.631
3800	7.599	86.934	59.711	0.000	60.323	60.323	17326.131
3900	7.529	87.674	59.334	0.000	58.534	58.534	18338.631
4000	7.459	88.407	58.947	0.000	56.685	56.685	19392.131
4100	7.389	89.134	58.551	0.000	54.776	54.776	20486.631
4200	7.319	89.857	58.147	0.000	52.807	52.807	21622.131
4300	7.249	90.574	57.734	0.000	50.778	50.778	22798.631
4400	7.179	91.287	57.307	0.000	48.689	48.689	24016.131
4500	7.109	91.994	56.867	0.000	46.540	46.540	25274.631
4600	7.039	92.697	56.411	0.000	44.331	44.331	26574.131
4700	6.969	93.397	55.941	0.000	42.062	42.062	27915.631
4800	6.899	94.094	55.457	0.000	39.733	39.733	29299.131
4900	6.829	94.787	54.959	0.000	37.344	37.344	30725.631
5000	6.759	95.477	54.447	0.000	34.895	34.895	32195.131
5100	6.689	96.164	53.921	0.000	32.386	32.386	33708.631
5200	6.619	96.847	53.381	0.000	29.817	29.817	35266.131
5300	6.549	97.524	52.827	0.000	27.188	27.188	36868.631
5400	6.479	98.197	52.259	0.000	24.509	24.509	38516.131
5500	6.409	98.867	51.677	0.000	21.780	21.780	40209.631
5600	6.339	99.534	51.083	0.000	19.001	19.001	41949.131
5700	6.269	100.197	50.477	0.000	16.172	16.172	43735.631
5800	6.199	100.857	49.859	0.000	13.293	13.293	45568.131
5900	6.129	101.514	49.227	0.000	10.364	10.364	47447.631
6000	6.059	102.167	48.583	0.000	7.395	7.395	49374.131

Fluorine Monoxide (FO)
(Ideal Gas)

GFW = 34.998

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	6.900	0.000	INF INFINITE	-	25.998	25.998	INF INFINITE
100	6.929	46.076	56.040	0.000	25.997	25.997	56.115
200	7.029	88.910	52.423	0.703	25.997	25.392	27.747
298	7.319	91.765	51.765	0.000	26.000	25.094	18.394
300	7.326	91.810	51.765	0.014	26.000	25.094	18.277
400	7.694	93.968	52.057	0.765	26.011	24.783	13.541
500	8.007	95.720	52.619	1.350	26.027	24.474	10.698
600	8.246	97.202	53.263	2.164	26.047	24.162	8.801
700	8.426	98.488	53.919	3.198	26.067	23.846	7.445
800	8.562	99.622	54.563	4.407	26.084	23.527	6.427
900	8.667	60.637	55.192	4.909	26.101	23.206	5.635
1000	8.750	61.334	55.774	5.760	26.116	22.884	5.001
1100	8.818	62.392	56.338	6.654	26.129	22.559	4.492
1200	8.875	63.161	56.875	7.543	26.141	22.236	4.050
1300	8.923	63.674	57.397	8.433	26.151	21.909	3.683
1400	8.965	64.037	57.874	9.324	26.160	21.582	3.389
1500	9.002	64.256	58.339	10.226	26.168	21.257	3.097
1600	9.035	65.738	58.783	11.128	26.173	20.929	2.859
1700	9.066	66.287	59.209	12.033	26.179	20.601	2.648
1800	9.093	66.806	59.617	12.941	26.181	20.272	2.461
1900	9.119	67.284	60.008	13.852	26.182	19.944	2.294
2000	9.144	67.727	60.384	14.765	26.182	19.615	2.143
2100	9.167	68.213	60.747	15.680	26.180	19.286	2.007
2200	9.189	68.640	61.096	16.598	26.175	18.959	1.883
2300	9.210	69.049	61.433	17.514	26.170	18.631	1.770
2400	9.230	69.442	61.756	18.440	26.162	18.303	1.667
2500	9.250	69.816	62.073	19.364	26.151	17.975	1.571
2600	9.269	70.192	62.378	20.290	26.139	17.649	1.484
2700	9.287	70.570	62.674	21.214	26.126	17.324	1.402
2800	9.306	70.947	62.961	22.147	26.110	16.999	1.327
2900	9.324	71.324	63.240	23.079	26.093	16.674	1.257
3000	9.341	71.514	63.510	24.012	26.073	16.346	1.191
3100	9.359	71.820	63.773	24.947	26.053	16.024	1.130
3200	9.376	72.118	64.029	25.884	26.030	15.699	1.072
3300	9.393	72.406	64.278	26.822	26.006	15.374	1.018
3400	9.410	72.687	64.522	27.762	25.980	15.056	0.966
3500	9.427	72.960	64.759	28.704	25.953	14.735	0.920
3600	9.444	73.226	64.990	29.644	25.925	14.416	0.875
3700	9.461	73.495	65.216	30.593	25.895	14.094	0.833
3800	9.478	73.767	65.437	31.540	25.865	13.781	0.793
3900	9.494	74.034	65.653	32.484	25.834	13.468	0.754
4000	9.512	74.224	65.865	33.439	25.800	13.144	0.718
4100	9.529	74.459	66.071	34.391	25.766	12.829	0.684
4200	9.547	74.699	66.274	35.345	25.732	12.513	0.651
4300	9.564	74.914	66.472	36.301	25.698	12.200	0.620
4400	9.581	75.124	66.667	37.257	25.664	11.887	0.590
4500	9.600	75.350	66.857	38.217	25.628	11.570	0.562
4600	9.618	75.561	67.044	39.174	25.589	11.260	0.535
4700	9.637	75.768	67.227	40.141	25.552	10.949	0.509
4800	9.656	75.971	67.408	41.105	25.516	10.641	0.484
4900	9.674	76.170	67.584	42.067	25.479	10.334	0.460
5000	9.694	76.366	67.758	43.040	25.442	10.019	0.438
5100	9.714	76.558	67.929	44.011	25.405	9.712	0.416
5200	9.733	76.747	68.096	44.983	25.368	9.404	0.395
5300	9.751	76.933	68.261	45.957	25.332	9.098	0.375
5400	9.769	77.116	68.424	46.931	25.295	8.793	0.355
5500	9.795	77.295	68.583	47.912	25.260	8.485	0.337
5600	9.816	77.471	68.741	48.893	25.224	8.184	0.319
5700	9.838	77.645	68.895	49.876	25.190	7.879	0.302
5800	9.860	77.816	69.047	50.860	25.156	7.573	0.286
5900	9.885	77.995	69.198	51.845	25.123	7.267	0.269
6000	9.908	78.152	69.349	52.837	25.090	6.967	0.254

Dec. 31, 1960; June 30, 1965; Dec. 31, 1966

FLUORINE MONOXIDE (FO)

(IDEAL GAS)

GFW = 34.998

Ground State Configuration [2Π]

S_{298.15} = 51.77 ± 0.3 gibbs/molΔH_f⁰ = [26 ± 10] kcal/molΔH_f⁰_{298.15} = [26 ± 10] kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	$\frac{g_i}{[29000]}$	$\frac{g_i}{[4]}$
0	[4]	[4]
1056 cm ⁻¹		
$w_e = 1056$ cm ⁻¹		
$B_e = [1.148]$ cm ⁻¹		
$w_{exe} = [15]$ cm ⁻¹		
$\alpha_e = [0.020]$ cm ⁻¹		
$r_e = [1.30]$ Å		
$\sigma = 1$		

Heat of Formation

Several values have been proposed for the heat of formation of FO(g). V. H. Dibeler, R. M. Reese and J. L. Franklin, J. Chem. Phys. 27, 1296 (1957), obtained D₀(FO,g) = 24 kcal from electron impact studies. However, theoretical estimates give D₀ values in the range 45 - 56 kcal. W. C. Price, T. R. Passmore and D. M. Roessler, Discussions Faraday Soc. 25, 207 (1963), estimated 52 kcal for D₀(FO,g).

From a consideration of the central bond energies in FNOH and HNOH with that in HOOH, using all JANAP values of 101, 109 and 50 kcal, we predict the bond dissociation energy in FO-OF to be 46 ± 4 kcal, which yields D₀(FO,g) = 51 ± 2 kcal. The average F-O bond dissociation energy in F₂O(g) is 49.8 ± 0.5 kcal. Also, since there is one less antibonding electron in FO than in F₂, we should expect the F-O bond to be greater than that in F₂(38 kcal). Thus a median value of D₀(FO,g) = 51.4 ± 10 kcal is adopted here which leads to ΔH_f⁰(FO) = 26 kcal/mol.

Heat Capacity and Entropy

The fundamental frequency is obtained by adding 2 $\omega_e x_e$ to the value reported by A. Arkell, R. R. Reinhard and L. P. Larson, J. Am. Chem. Soc. 87, 1016 (1965), from matrix isolation studies. The bond length was taken equal to that in the isoelectronic molecule O₂(g). The value of $\omega_e x_e$ was obtained from the Morse potential function and the assumed dissociation energy. The rotational constant α_e was also estimated from the above parameters and the Morse potential curve. The 2Π ground state is that predicted by molecular orbital theory and the first excited state would also be 2Π. By analogy with the isoelectronic O₂⁻(g) states, the first excited level was estimated at 29000 cm⁻¹.

T, K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	7.000	∞	INFINITE	-	-	-	INFINITE
100	7.000	45.587	63.447	2.468	-102.996	-103.127	6.730
200	10.102	55.587	63.447	1.069	-103.127	-103.275	6.730
298	11.585	59.887	63.447	0.000	-103.540	-104.689	6.730
300	11.608	59.958	63.447	0.021	-103.543	-104.689	6.730
400	12.618	63.447	63.447	1.236	-103.669	-105.304	6.730
500	13.267	66.337	61.271	2.533	-103.810	-105.374	6.730
600	13.690	68.796	62.326	3.882	-103.927	-105.676	6.730
700	13.975	70.929	63.406	5.267	-104.051	-105.958	6.730
800	14.173	72.809	64.666	6.674	-104.186	-106.222	6.730
900	14.315	74.487	65.888	8.099	-104.331	-106.467	6.730
1000	14.420	76.001	66.965	9.536	-104.490	-106.696	6.730
1100	14.500	77.379	67.395	10.982	-104.663	-106.910	6.730
1200	14.562	78.644	68.281	12.436	-104.798	-107.068	6.730
1300	14.611	79.811	68.912	13.894	-104.908	-107.165	6.730
1400	14.650	80.896	69.326	15.357	-105.010	-107.248	6.730
1500	14.682	81.907	70.691	16.824	-105.110	-107.314	6.730
1600	14.708	82.856	71.422	18.294	-105.207	-107.364	6.730
1700	14.730	83.748	72.121	19.766	-105.291	-107.401	6.730
1800	14.749	84.591	72.791	21.240	-105.363	-107.422	6.730
1900	14.764	85.388	73.433	22.715	-105.428	-107.427	6.730
2000	14.778	86.146	74.050	24.192	-105.480	-107.425	6.730
2100	14.789	86.867	74.643	25.671	-105.529	-107.413	6.730
2200	14.799	87.556	75.215	27.150	-105.575	-107.392	6.730
2300	14.808	88.214	75.766	28.631	-105.618	-107.363	6.730
2400	14.816	88.844	76.298	30.117	-105.657	-107.324	6.730
2500	14.823	89.449	76.812	31.594	-105.692	-107.275	6.730
2600	14.829	90.031	77.309	33.076	-105.723	-107.217	6.730
2700	14.834	90.590	77.791	34.560	-105.751	-107.150	6.730
2800	14.839	91.130	78.257	36.043	-105.775	-107.075	6.730
2900	14.844	91.651	78.710	37.527	-105.796	-107.002	6.730
3000	14.848	92.154	79.150	39.012	-105.813	-106.922	6.730
3100	14.851	92.641	79.577	40.497	-105.827	-106.837	6.730
3200	14.854	93.112	79.993	41.982	-105.838	-106.747	6.730
3300	14.857	93.570	80.398	43.468	-105.846	-106.652	6.730
3400	14.860	94.013	80.792	44.954	-105.851	-106.553	6.730
3500	14.863	94.444	81.175	46.440	-105.854	-106.450	6.730
3600	14.865	94.863	81.550	47.926	-105.856	-106.343	6.730
3700	14.867	95.270	81.915	49.413	-105.856	-106.232	6.730
3800	14.869	95.667	82.272	50.900	-105.854	-106.117	6.730
3900	14.871	96.053	82.620	52.387	-105.851	-106.000	6.730
4000	14.872	96.429	82.961	53.874	-105.846	-105.882	6.730
4100	14.874	96.797	83.294	55.361	-105.839	-105.760	6.730
4200	14.875	97.155	83.620	56.848	-105.830	-105.633	6.730
4300	14.877	97.505	83.939	58.336	-105.819	-105.500	6.730
4400	14.878	97.847	84.251	59.824	-105.806	-105.363	6.730
4500	14.879	98.181	84.557	61.312	-105.791	-105.222	6.730
4600	14.880	98.508	84.856	62.800	-105.775	-105.077	6.730
4700	14.881	98.828	85.150	64.288	-105.758	-104.928	6.730
4800	14.882	99.142	85.438	65.776	-105.739	-104.775	6.730
4900	14.883	99.449	85.721	67.264	-105.719	-104.617	6.730
5000	14.884	99.749	85.999	68.752	-105.698	-104.455	6.730
5100	14.885	100.044	86.271	70.241	-105.675	-104.289	6.730
5200	14.885	100.333	86.539	71.729	-105.650	-104.117	6.730
5300	14.886	100.617	86.802	73.218	-105.623	-103.940	6.730
5400	14.887	100.895	87.060	74.707	-105.595	-103.758	6.730
5500	14.887	101.168	87.314	76.195	-105.566	-103.571	6.730
5600	14.888	101.436	87.564	77.684	-105.535	-103.379	6.730
5700	14.889	101.700	87.810	79.173	-105.502	-103.182	6.730
5800	14.889	101.959	88.052	80.662	-105.467	-102.971	6.730
5900	14.890	102.213	88.290	82.151	-105.430	-102.755	6.730
6000	14.890	102.464	88.524	83.640	-105.392	-102.535	6.730

Sept. 30, 1963

MOL. WT. = 82.9

TITANIUM OXIDE FLUORIDE (TiOF)

(IDEAL GAS)

Point Group [C_{2v}]S°_{298.15} = [59.887] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [2]

ΔH°_f 0 = [-103.0] kcal. mole⁻¹ΔH°_f 298.15 = [-103.5] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

 ω_e , cm.⁻¹

[880] (1)

[300] (2)

[740] (1)

Bond Distances: Ti-O = [1.62] Å Ti-F = [1.74] Å

Bond Angle: O-Ti-F = [180°]

Rotational Constant: B₀ = [0.1705] cm.⁻¹

Heat of Formation.

ΔH°_f 0 was estimated as -103 kcal. mole⁻¹ by J. S. Gordon, AstroSystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH°_f 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. Principal moment was 16.419 X 10⁻³⁹ g. cm.²

Monofluorine Dioxide (F₀₂)
(Ideal Gas) GFW = 50.9972

T, °K	C _p ^o	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH _f ^o	ΔG ^o	Log K _p
0	∞	INFINITE	- 2.688	3.442	3.442	INFINITE
100	8.242	51.736	70.617	3.200	4.201	9.181
200	9.611	57.864	79.966	3.047	5.272	5.761
298	10.611	61.903	84.906	3.000	6.376	4.674
300	10.626	61.968	85.020	3.000	6.397	4.660
400	11.319	65.125	92.329	3.003	7.530	4.114
500	11.843	67.710	98.154	3.027	8.660	3.785
600	12.257	69.907	103.101	3.062	9.783	3.563
700	12.590	71.751	107.254	3.109	10.903	3.403
800	12.860	73.252	110.671	3.133	12.013	3.283
900	13.086	74.531	113.378	3.147	13.119	3.186
1000	13.273	75.631	115.391	3.211	14.223	3.108
1100	13.426	76.585	116.657	3.245	15.321	3.044
1200	13.558	77.408	117.188	3.268	16.419	2.990
1300	13.676	78.092	117.576	3.283	17.519	2.946
1400	13.778	78.659	117.829	3.300	18.603	2.904
1500	13.859	79.121	117.960	3.319	19.693	2.869
1600	13.922	79.496	118.000	3.380	20.782	2.839
1700	13.970	79.792	118.046	3.486	21.869	2.812
1800	14.005	79.999	118.097	3.586	22.952	2.787
1900	14.030	80.125	118.153	3.681	24.040	2.765
2000	14.048	80.178	118.213	3.769	25.124	2.745
2100	14.060	80.259	118.279	3.850	26.210	2.728
2200	14.066	80.361	118.350	3.923	27.295	2.711
2300	14.067	80.484	118.425	3.990	28.378	2.694
2400	14.064	80.629	118.504	4.051	29.460	2.678
2500	14.057	80.794	118.587	4.107	30.541	2.661
2600	14.046	80.979	118.674	4.158	31.621	2.644
2700	14.032	81.183	118.764	4.204	32.700	2.627
2800	14.015	81.406	118.857	4.245	33.778	2.610
2900	13.996	81.647	118.953	4.281	34.855	2.593
3000	13.975	81.904	119.052	4.312	35.930	2.576
3100	13.951	82.176	119.154	4.338	37.003	2.559
3200	13.924	82.462	119.259	4.359	38.074	2.542
3300	13.895	82.762	119.367	4.375	39.143	2.525
3400	13.864	83.074	119.477	4.387	40.210	2.508
3500	13.831	83.397	119.589	4.395	41.274	2.491
3600	13.796	83.731	119.703	4.400	42.337	2.474
3700	13.760	84.074	119.818	4.402	43.398	2.457
3800	13.723	84.426	119.934	4.401	44.457	2.440
3900	13.685	84.786	120.051	4.397	45.513	2.423
4000	13.646	85.153	120.168	4.390	46.566	2.406
4100	13.606	85.526	120.285	4.379	47.616	2.389
4200	13.565	85.904	120.402	4.365	48.663	2.372
4300	13.523	86.286	120.518	4.348	49.707	2.355
4400	13.480	86.671	120.633	4.328	50.748	2.338
4500	13.436	87.059	120.747	4.305	51.785	2.321
4600	13.391	87.450	120.860	4.279	52.818	2.304
4700	13.345	87.843	120.971	4.250	53.847	2.287
4800	13.298	88.238	121.080	4.218	54.872	2.270
4900	13.250	88.634	121.187	4.183	55.893	2.253
5000	13.201	89.031	121.291	4.145	56.910	2.236
5100	13.151	89.428	121.393	4.105	57.923	2.219
5200	13.100	89.825	121.493	4.063	58.932	2.202
5300	13.048	90.221	121.590	4.019	59.937	2.185
5400	12.995	90.616	121.684	3.973	60.938	2.168
5500	12.941	91.010	121.776	3.925	61.934	2.151
5600	12.886	91.403	121.865	3.875	62.926	2.134
5700	12.830	91.795	121.951	3.823	63.914	2.117
5800	12.773	92.186	122.034	3.769	64.898	2.100
5900	12.715	92.575	122.114	3.713	65.878	2.083
6000	12.656	92.962	122.191	3.655	66.853	2.066

Sept. 30, 1966

F₀₂

OPW = 50.9972

(IDEAL GAS)

MONOFLUORINE DIOXIDE (F₀₂)

Point Group C_{2v}
S_{298.15} = 51.9 gibbs/mol
Ground State Quantum Weight = 2
ΔH_f^o = 3.4 ± 5 kcal/mol
ΔH_f^o_{298.15} = 3.0 ± 5 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
1495.0 (1)	
584.5 (1)	
376.0 (1)	

Bond Distance: O-O = 1.22 Å O-P = 1.58 Å

Bond Angle: O-O-P = 109.5°

Product of the Moments of Inertia: I_AI_BI_C = 7.7504 × 10⁻¹¹⁶ g³cm⁶

G° = 1

Heat of Formation.

The heat of formation for F₂O₂(g) is unavailable in the literature. Based on a kinetic study of the thermal decomposition of F₂O₂(g) reported by H. J. Schumacher and P. Frieck, Z. physik. Chem. **B24**, 332 (1934), the enthalpy change for the reaction F₂O₂(g) = F(g) + O₂(g) was estimated to be + 17.3 kcal/mol by J. B. Levy and B. K. Healey, J. Phys. Chem. **69**, 408 (1965), assuming that the activation energy for the reverse reaction is negligible. From this data the value of ΔH_f^o_{298.15}(F₂O₂, g) was calculated as + 3.2 kcal/mol, using ΔH_f^o_{298.15} = + 4.73 kcal/mol for F₂O₂(g) determined calorimetrically by A. D. Kirshenbaum, A. V. Grosse and J. G. Aston, J. Am. Chem. Soc. **81**, 6398 (1959).

Based on the assumption that the enthalpy change for the reaction F₂O₂(g) = F(g) + O₂(g) is 16.5 kcal/mol, which is half of the enthalpy change for the reaction F₂O₂(g) = 2F(g) + O₂(g), the heat of formation (ΔH_f^o_{298.15}) for F₂O₂(g) was derived as + 2.4 kcal/mol.

The value of ΔH_f^o_{298.15}(F₂O₂, g) adopted is 3 ± 5 kcal/mol.

Heat Capacity and Entropy.

The vibrational frequencies for F₂O₂(g) were assumed to be the same as those obtained from matrix isolation by P. N. Noble and G. C. Pimentel, J. Chem. Phys. **44**, 3641 (1966). These authors have observed two more frequencies for isotopically substituted F₂O₂ and combined them with those observed by R. D. Spratley, J. J. Turner and G. C. Pimentel, J. Chem. Phys. **44**, 2063 (1966), and performed a normal coordinate analysis. The results confirm the fact that the bond distances and angles in F₂O₂ are essentially the same as those reported for F₂O₂(g) by R. H. Jackson, J. Chem. Soc., 4585 (1962). The same molecular structure for F₂O₂ was also deduced from electron spin resonance and electron paramagnetic resonance data reported by R. W. Fessenden and R. H. Schuler, J. Chem. Phys. **44**, 434 (1966) and P. H. Kasal and A. D. Kirshenbaum, J. Am. Chem. Soc. **87**, 3069 (1965), respectively. Hence this molecular structure was adopted. Two vibrational frequencies, ν₁ and ν₃, for F₂O₂ molecule were also observed by A. Arkell, J. Am. Chem. Soc. **87**, 4057 (1965).

The three principal moments of inertia are: I_A = 1.1103 × 10⁻³⁹, I_B = 7.8182 × 10⁻³⁹ and I_C = 8.9285 × 10⁻³⁹ g cm².

F₀₂

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 49.975

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0	0.000	0.000	INFINITE	-2.117	-14.200	-14.200	-14.200	INFINITE
100	6.959	60.183	-1.422	-1.422	-13.964	-13.964	-13.964	55.743
200	7.135	56.819	-0.720	-0.720	-13.910	-13.910	-13.910	40.536
298	7.257	53.744	0.000	0.000	-14.000	-14.000	-14.117	35.222
300	7.266	53.791	0.014	0.014	-14.002	-14.002	-14.117	35.222
400	7.956	56.023	5.046	7.951	-14.143	-14.143	-14.306	15.459
500	8.277	57.831	5.628	1.601	-14.307	-14.307	-14.595	12.807
600	8.430	59.350	5.520	2.326	-14.490	-14.490	-14.868	11.344
700	8.566	60.660	5.567	3.286	-14.698	-14.698	-15.134	10.296
800	8.664	61.811	5.627	4.117	-14.933	-14.933	-15.393	9.537
900	8.737	62.836	5.761	5.017	-15.197	-15.197	-15.649	9.037
1000	8.794	63.760	5.865	5.894	-15.484	-15.484	-15.894	8.678
1100	8.839	64.600	5.940	6.776	-15.787	-15.787	-16.138	8.400
1200	8.876	65.371	6.000	7.662	-16.100	-16.100	-16.380	8.190
1300	8.907	66.082	6.050	8.551	-16.422	-16.422	-16.620	8.000
1400	8.933	66.743	6.099	9.443	-16.753	-16.753	-16.859	7.826
1500	8.956	67.361	6.146	10.337	-17.092	-17.092	-17.092	7.666
1600	8.976	67.930	6.188	11.234	-17.439	-17.439	-17.338	7.517
1700	8.994	68.464	6.229	12.132	-17.794	-17.794	-17.584	7.376
1800	9.011	68.968	6.268	13.033	-18.157	-18.157	-17.830	7.242
1900	9.026	69.446	6.305	13.935	-18.528	-18.528	-18.076	7.115
2000	9.041	69.899	6.339	14.838	-18.906	-18.906	-18.322	7.000
2100	9.054	70.331	6.370	15.743	-19.292	-19.292	-18.568	6.894
2200	9.067	70.741	6.398	16.650	-19.685	-19.685	-18.814	6.797
2300	9.079	71.126	6.424	17.558	-20.085	-20.085	-19.060	6.707
2400	9.091	71.492	6.449	18.465	-20.492	-20.492	-19.306	6.623
2500	9.102	71.837	6.472	19.374	-20.906	-20.906	-19.552	6.544
2600	9.113	72.161	6.493	20.285	-21.326	-21.326	-19.798	6.470
2700	9.123	72.471	6.511	21.197	-21.752	-21.752	-20.044	6.401
2800	9.133	72.767	6.526	22.110	-22.184	-22.184	-20.290	6.336
2900	9.143	73.048	6.539	23.023	-22.622	-22.622	-20.536	6.275
3000	9.153	73.313	6.550	23.938	-23.066	-23.066	-20.782	6.217
3100	9.163	73.563	6.559	24.853	-23.516	-23.516	-21.028	6.162
3200	9.172	73.798	6.566	25.768	-23.972	-23.972	-21.274	6.110
3300	9.181	74.018	6.572	26.683	-24.434	-24.434	-21.520	6.060
3400	9.191	74.223	6.576	27.600	-24.902	-24.902	-21.766	6.011
3500	9.200	74.413	6.579	28.517	-25.376	-25.376	-22.012	5.964
3600	9.209	74.588	6.581	29.434	-25.856	-25.856	-22.258	5.919
3700	9.218	74.748	6.582	30.351	-26.342	-26.342	-22.504	5.875
3800	9.227	74.893	6.583	31.268	-26.834	-26.834	-22.750	5.832
3900	9.235	75.023	6.584	32.185	-27.332	-27.332	-23.000	5.790
4000	9.244	75.138	6.584	33.102	-27.836	-27.836	-23.250	5.748
4100	9.253	75.238	6.584	34.019	-28.346	-28.346	-23.500	5.707
4200	9.261	75.323	6.584	34.936	-28.862	-28.862	-23.750	5.667
4300	9.270	75.393	6.584	35.853	-29.384	-29.384	-24.000	5.627
4400	9.278	75.448	6.584	36.770	-29.912	-29.912	-24.250	5.587
4500	9.287	75.498	6.584	37.687	-30.446	-30.446	-24.500	5.547
4600	9.295	75.543	6.584	38.604	-30.986	-30.986	-24.750	5.507
4700	9.303	75.583	6.584	39.521	-31.532	-31.532	-25.000	5.467
4800	9.312	75.618	6.584	40.438	-32.084	-32.084	-25.250	5.427
4900	9.320	75.648	6.584	41.355	-32.642	-32.642	-25.500	5.387
5000	9.329	75.673	6.584	42.272	-33.206	-33.206	-25.750	5.347
5100	9.337	75.693	6.584	43.189	-33.776	-33.776	-26.000	5.307
5200	9.345	75.708	6.584	44.106	-34.352	-34.352	-26.250	5.267
5300	9.353	75.718	6.584	45.023	-34.934	-34.934	-26.500	5.227
5400	9.362	75.723	6.584	45.940	-35.522	-35.522	-26.750	5.187
5500	9.370	75.723	6.584	46.857	-36.116	-36.116	-27.000	5.147
5600	9.378	75.718	6.584	47.774	-36.716	-36.716	-27.250	5.107
5700	9.386	75.708	6.584	48.691	-37.322	-37.322	-27.500	5.067
5800	9.394	75.693	6.584	49.608	-37.934	-37.934	-27.750	5.027
5900	9.403	75.673	6.584	50.525	-38.552	-38.552	-28.000	4.987
6000	9.411	75.648	6.584	51.442	-39.176	-39.176	-28.250	4.947

Dec. 31, 1960; Sept. 30, 1962

Phosphorus Monofluoride (PF) (Ideal Gas)

Mol. Wt. = 49.975

 $\Delta H_f^\circ 298.15 = -14 \pm 3 \text{ kcal. mole}^{-1}$ $S^\circ 298.15 = 53.7 \text{ cal. deg}^{-1} \text{ mole}^{-1}$ Ground State Configuration \sum

Electronic Level and Multiplicity

 $\epsilon, \text{ cm}^{-1}$ g_1 0 3 $\omega_e X_e = 4.409 \text{ cm}^{-1}$ $B_e = 0.5665 \text{ cm}^{-1}$ $\alpha_e = 0.00456 \text{ cm}^{-1}$ $r_e = 1.590 \text{ \AA}$ $\sigma = 1$

Heat of Formation, $\Delta H_f^\circ 298.15$ was derived from a D_0° calculated with spectroscopic constants reported by A. E. Douglas and M. Preckowiak, Can. J. Phys. 40, 832 (1962). The D_0° value was calculated using the dissociation and spectroscopic relations given by G. Herzberg in "Spectra of Diatomic Molecules", D. van Nostrand Co., N. Y., 2nd Ed. (1950) pages 93 and 100. If the PF molecule dissociates to the ground state atoms, $F(3s/2) + F(2p_{3/2})$, the corresponding $\Delta H_f^\circ 298.15$ is $-15 \pm 3 \text{ kcal. mole}^{-1}$. If the dissociation is to the phosphorus ground state and the excited fluorine state, $F(3s/2) + F(2p_{1/2})$, the corresponding $\Delta H_f^\circ 298.15$ is $-14 \pm 3 \text{ kcal. mole}^{-1}$. The dissociation to an excited $F(2p_{1/2})$ atom was assumed to obtain the selected $\Delta H_f^\circ 298.15 = -14 \pm 3 \text{ kcal. mole}^{-1}$.

The heat of formation was estimated to be $-17 \text{ kcal. mole}^{-1}$ by J. S. Gordon, "Thermodynamic Data for Combustion Products", January, 1960, Thiokol Chemical Corp. This estimate when changed from white(Ox) to red(V) phosphorus reference state ($-13 \text{ kcal. mole}^{-1}$) agrees within uncertainty limits with the derived $\Delta H_f^\circ 298.15$ values.

Heat Capacity and Entropy. The molecular constants were reported by Douglas and Preckowiak (loc. cit.). They photographed and analyzed the electronic spectra of PF in the emission spectrum of a discharge through a mixture of PF_3 and He.

Phosphorus Sulfide Fluoride (PSF)
(Ideal Gas) Mol. Wt. = 82.041 INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH°	ΔF°	Log K _p
0	8.100	INFINITE	INFINITE	2.654	-35.484	-35.484	INFINITE	
100	8.165	56.356	7.074	1.956	-35.488	-35.488	86.638	
200	9.371	62.368	57.283	.983	-35.476	-35.476	46.710	
298	10.621	66.350	60.350	.000	-37.500	-37.500	35.468	
300	10.642	66.416	60.360	.020	-37.506	-37.506	35.300	
400	11.500	69.615	64.780	1.134	-37.509	-37.509	26.519	
500	12.222	72.275	67.550	2.427	-38.438	-38.438	21.341	
600	12.652	74.545	69.500	3.373	-39.257	-39.257	19.505	
700	12.920	76.240	70.525	4.093	-39.835	-39.835	17.440	
800	13.116	77.416	71.525	4.625	-40.200	-40.200	15.630	
900	13.293	78.087	72.506	5.000	-40.400	-40.400	14.060	
1000	13.402	78.224	72.506	5.114	-40.400	-40.400	13.637	
1100	13.455	78.259	72.506	5.166	-40.400	-40.400	12.170	
1200	13.461	78.269	72.506	5.172	-40.400	-40.400	10.948	
1300	13.461	78.269	72.506	5.172	-40.400	-40.400	9.948	
1400	13.462	78.269	72.506	5.172	-40.400	-40.400	9.028	
1500	13.466	78.269	72.506	5.172	-40.400	-40.400	8.260	
1600	13.466	78.269	72.506	5.172	-40.400	-40.400	7.588	
1700	13.466	78.269	72.506	5.172	-40.400	-40.400	6.996	
1800	13.466	78.269	72.506	5.172	-40.400	-40.400	6.465	
1900	13.466	78.269	72.506	5.172	-40.400	-40.400	5.988	
2000	13.466	78.269	72.506	5.172	-40.400	-40.400	5.575	
2100	13.466	78.269	72.506	5.172	-40.400	-40.400	5.201	
2200	13.466	78.269	72.506	5.172	-40.400	-40.400	4.865	
2300	13.466	78.269	72.506	5.172	-40.400	-40.400	4.565	
2400	13.466	78.269	72.506	5.172	-40.400	-40.400	4.293	
2500	13.466	78.269	72.506	5.172	-40.400	-40.400	4.045	
2600	13.466	78.269	72.506	5.172	-40.400	-40.400	3.817	
2700	13.466	78.269	72.506	5.172	-40.400	-40.400	3.607	
2800	13.466	78.269	72.506	5.172	-40.400	-40.400	3.415	
2900	13.466	78.269	72.506	5.172	-40.400	-40.400	3.237	
3000	13.466	78.269	72.506	5.172	-40.400	-40.400	3.077	
3100	13.466	78.269	72.506	5.172	-40.400	-40.400	2.932	
3200	13.466	78.269	72.506	5.172	-40.400	-40.400	2.799	
3300	13.466	78.269	72.506	5.172	-40.400	-40.400	2.677	
3400	13.466	78.269	72.506	5.172	-40.400	-40.400	2.565	
3500	13.466	78.269	72.506	5.172	-40.400	-40.400	2.462	
3600	13.466	78.269	72.506	5.172	-40.400	-40.400	2.371	
3700	13.466	78.269	72.506	5.172	-40.400	-40.400	2.291	
3800	13.466	78.269	72.506	5.172	-40.400	-40.400	2.221	
3900	13.466	78.269	72.506	5.172	-40.400	-40.400	2.161	
4000	13.466	78.269	72.506	5.172	-40.400	-40.400	2.112	
4100	13.466	78.269	72.506	5.172	-40.400	-40.400	2.072	
4200	13.466	78.269	72.506	5.172	-40.400	-40.400	2.041	
4300	13.466	78.269	72.506	5.172	-40.400	-40.400	2.018	
4400	13.466	78.269	72.506	5.172	-40.400	-40.400	2.000	
4500	13.466	78.269	72.506	5.172	-40.400	-40.400	1.985	
4600	13.466	78.269	72.506	5.172	-40.400	-40.400	1.972	
4700	13.466	78.269	72.506	5.172	-40.400	-40.400	1.961	
4800	13.466	78.269	72.506	5.172	-40.400	-40.400	1.951	
4900	13.466	78.269	72.506	5.172	-40.400	-40.400	1.942	
5000	13.466	78.269	72.506	5.172	-40.400	-40.400	1.934	
5100	13.466	78.269	72.506	5.172	-40.400	-40.400	1.927	
5200	13.466	78.269	72.506	5.172	-40.400	-40.400	1.921	
5300	13.466	78.269	72.506	5.172	-40.400	-40.400	1.916	
5400	13.466	78.269	72.506	5.172	-40.400	-40.400	1.911	
5500	13.466	78.269	72.506	5.172	-40.400	-40.400	1.907	
5600	13.466	78.269	72.506	5.172	-40.400	-40.400	1.903	
5700	13.466	78.269	72.506	5.172	-40.400	-40.400	1.900	
5800	13.466	78.269	72.506	5.172	-40.400	-40.400	1.897	
5900	13.466	78.269	72.506	5.172	-40.400	-40.400	1.894	
6000	13.466	78.269	72.506	5.172	-40.400	-40.400	1.891	

Dec. 31, 1960; Sept. 30, 1962

PHOSPHORUS SULFIDE FLUORIDE (PSF)

(Ideal Gas)

Mol. Wt. = 82.041

ΔH°_f 298.15 = [-37 ± 15] kcal. mole⁻¹

S°_{298.15} = [86.35 ± 3] cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω cm. ⁻¹	[940] (1)	[740] (1)	[400] (1)
940	1	1	1
740	1	1	1
400	1	1	1

Product of the Moments of Inertia: I_AI_BI_C = [7.999 X 10⁻¹¹] g.³ cm.⁶ σ = 1

Heat of Formation. The ΔH°_f 298.15 was estimated by C. B. Henderson and R. S. Scheffee, Atlantic Research Corp., Alexandria, Virginia, "Survey of Thermochemical Data," January, 1960. This estimated ΔH°_f 298.15 was corrected for the change in the reference state of phosphorus from white α to red γ.

Heat Capacity and Entropy. The vibrational frequencies were estimated by comparison with the corresponding frequencies of PF₃(g), PS(g), and PF₂(g). The vibrational levels of PF₂(g) in turn were estimated by J. S. Gordon, Thokol Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products," January, 1960. The entropy was estimated by C. B. Henderson and R. S. Scheffee (loc. cit.). The product of the moment of inertia was derived from the estimated entropy.

INTERIM TABLE

Mol. Wt. = 226.21

T. °K.	C _p	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	-2.215	8.516	-	INFINITE
100	7.073	51.377	60.561	-1.519	8.891	-12.813	22.131
200	7.470	56.444	60.366	-0.784	8.809	-12.949	14.149
298	8.224	59.627	59.627	0.000	9.000	-14.939	10.950
300	8.231	59.678	59.677	0.015	9.004	-14.976	10.909
400	8.208	59.956	59.954	0.054	9.002	-14.936	9.253
500	8.080	60.000	60.279	1.115	9.048	-18.847	8.236
600	8.781	65.001	61.287	2.588	9.650	-20.710	7.543
700	8.849	66.960	62.003	3.470	11.064	-22.343	6.975
800	8.899	68.145	62.699	4.357	11.331	-23.936	6.539
900	8.933	69.193	63.283	5.249	11.581	-25.498	6.191
1000	8.968	70.138	63.996	6.144	11.844	-27.028	5.907
1100	8.997	70.994	64.592	7.043	12.091	-28.535	5.669
1200	9.024	71.778	65.159	7.944	12.329	-30.018	5.467
1300	9.052	72.502	65.696	8.847	12.563	-31.482	5.292
1400	9.081	73.174	66.206	9.754	12.795	-32.930	5.140
1500	9.113	73.801	66.692	10.664	13.025	-34.358	5.006
1600	9.149	74.391	67.155	11.577	13.256	-35.774	4.886
1700	9.188	74.946	67.597	12.494	13.487	-37.173	4.779
1800	9.230	75.473	68.020	13.415	13.721	-38.562	4.682
1900	9.273	75.976	68.426	14.340	13.956	-39.936	4.593
2000	9.323	76.450	68.815	15.270	14.193	-41.296	4.512
2100	9.373	76.906	69.190	16.204	14.431	-42.643	4.439
2200	9.424	77.343	69.550	17.144	14.670	-43.978	4.372
2300	9.477	77.763	69.898	18.089	14.911	-45.303	4.310
2400	9.532	78.168	70.236	19.040	15.154	-46.618	4.252
2500	9.582	78.558	70.566	19.995	15.399	-47.924	4.198
2600	9.635	78.935	70.875	20.956	15.646	-49.221	4.148
2700	9.686	79.299	71.180	21.922	15.894	-50.510	4.100
2800	9.737	79.652	71.476	22.893	16.143	-51.794	4.054
2900	9.786	79.995	71.764	23.869	16.393	-53.073	4.010
3000	9.833	80.327	72.044	24.850	16.644	-54.347	3.968
3100	9.878	80.651	72.316	25.836	16.896	-55.616	3.927
3200	9.921	80.965	72.582	26.826	17.149	-56.880	3.887
3300	9.962	81.271	72.840	27.820	17.403	-58.139	3.848
3400	10.001	81.569	73.093	28.818	17.658	-59.393	3.810
3500	10.038	81.859	73.339	29.820	17.914	-60.642	3.772
3600	10.074	82.142	73.580	30.826	18.171	-61.886	3.735
3700	10.109	82.419	73.815	31.834	18.429	-63.125	3.698
3800	10.144	82.689	74.045	32.846	18.687	-64.359	3.662
3900	10.178	82.952	74.270	33.861	18.946	-65.588	3.627
4000	10.189	83.210	74.490	34.879	19.206	-66.812	3.592
4100	10.213	83.462	74.706	35.899	19.467	-68.031	3.558
4200	10.235	83.708	74.917	36.921	19.729	-69.245	3.524
4300	10.256	83.949	75.125	37.946	19.992	-70.454	3.491
4400	10.275	84.185	75.328	38.972	20.256	-71.658	3.458
4500	10.292	84.416	75.527	40.001	20.521	-72.857	3.425
4600	10.308	84.643	75.727	41.031	20.787	-74.051	3.392
4700	10.323	84.865	75.915	42.062	21.054	-75.240	3.360
4800	10.337	85.082	76.104	43.095	21.322	-76.424	3.328
4900	10.349	85.295	76.289	44.130	21.591	-77.603	3.296
5000	10.360	85.503	76.472	45.165	21.861	-78.777	3.264
5100	10.370	85.710	76.651	46.202	22.132	-79.946	3.232
5200	10.379	85.911	76.827	47.239	22.404	-81.110	3.200
5300	10.388	86.109	77.000	48.278	22.677	-82.270	3.168
5400	10.396	86.303	77.171	49.317	22.951	-83.425	3.136
5500	10.402	86.494	77.338	50.357	23.226	-84.576	3.104
5600	10.409	86.682	77.504	51.397	23.502	-85.722	3.072
5700	10.415	86.866	77.666	52.438	23.779	-86.863	3.040
5800	10.420	87.047	77.826	53.480	24.057	-88.000	3.008
5900	10.425	87.225	77.984	54.522	24.336	-89.132	2.976
6000	10.429	87.401	78.140	55.565	24.616	-90.260	2.944

June 30, 1962

FPb

Lead Monofluoride (PbF)

(Ideal Gas)

Mol. Wt. = 226.21

 ΔH_f^0 298.15 = -9.0 ± 9.2 kcal. mole⁻¹ $S_{298.15}^0$ = 59.627 cal. deg.⁻¹ mole⁻¹Ground State Configuration 2Π

Electronic Levels and Multiplicities

ϵ , cm. ⁻¹	E_1
0	2
8268	2

 $\omega_e = 507.2$ cm.⁻¹ $\omega_e x_e = 2.30$ cm.⁻¹ $B_e = [0.2597]$ cm.⁻¹ $d_e = [0.0017]$ cm.⁻¹Heat of Formation. ΔH_f^0 298.15 was calculated from the dissociation

energy of PbF(g) reported by A. G. Gaydon, "Dissociation Energies

and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London,

1953.

Heat Capacity and Entropy. Ground state configuration, ϵ , ω_e and $\omega_e x_e$ were given by G. Herzberg, "Spectra of Diatomic Mole-cules," Van Nostrand, New York, 1950. B_e and d_e were estimated

by J. S. Gordon, AstroSystems, Inc., private communication, May,

1962.

Silicon Monofluoride (SiF)

(Ideal Gas) $GFW = 47.0844$

T, °K	Cp°	S°	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔHf°	ΔGf°	Log Kp
0	7.000	∞	INFINITE	-2.261	5.037	5.037	5.037	INFINITE
100	7.630	45.521	60.769	1.525	4.713	4.713	4.713	15.600
200	7.850	48.510	58.810	1.250	4.580	4.580	4.580	16.400
298	7.803	51.937	55.937	1.000	4.400	4.400	4.400	8.663
300	7.809	53.985	53.937	.014	4.402	4.402	4.402	8.662
400	8.096	56.272	51.247	.810	4.698	4.698	4.698	8.017
500	8.326	58.104	50.104	1.632	4.824	4.824	4.824	7.497
600	8.492	59.638	55.516	2.473	4.967	4.967	4.967	7.141
700	8.611	60.958	56.201	3.328	5.122	5.122	5.122	6.878
800	8.699	62.112	56.869	4.194	5.289	5.289	5.289	6.676
900	8.765	63.141	57.510	5.067	5.466	5.466	5.466	6.512
1000	8.817	64.067	58.120	5.947	5.653	5.653	5.653	6.376
1100	8.858	64.909	58.700	6.830	5.850	5.850	5.850	6.263
1200	8.893	65.682	59.250	7.718	6.056	6.056	6.056	6.165
1300	8.921	66.395	59.772	8.609	6.272	6.272	6.272	6.079
1400	8.946	67.057	60.269	9.502	6.497	6.497	6.497	6.002
1500	8.968	67.675	60.743	10.398	6.732	6.732	6.732	5.933
1600	8.987	68.254	61.194	11.296	6.976	6.976	6.976	5.871
1700	9.005	68.799	61.626	12.195	7.224	7.224	7.224	5.800
1800	9.021	69.315	62.039	13.097	7.473	7.473	7.473	5.662
1900	9.036	69.803	62.435	13.999	7.724	7.724	7.724	5.537
2000	9.050	70.267	62.815	14.904	7.976	7.976	7.976	5.424
2100	9.063	70.708	63.180	15.809	8.230	8.230	8.230	5.320
2200	9.075	71.130	63.532	16.716	8.486	8.486	8.486	5.224
2300	9.087	71.534	63.871	17.624	8.743	8.743	8.743	5.136
2400	9.099	71.921	64.199	18.534	9.000	9.000	9.000	5.055
2500	9.110	72.293	64.515	19.444	9.258	9.258	9.258	4.979
2600	9.121	72.650	64.821	20.356	9.516	9.516	9.516	4.909
2700	9.132	72.995	65.117	21.266	9.774	9.774	9.774	4.843
2800	9.142	73.327	65.405	22.182	10.032	10.032	10.032	4.781
2900	9.153	73.648	65.683	23.097	10.290	10.290	10.290	4.722
3000	9.164	73.958	65.954	24.013	10.548	10.548	10.548	4.668
3100	9.174	74.259	66.217	24.930	10.806	10.806	10.806	4.616
3200	9.185	74.550	66.473	25.847	11.064	11.064	11.064	4.567
3300	9.195	74.833	66.722	26.766	11.322	11.322	11.322	4.520
3400	9.206	75.108	66.965	27.687	11.580	11.580	11.580	4.476
3500	9.217	75.375	67.201	28.608	11.838	11.838	11.838	4.434
3600	9.229	75.635	67.432	29.530	12.096	12.096	12.096	4.392
3700	9.241	75.886	67.657	30.454	12.354	12.354	12.354	4.350
3800	9.253	76.134	67.877	31.378	12.612	12.612	12.612	4.308
3900	9.265	76.378	68.092	32.304	12.870	12.870	12.870	4.266
4000	9.276	76.610	68.302	33.231	13.128	13.128	13.128	4.224
4100	9.291	76.839	68.507	34.160	13.386	13.386	13.386	4.182
4200	9.305	77.063	68.708	35.090	13.644	13.644	13.644	4.140
4300	9.320	77.282	68.905	36.021	13.902	13.902	13.902	4.098
4400	9.335	77.496	69.098	36.954	14.160	14.160	14.160	4.056
4500	9.350	77.706	69.287	37.886	14.418	14.418	14.418	4.014
4600	9.367	77.912	69.472	38.824	14.676	14.676	14.676	3.972
4700	9.384	78.114	69.654	39.761	14.934	14.934	14.934	3.930
4800	9.401	78.311	69.832	40.700	15.192	15.192	15.192	3.888
4900	9.420	78.505	70.007	41.641	15.450	15.450	15.450	3.846
5000	9.439	78.696	70.179	42.584	15.708	15.708	15.708	3.804
5100	9.459	78.883	70.348	43.529	15.966	15.966	15.966	3.762
5200	9.479	79.067	70.514	44.476	16.224	16.224	16.224	3.720
5300	9.501	79.248	70.677	45.425	16.482	16.482	16.482	3.678
5400	9.523	79.426	70.837	46.376	16.740	16.740	16.740	3.636
5500	9.546	79.600	70.995	47.330	17.000	17.000	17.000	3.594
5600	9.570	79.773	71.150	48.286	17.258	17.258	17.258	3.552
5700	9.595	79.942	71.303	49.244	17.516	17.516	17.516	3.510
5800	9.621	80.109	71.453	50.205	17.774	17.774	17.774	3.468
5900	9.647	80.274	71.602	51.168	18.032	18.032	18.032	3.426
6000	9.674	80.436	71.747	52.134	18.290	18.290	18.290	3.384

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1963; Dec. 31, 1969

SILICON MONOFLOURIDE (SiF)

(IDEAL GAS)

GFW = 47.0844

Ground State Configuration $2^1\Pi$ $\Delta H_f^\circ = -5.0 \pm 3$ kcal/mol $S_{298.15}^\circ = 53.937 \pm 0.01$ gibbs/mol $\Delta H_f^\circ = -4.6 \pm 3$ kcal/mol

Electronic Levels and Quantum Weights

State	ϵ_i , cm ⁻¹	g_i
$X^1\Pi$	0	2
$A^2\Sigma^-$	161.93	2
$4^2\Sigma^-$	22787.6	2
$4^2\Sigma$	23808.4	4
$B^2\Sigma$	34638.3	2
$C^2\Delta$	39537	4
$C^2\Pi$	41985	4
$D^2\Pi$	46607	4
$D^2\Sigma^+$	47491	2

 $\omega_e X_e^\circ = 4.74 \pm 0.03$ cm⁻¹ $\sigma = 1$ $B_e = 0.58138$ cm⁻¹ $r_e = 1.6008$ Å

Heat of Formation

Ehlert and Margrave (1) have studied mass-spectrometrically the reaction $Si(g) + SiF_2(g) \rightarrow 2SiF(g)$ by monitoring the intensities of the Si^+ , SiF_2^+ , and SiF^+ ions in an equilibrium system containing CaF_2 and Si. The ionization cross-sections are assumed to cancel so that equilibrium constants can be obtained directly from the ion intensities. We have analysed the above data using present JANAF functions and obtain $\Delta H_{298}^\circ = 23.5 \pm 3$ kcal by the third law technique with a drift of -0.8 ± 1.1 eu, the second law value is 23.9 ± 7 kcal. We adopt the third law value which with JANAF auxiliary data gives $\Delta H_f^\circ(SiF, g) = -4.6 \pm 3$ kcal/mol.

Johns and Barrow (2) have selected $\Delta H_f^\circ(SiF, g) = 115 \pm 10$ kcal/mol, from Birge-Sponer extrapolations of several states, this gives $\Delta H_f^\circ = 0.1 \pm 10$ kcal/mol in good agreement with the adopted value.

Heat Capacity and Entropy

The molecular constants of the various electronic levels have been documented by Johns and Barrow (2), Verma (3), Barrow et al. (4), and Appelblad et al. (5). The approximation involving the use of the ground state constants for all electronic levels is used since it introduces negligible error in this molecule.

References

1. T. C. Ehlert and J. L. Margrave, J. Chem. Phys. **43**, 1066 (1964).
2. J. W. C. Johns and R. F. Barrow, Proc. Phys. Soc. (London) **71**, 476 (1958).
3. R. D. Verma, Can. J. Phys. **40**, 586 (1962).
4. R. F. Barrow, D. Butler, J. W. C. Johns and J. L. Powell, Proc. Phys. Soc. (London) **73**, 317 (1959).
5. O. Appelblad, R. F. Barrow, and R. D. Verma, J. Phys. B (Proc. Phys. Soc. (London)) Series 2, **1**, 274 (1968).

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	enthalpy/mol H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	4.000	INFINITE	-	16.001	16.001	INFINITE
100	6.002	48.321	2.208	15.793	15.793	17.250
200	7.602	57.638	1.786	15.671	15.671	22.950
298	8.466	56.692	.000	16.000	23.497	17.223
300	8.461	56.744	.016	16.002	23.543	17.151
400	9.156	59.279	.898	16.123	26.507	14.258
500	9.636	61.377	1.680	16.231	28.304	12.459
600	9.942	63.163	2.420	16.333	30.950	11.273
700	10.128	64.711	3.124	16.440	33.377	10.421
800	10.236	66.071	3.843	16.564	35.789	9.777
900	10.298	67.281	4.579	16.711	38.183	9.272
1000	10.334	68.366	5.302	16.866	40.560	8.864
1100	10.357	69.354	6.019	17.036	42.917	8.527
1200	10.373	70.256	6.719	17.220	45.218	8.235
1300	10.387	71.087	7.406	17.418	47.460	7.979
1400	10.401	71.857	8.081	17.629	49.643	7.757
1500	10.417	72.575	8.754	17.860	51.793	7.564
1600	10.433	73.248	9.426	18.110	53.921	7.393
1700	10.450	73.881	10.097	18.378	56.038	7.241
1800	10.469	74.479	10.766	18.665	58.146	7.104
1900	10.487	75.045	11.433	18.969	60.248	6.980
2000	10.506	75.584	12.100	19.289	62.348	6.850
2100	10.525	76.097	12.767	19.623	64.442	6.723
2200	10.543	76.587	13.434	19.971	66.531	6.607
2300	10.561	77.056	14.101	20.332	68.616	6.499
2400	10.577	77.506	14.768	20.707	70.698	6.400
2500	10.593	77.938	15.435	21.097	72.778	6.307
2600	10.607	78.354	16.102	21.500	74.858	6.221
2700	10.620	78.754	16.769	21.916	76.938	6.140
2800	10.633	79.141	17.436	22.345	79.018	6.064
2900	10.644	79.514	18.103	22.787	81.098	5.993
3000	10.654	79.875	18.770	23.242	83.178	5.926
3100	10.662	80.224	19.437	23.710	85.258	5.863
3200	10.670	80.563	20.104	24.191	87.338	5.803
3300	10.677	80.891	20.771	24.684	89.418	5.746
3400	10.683	81.210	21.438	25.189	91.498	5.692
3500	10.689	81.520	22.105	25.706	93.578	5.640
3600	10.694	81.821	22.772	26.234	95.658	5.595
3700	10.698	82.114	23.440	26.773	97.738	5.557
3800	10.701	82.400	24.107	27.323	99.818	5.522
3900	10.705	82.678	24.774	27.884	101.898	5.489
4000	10.707	82.949	25.445	28.456	103.978	5.458
4100	10.710	83.213	26.116	29.039	106.058	5.428
4200	10.712	83.471	26.787	29.633	108.138	5.398
4300	10.714	83.723	27.458	30.237	110.218	5.369
4400	10.717	83.970	28.129	30.852	112.298	5.340
4500	10.718	84.211	28.800	31.477	114.378	5.311
4600	10.720	84.446	29.471	32.112	116.458	5.282
4700	10.722	84.677	30.142	32.757	118.538	5.253
4800	10.724	84.902	30.813	33.412	120.618	5.224
4900	10.726	85.124	31.484	34.077	122.698	5.195
5000	10.729	85.340	32.155	34.752	124.778	5.166
5100	10.731	85.553	32.826	35.427	126.858	5.137
5200	10.733	85.761	33.497	36.102	128.938	5.108
5300	10.736	85.966	34.168	36.777	131.018	5.079
5400	10.739	86.166	34.839	37.452	133.098	5.050
5500	10.742	86.363	35.510	38.127	135.178	5.021
5600	10.745	86.557	36.181	38.802	137.258	4.992
5700	10.748	86.748	36.852	39.477	139.338	4.963
5800	10.752	86.934	37.523	40.152	141.418	4.934
5900	10.756	87.118	38.194	40.827	143.498	4.905
6000	10.760	87.299	38.865	41.502	145.578	4.876

June 30, 1961; June 30, 1964; Sept. 30, 1964; Dec. 31, 1967

Ground State Configuration (°Σ)
 $S_{298.15}^{\circ} = 56.7 \pm 2.0$ gibbs/mol
 $\Delta H_{298.15}^{\circ} = [-16 \pm 10]$ kcal/mol
 $\Delta H_{298.15}^{\circ} = [-16 \pm 10]$ kcal/mol

Electronic Levels and Quantum Weights			
ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	[4]	[6000]	[4]
[1000]	[4]	[8000]	[4]
[2000]	[4]	[10000]	[4]
[4000]	[4]		

$\omega_e = [590]$ cm⁻¹
 $\omega_e x_e = [6.6]$ cm⁻¹
 $\sigma = 1$
 $r_e = [1.95]$ Å

Heat of Formation

The heat of formation, ΔH_{298}° , of TiF(g) is calculated from the dissociation energy, D_0° . The dissociation energy is estimated as 148 ± 6 kcal/mol using the corresponding quantity for TiF₂(g) and the relation $D(\text{HF})/D(\text{HF}_2) = 0.46 \pm 0.02$ which Zmbov and Margrave (1) found held for other mono- and di-fluorides.

Heat Capacity and Entropy

The vibrational frequency, ω_e , and anharmonic vibrational term, $\omega_e x_e$, are estimated from those of the alkali and mercury monohalides. The interatomic distance, r_e , is estimated from those of TiCl(g), TiF₂(g) and TiF₃(g). B_e is calculated from r_e . The ground state term and electronic levels are estimated from the ground state multiplet of Ti²⁺ (2).

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. 71, 2893 (1967).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

(Ideal Gas) GFW = 202.8484

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H _T ^o	kcal/mol ΔH _f ^o	ΔG _f ^o	Log K _p
0	0.000	INFINITE	- 2.140	92.404	92.404	INFINITE
100	6.963	52.019	66.466	89.558	89.558	- 195.046
200	14.755	66.466	70.777	87.720	87.720	- 194.605
298	7.855	59.903	70.777	87.720	87.720	- 194.605
300	7.764	59.951	59.904	92.295	83.938	- 61.468
400	8.140	62.240	60.213	92.119	81.179	- 84.354
500	8.386	64.085	60.809	91.942	78.463	- 34.296
600	8.547	65.429	61.487	91.744	75.744	- 27.604
700	8.659	66.956	62.176	91.576	73.136	- 22.834
800	8.743	68.118	62.847	91.380	70.518	- 19.264
900	8.811	69.151	63.491	91.178	67.920	- 16.493
1000	8.872	70.083	64.105	90.966	65.346	- 14.281
1100	8.930	70.931	64.687	90.746	62.794	- 12.375
1200	8.985	71.711	65.241	90.518	60.264	- 10.376
1300	9.040	72.432	65.766	90.282	57.753	- 9.709
1400	9.094	73.104	66.267	90.038	55.253	- 9.026
1500	9.146	73.733	66.744	89.786	52.784	- 8.291
1600	9.197	74.325	67.199	89.527	50.326	- 7.474
1700	9.247	74.884	67.635	89.259	47.884	- 6.556
1800	9.295	75.414	68.053	88.984	45.457	- 5.519
1900	9.342	75.918	68.453	88.700	43.046	- 4.351
2000	9.389	76.398	68.839	88.405	40.553	- 4.042
2100	9.436	76.857	69.210	88.108	38.273	- 3.563
2200	9.483	77.298	69.567	87.798	35.902	- 3.067
2300	9.531	77.720	69.913	87.481	33.553	- 2.563
2400	9.581	78.127	70.247	87.155	31.215	- 2.043
2500	9.633	78.519	70.570	86.822	28.891	- 1.526
2600	9.688	78.898	70.893	86.481	26.581	- 1.004
2700	9.747	79.265	71.186	86.127	24.283	- 0.476
2800	9.808	79.620	71.481	85.752	22.002	- 0.171
2900	9.872	79.965	71.768	85.346	19.731	- 0.187
3000	9.940	80.301	72.047	84.904	17.476	- 0.273
3100	10.011	80.628	72.318	84.415	15.234	- 0.369
3200	10.084	80.947	72.585	83.874	13.011	- 0.469
3300	10.160	81.259	72.841	83.272	10.804	- 0.576
3400	10.238	81.563	73.093	82.603	8.621	- 0.694
3500	10.319	81.861	73.340	81.852	6.456	- 0.823
3600	10.400	82.153	73.580	81.094	4.312	- 0.962
3700	10.482	82.439	73.816	80.322	2.242	- 1.112
3800	10.565	82.720	74.047	79.548	0.169	- 1.271
3900	10.648	82.995	74.273	78.772	- 1.896	- 1.439
4000	10.730	83.266	74.494	77.994	- 3.935	- 1.613
4100	10.812	83.532	74.711	77.209	- 5.209	- 1.796
4200	10.892	83.793	74.924	76.416	- 6.702	- 1.989
4300	10.970	84.050	75.134	75.616	- 8.391	- 2.192
4400	11.046	84.304	75.339	74.813	- 10.271	- 2.404
4500	11.120	84.553	75.541	74.004	- 12.351	- 2.626
4600	11.192	84.798	75.740	73.193	- 14.533	- 2.858
4700	11.260	85.039	75.935	72.379	- 16.816	- 3.100
4800	11.326	85.277	76.127	71.562	- 19.201	- 3.354
4900	11.389	85.511	76.316	70.742	- 21.684	- 3.614
5000	11.447	85.742	76.502	69.916	- 24.266	- 3.881
5100	11.502	85.969	76.686	69.084	- 26.946	- 4.154
5200	11.554	86.193	76.867	68.245	- 29.721	- 4.434
5300	11.602	86.413	77.045	67.400	- 32.591	- 4.719
5400	11.646	86.631	77.220	66.550	- 35.557	- 5.009
5500	11.687	86.845	77.394	65.694	- 38.619	- 5.304
5600	11.725	87.056	77.564	64.834	- 41.776	- 5.604
5700	11.758	87.264	77.732	63.968	- 45.028	- 5.909
5800	11.789	87.468	77.898	63.096	- 48.374	- 6.219
5900	11.818	87.668	78.062	62.218	- 51.814	- 6.534
6000	11.839	87.869	78.224	61.334	- 55.346	- 6.854

Sept. 30, 1962; Mar. 31, 1967

TUNGSTEN MONOFLUORIDE (WF)

(IDEAL GAS)

GFW = 202.8484

Ground State Configuration [2Δ]

ΔH_f^o = [92.4 ± 15] kcal/molS_{298.15}^o = [59.9] gibbs/molΔH_f^o_{298.15} = [92.3 ± 15] kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	G _i
0	[4]
[5000] [2]	
[15000] [20]	

$w_e x_e = [2.9] \text{ cm}^{-1}$ $\sigma = 1$
 $w_e = [728.5] \text{ cm}^{-1}$ $\sigma_e = [0.0015] \text{ cm}^{-1}$ $r_e = [1.83] \text{ Å}$
 $B_e = [0.2923] \text{ cm}^{-1}$

Heat of Formation

The heat of formation, ΔH_f^o₂₉₈(WF, g) = 92.3 kcal/mol, is calculated from the bond dissociation energy D₂₉₈^o(WF) = 130 ± 15 kcal/mol. This value of D₂₉₈^o is estimated to be slightly higher than the average bond dissociation energy of WF₆(g) by analogy with the MO_x system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WF₆(g). This distance is then used with Ouggenheimer's relation to calculate the fundamental vibrational frequency, w_e (K. M. Ouggenheimer, Proc. Phys. Soc. 58, 456 (1946)). The anharmonicity correction x_e is estimated roughly by assuming $x_e = w_e/(D_0 + 0.5 w_e) = 0.0042$. The rotational constant B_e is calculated from the estimated bond distance. The value of w_e is calculated from the Morse potential function. The moment of inertia is $9.575 \times 10^{-39} \text{ g cm}^2$.

The ground state configuration, low lying electronic levels and their quantum weights are estimated based on the tentative molecular orbital diagram for TaO given by M. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. 42, 882 (1965). Using this scheme, we obtain the ground state configuration as $\pi^2 \sigma^2$, which yields a $^2\Delta$ ground state. The first excited state is assumed to have $\pi^2 \sigma^2$, which yields a $^2\Delta$ state. Higher levels are considered to be formed by transition to π^* antibonding orbitals, and by analogy with TaO these are assumed to lie in the 15000 cm⁻¹ region. The degeneracy of these levels is estimated roughly from the large number of possible configurations.

$$\Delta H_f^\circ = (20.0 \pm 5) \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = (19.8 \pm 5) \text{ kcal/mol}$$

$$\Delta H_f^\circ = (20.0 \pm 5) \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = (19.8 \pm 5) \text{ kcal/mol}$$

Electronic Levels and Quantum Weights			
ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	[4]	[18000]	[4]
[3000]	[4]	[24000]	[4]
[6000]	[4]	[30000]	[4]
[12000]	[4]		

$$\omega_e = (628.0) \text{ cm}^{-1} \quad \sigma = 1 \quad \omega_e x_e = [4.0] \text{ cm}^{-1}$$

$$B_e = [0.29899] \text{ cm}^{-1} \quad r_e = [1.90] \text{ \AA}$$

Heat of Formation

Based on $[D(ZrF_2)/D(ZrF_2)] = 0.46$, as indicated by recent work on the fluorides of Groups II and IV elements (1, 2, 3, 4, 5), and $D_0(ZrF_2) = 318.1 \text{ kcal/mol}$, the $D_0(ZrF)$ is calculated as 146.3 kcal/mol . Using $\Delta H_f^\circ(Zr, g) = 147.99$, $\Delta H_f^\circ(F, g) = 18.36$, and $D_0(ZrF, g) = 146.3 \text{ kcal/mol}$, we derive $\Delta H_f^\circ(ZrF, g) = 20.0$ or $\Delta H_f^\circ(ZrF, g) = 19.8 \pm 5 \text{ kcal/mol}$ which is adopted. The ΔH_{298}° for $ZrF(g)$ was evaluated as approximately $16 \pm 5 \text{ kcal/mol}$ by Nard and Hildenbrand (8), employing different $D(ZrF_2)$ values. Their value is in agreement with the adopted one, within the assigned uncertainty.

Heat Capacity and Entropy

The ground state configuration is taken from the ground state multiplet of Zr^+ (6). The electronic levels are estimated as three times higher than those of $TiF(g)$ and the quantum weights are assumed to be the same. ω_e is taken to be approximately the same as the $Zr-F$ stretching frequency ν_1 for $ZrF_4(g)$. B_e is calculated from the formula $B_e = (2.798076 \times 10^{-39})(I_e)^{-1}$ where $I_e = \mu r_e^2$, μ = reduced mass of $ZrF(g)$, $r_e = 1.90 \text{ \AA}$ which is estimated from those of ZrF_2 , CF_4 , CF and other related gaseous molecules. σ_0 is derived from B_e , ω_e , and $\omega_e x_e$ (estimated), according to the method suggested by Herzberg (7). The moment of inertia is $9.475 \times 10^{-39} \text{ c cm}^2$.

References

1. G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, J. Phys. Chem. **67**, 877 (1963).
2. H. L. Hildenbrand and E. Murad, J. Chem. Phys. **44**, 1524 (1966).
3. G. D. Blue, J. W. Green, T. C. Ehler, and J. L. Margrave, Nature **193**, 804 (1963).
4. T. C. Ehler and J. L. Margrave, J. Chem. Phys. **41**, 1056 (1964).
5. R. A. Kant, T. C. Ehler, and J. L. Margrave, J. Am. Chem. Soc. **86**, 5080 (1964).
6. C. E. Moore, "Atomic Energy Levels," Vol. II, Natl. Bur. Std. Circ. 467, 1952.
7. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
8. E. Murad and D. L. Hildenbrand, J. Chem. Phys. **45**, 4751 (1966).

Zirconium Monofluoride (ZrF)₂

$$GFW = 110.2184$$

T, °K	Cp°	S° -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	6.000	0.000	0.000	20.085	20.085	IMF WHITE
100	6.979	50.198	2.171	20.181	17.491	-18.227
200	7.442	55.148	1.759	19.942	14.694	-16.277
298	7.949	58.227	1.000	19.800	12.439	-9.116
300	7.998	58.277	-0.015	19.797	12.393	-9.078
400	8.364	60.632	1.648	19.404	10.561	-5.106
500	8.611	62.358	1.684	19.401	7.563	-3.306
600	8.809	64.114	2.555	19.180	5.216	-1.900
700	8.993	65.845	3.445	18.930	2.907	-0.806
800	9.176	66.998	4.353	18.681	1.634	-0.173
900	9.355	67.789	5.280	18.408	0.306	0.390
1000	9.528	68.184	6.224	18.121	-1.014	0.834
1100	9.691	69.700	7.185	17.819	-2.393	1.191
1200	9.842	70.550	8.176	17.511	-3.802	1.474
1300	9.979	71.343	9.153	17.206	-5.234	1.706
1400	10.102	72.087	10.117	16.907	-6.691	1.893
1500	10.212	72.788	11.113	16.617	-8.173	2.072
1600	10.309	73.450	12.199	16.327	-9.686	2.219
1700	10.393	74.078	13.234	16.027	-11.224	2.347
1800	10.467	74.674	14.278	15.724	-12.786	2.460
1900	10.531	75.242	15.328	15.424	-14.364	2.560
2000	10.587	75.783	16.383	15.145	-15.954	2.649
2100	10.635	76.301	17.445	14.866	-17.554	2.726
2200	10.677	76.797	18.510	14.586	-19.164	2.782
2300	10.713	77.272	19.580	14.306	-20.782	2.824
2400	10.745	77.729	20.653	14.026	-22.406	2.863
2500	10.773	78.168	21.729	13.746	-24.036	2.897
2600	10.798	78.591	22.807	13.466	-25.674	2.924
2700	10.821	78.999	23.888	13.186	-27.322	2.956
2800	10.842	79.393	24.971	12.906	-28.976	2.982
2900	10.861	79.774	26.057	12.626	-30.636	3.006
3000	10.880	80.142	27.144	12.346	-32.302	3.027
3100	10.897	80.499	28.232	12.066	-33.972	3.047
3200	10.914	80.845	29.323	11.786	-35.646	3.065
3300	10.930	81.181	30.415	11.506	-37.322	3.081
3400	10.946	81.508	31.508	11.226	-38.998	3.096
3500	10.962	81.825	32.604	10.946	-40.674	3.110
3600	10.978	82.135	33.701	10.666	-42.350	3.123
3700	10.994	82.436	34.800	10.386	-44.026	3.135
3800	11.010	82.729	35.891	10.106	-45.702	3.145
3900	11.027	83.015	36.977	9.826	-47.378	3.156
4000	11.043	83.294	38.065	9.546	-49.054	3.165
4100	11.060	83.567	39.151	9.266	-50.730	3.174
4200	11.077	83.834	40.237	8.986	-52.406	3.181
4300	11.095	84.095	41.324	8.706	-54.082	3.189
4400	11.112	84.350	42.411	8.426	-55.758	3.196
4500	11.130	84.600	43.498	8.146	-57.434	3.202
4600	11.149	84.845	44.582	7.866	-59.110	3.208
4700	11.167	85.085	45.666	7.586	-60.786	3.213
4800	11.186	85.320	46.750	7.306	-62.462	3.219
4900	11.205	85.551	47.832	7.026	-64.138	3.224
5000	11.224	85.778	48.915	6.746	-65.814	3.229
5100	11.243	86.000	50.000	6.466	-67.490	3.234
5200	11.263	86.219	51.085	6.186	-69.166	3.239
5300	11.283	86.433	52.169	5.906	-70.842	3.244
5400	11.302	86.644	53.254	5.626	-72.518	3.249
5500	11.322	86.852	54.339	5.346	-74.194	3.254
5600	11.342	87.056	55.424	5.066	-75.870	3.259
5700	11.362	87.257	56.509	4.786	-77.546	3.264
5800	11.383	87.455	57.594	4.506	-79.222	3.269
5900	11.403	87.650	58.679	4.226	-80.898	3.274
6000	11.423	87.841	59.764	3.946	-82.574	3.279

June 30, 1961; Sept. 30, 1964; June 30, 1969

Fluorine, Diatomic (F₂)
(Reference State - Ideal Gas)

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
200	7.499	48.487	0.000	0.000	0.000	0.000
250	7.499	48.487	0.000	0.000	0.000	0.000
300	7.499	48.487	0.000	0.000	0.000	0.000
350	7.499	48.487	0.000	0.000	0.000	0.000
400	7.499	48.487	0.000	0.000	0.000	0.000
450	7.499	48.487	0.000	0.000	0.000	0.000
500	7.499	48.487	0.000	0.000	0.000	0.000
550	7.499	48.487	0.000	0.000	0.000	0.000
600	7.499	48.487	0.000	0.000	0.000	0.000
650	7.499	48.487	0.000	0.000	0.000	0.000
700	7.499	48.487	0.000	0.000	0.000	0.000
750	7.499	48.487	0.000	0.000	0.000	0.000
800	7.499	48.487	0.000	0.000	0.000	0.000
850	7.499	48.487	0.000	0.000	0.000	0.000
900	7.499	48.487	0.000	0.000	0.000	0.000
950	7.499	48.487	0.000	0.000	0.000	0.000
1000	7.499	48.487	0.000	0.000	0.000	0.000
1100	7.499	48.487	0.000	0.000	0.000	0.000
1200	7.499	48.487	0.000	0.000	0.000	0.000
1300	7.499	48.487	0.000	0.000	0.000	0.000
1400	7.499	48.487	0.000	0.000	0.000	0.000
1500	7.499	48.487	0.000	0.000	0.000	0.000
1600	7.499	48.487	0.000	0.000	0.000	0.000
1700	7.499	48.487	0.000	0.000	0.000	0.000
1800	7.499	48.487	0.000	0.000	0.000	0.000
1900	7.499	48.487	0.000	0.000	0.000	0.000
2000	7.499	48.487	0.000	0.000	0.000	0.000
2100	7.499	48.487	0.000	0.000	0.000	0.000
2200	7.499	48.487	0.000	0.000	0.000	0.000
2300	7.499	48.487	0.000	0.000	0.000	0.000
2400	7.499	48.487	0.000	0.000	0.000	0.000
2500	7.499	48.487	0.000	0.000	0.000	0.000
2600	7.499	48.487	0.000	0.000	0.000	0.000
2700	7.499	48.487	0.000	0.000	0.000	0.000
2800	7.499	48.487	0.000	0.000	0.000	0.000
2900	7.499	48.487	0.000	0.000	0.000	0.000
3000	7.499	48.487	0.000	0.000	0.000	0.000
3100	7.499	48.487	0.000	0.000	0.000	0.000
3200	7.499	48.487	0.000	0.000	0.000	0.000
3300	7.499	48.487	0.000	0.000	0.000	0.000
3400	7.499	48.487	0.000	0.000	0.000	0.000
3500	7.499	48.487	0.000	0.000	0.000	0.000
3600	7.499	48.487	0.000	0.000	0.000	0.000
3700	7.499	48.487	0.000	0.000	0.000	0.000
3800	7.499	48.487	0.000	0.000	0.000	0.000
3900	7.499	48.487	0.000	0.000	0.000	0.000
4000	7.499	48.487	0.000	0.000	0.000	0.000
4100	7.499	48.487	0.000	0.000	0.000	0.000
4200	7.499	48.487	0.000	0.000	0.000	0.000
4300	7.499	48.487	0.000	0.000	0.000	0.000
4400	7.499	48.487	0.000	0.000	0.000	0.000
4500	7.499	48.487	0.000	0.000	0.000	0.000
4600	7.499	48.487	0.000	0.000	0.000	0.000
4700	7.499	48.487	0.000	0.000	0.000	0.000
4800	7.499	48.487	0.000	0.000	0.000	0.000
4900	7.499	48.487	0.000	0.000	0.000	0.000
5000	7.499	48.487	0.000	0.000	0.000	0.000
5100	7.499	48.487	0.000	0.000	0.000	0.000
5200	7.499	48.487	0.000	0.000	0.000	0.000
5300	7.499	48.487	0.000	0.000	0.000	0.000
5400	7.499	48.487	0.000	0.000	0.000	0.000
5500	7.499	48.487	0.000	0.000	0.000	0.000
5600	7.499	48.487	0.000	0.000	0.000	0.000
5700	7.499	48.487	0.000	0.000	0.000	0.000
5800	7.499	48.487	0.000	0.000	0.000	0.000
5900	7.499	48.487	0.000	0.000	0.000	0.000
6000	7.499	48.487	0.000	0.000	0.000	0.000

December 31, 1960.

Fluorine, Diatomic (F₂) (Reference State - Ideal Gas)

Mol. Wt. = 38.00
 ΔH_f^0 298.15 = 0 kcal. mole⁻¹
 S_f^0 298.15 = 48.45 cal. deg⁻¹ mole⁻¹
 Ground State Configuration: \sum
 $\omega_e = 923.1$ cm⁻¹ $\omega_e x_e = 15.04$ cm⁻¹
 $B_e = 0.6938$ cm⁻¹ $\alpha_e = 0.022$ cm⁻¹
 $D_e = 3.346 \times 10^{-6}$ cm⁻¹ $r_e = 1.409$ Å
 $\sigma = 2$

Heat Capacities and Entropies. Molecular and spectroscopic constants calculated from Raman measurements of D. Andrychuk, Can. J. Phys. 29, 151 (1951), and the dissociation energy listed by J. O. Stanger and R. P. Barrow, Trans. Faraday Soc. 54, 1592 (1958).

IRON DIFLUORIDE (FeF₂) (CRYSTAL) MOL. WT. = 93.8438

T, °K.	C _p ^o	S ^o	-(F ^o -H _{298^o)/T}	H-H _{298^o}	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	-	3.069	-168.564	-168.564	INFINITE
100	7.994	7.374	33.204	-2.583	-168.896	-165.417	361.502
200	13.530	14.824	22.204	-1.476	-168.931	-165.452	361.502
298	16.280	20.790	0.000	-	-168.700	-165.227	116.184
300	16.300	20.891	0.030	-	-168.695	-158.444	115.421
400	17.200	25.708	21.441	1.707	-168.414	-155.069	64.722
500	17.900	29.624	22.698	3.463	-168.140	-151.765	66.333
600	18.440	32.938	24.135	5.281	-167.884	-148.515	54.094
700	18.850	35.812	25.603	7.146	-167.659	-145.305	45.364
800	19.180	38.351	27.041	9.048	-167.491	-142.125	38.825
900	19.440	40.626	28.426	10.980	-167.411	-138.959	33.742
1000	19.630	42.684	29.751	12.934	-167.499	-135.796	29.077
1100	19.769	44.562	31.013	14.904	-167.796	-132.607	26.345
1200	19.880	46.287	32.215	16.887	-167.873	-129.410	23.568
1300	19.955	47.881	33.359	18.879	-167.697	-126.214	21.218
1400	20.020	49.363	34.450	20.877	-167.355	-123.040	19.207
1500	20.072	50.746	35.491	22.882	-167.114	-119.883	17.466
1600	20.120	52.043	36.485	24.892	-166.888	-116.743	15.946
1700	20.164	53.264	37.437	26.906	-166.967	-113.609	14.600
1800	20.200	54.418	38.348	28.924	-166.862	-110.475	13.413
1900	20.229	55.510	39.223	30.946	-170.441	-107.158	12.325
2000	20.250	56.549	40.064	32.970	-170.400	-103.830	11.345

Heat of Formation.
The equilibrium pressures for the reaction $\text{FeF}_2(\text{c}) + \text{H}_2(\text{g}) = \text{Fe}(\text{c}) + 2\text{HF}(\text{g})$ have been measured by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928) at 773, 875 and 973°K. The enthalpy change (ΔH_f° 298.15) of the reaction was evaluated by the second and third law methods to be 27.19 and 39.08 kcal. mole⁻¹, respectively. Based on the third law value of ΔH_f° 298.15, the ΔF_f° 298.15 (FeF₂, c) was calculated to be -168.7 + 10 kcal. mole⁻¹. The drift in the third law values of ΔH_f° 298.15 was evaluated to be 13.3 ± 1.8 e.u.

Heat Capacity and Entropy.
The low temperature (11.35 - 307.50°K.) heat capacities were determined by E. Catalano and J. W. Stout, J. Chem. Phys. 23, 1803 (1955). The heat capacities above 307°K. were estimated by comparison with those of FeCl₂(c), MgCl₂(c) and MgF₂(c). The value of S_{298.15} was obtained from E. Catalano and J. W. Stout, loc. cit., in which a sharp maximum C_p of 17.8 cal. deg.⁻¹ mole⁻¹ at 78.35°K. was reported. The S_{298.15} value was based on S₁₅ = 0.039 e.u.

Melting Data.
T_m was estimated as 1100°C based on the data reported by W. Biltz and E. Rehlf, Z. anorg. allgem. Chem. 166, 363 (1927). The value of ΔH_m° was calculated using $\Delta S_m^\circ = 9$ e.u. which was assumed to be the same as the corresponding value for MgF₂(c).

Heat of Sublimation.
The value of ΔH_s° 298.15 was obtained from J. I. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William Marsh Rice University, Houston, Texas. See FeF₂(g) table for details.

Iron Difluoride (FeF₂)

Mol. wt. = 93.8438

(Liquid)

F₂Fe

MOL. WT. = 93.8438

(LIQUID)

IRON DIFLUORIDE (FeF₂)

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ ^o)/T	H° - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _f
0						
100						
200						
298	23.500	21.951	21.951	-161.229	-151.383	110.961
300	23.500	22.096	21.951	-161.211	-151.322	110.232
400	23.500	26.857	22.673	-160.257	-148.171	80.953
500	23.500	34.101	24.614	-159.168	-145.253	63.487
600	23.500	38.385	26.563	-158.601	-142.500	51.903
700	23.500	42.008	28.517	-157.891	-139.874	43.669
800	23.500	45.146	30.404	-157.275	-137.345	37.519
900	23.500	47.914	32.199	-156.777	-134.884	32.753
1000	23.500	50.390	33.896	-156.469	-132.472	28.950
1100	23.500	52.630	35.499	-156.386	-130.071	25.842
1200	23.500	54.674	37.013	-156.086	-127.696	23.256
1300	23.500	56.552	38.445	-155.472	-125.354	21.073
1400	23.500	58.297	39.801	-154.868	-123.061	19.210
1500	23.500	59.918	41.089	-154.282	-120.809	17.601
1600	23.500	61.435	42.314	-153.716	-118.597	16.199
1700	23.500	62.859	43.481	-153.459	-116.412	14.965
1800	23.500	64.203	44.595	-153.022	-114.248	13.871
1900	23.500	65.473	45.661	-152.673	-111.919	12.873
2000	23.500	66.679	46.682	-152.406	-109.596	11.975
2100	23.500	67.825	47.662	-152.286	-107.288	11.165
2200	23.500	68.918	48.603	-152.193	-104.987	10.430
2300	23.500	69.963	49.509	-152.103	-102.725	9.761
2400	23.500	70.963	50.383	-152.056	-100.467	9.148
2500	23.500	71.923	51.225	-152.173	-98.223	8.586
2600	23.500	72.844	52.039	-152.446	-95.990	8.068
2700	23.500	73.731	52.826	-152.855	-93.771	7.590
2800	23.500	74.586	53.588	-153.393	-91.565	7.147
2900	23.500	75.410	54.326	-153.210	-89.365	6.734
3000	23.500	76.207	55.043	-152.902	-87.163	6.351

$$\Delta H_f^{\circ} 298.15 = [21.951] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^{\circ} = [12.4] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = [53.64] \text{ kcal. mole}^{-1}$$

$$T_m^{\circ} = [1373]^{\circ}\text{K.}$$

$$T_b^{\circ} = [2110]^{\circ}\text{K.}$$

Heat of Formation.

The value of $\Delta H_f^{\circ} 298.15$ (FeF₂, l) was obtained from $\Delta H_f^{\circ} 298.15$ (FeF₂, c) by adding ΔH_m° and the difference between $H_m^{\circ} - H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity for FeF₂(l) was estimated by comparison with those for FeCl₂(c), MgCl₂(c), MgF₂(c), CaCl₂(c) and CaF₂(c). The C_p (FeF₂, l) value was assumed to be constant in the temperature range, 298.15 - 3000°K. The entropy ($S_{298.15}^{\circ}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See the FeF₂(c) table for details.

Vaporization Data.

T_b is calculated as the temperature at which the free energy change of the reaction $\text{FeF}_2(\text{l}) = \text{FeF}_2(\text{g})$ approaches zero. The difference between ΔH_f° for FeF₂(l) and FeF₂(g) at T_b is ΔH_v° .

F₂Fe

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	+0.00	INFINITE	- 3.029	- 92.944	-	INFINITE
100	9.2216	51.3119	73.890	- 92.970	- 93.886	205.178
200	11.4449	58.4271	64.522	- 93.054	- 94.770	103.555
298	13.324	63.361	+0.00	- 93.100	- 95.600	70.073
300	13.325	63.466	+0.25	- 93.100	- 95.653	69.653
400	14.673	67.482	63.903	- 93.089	- 95.634	52.997
500	15.365	70.841	84.065	- 93.065	- 97.299	42.527
600	15.667	73.672	66.186	- 93.074	- 98.146	35.748
700	15.723	76.051	67.433	- 93.144	- 98.986	30.903
800	15.738	78.011	68.516	- 93.215	- 99.816	27.266
900	15.679	80.040	69.814	- 93.286	- 100.636	24.448
1000	15.644	81.690	70.921	- 94.054	- 101.367	22.153
1100	15.617	83.179	71.968	- 94.768	- 102.058	20.276
1200	15.600	84.537	73.060	- 95.267	- 102.704	18.704
1300	15.590	85.785	74.196	- 95.624	- 103.317	17.368
1400	15.588	86.941	75.280	- 95.826	- 103.897	16.146
1500	15.590	88.016	75.636	- 95.826	- 104.501	15.225
1600	15.594	89.023	76.442	- 96.051	- 105.073	14.352
1700	15.599	89.968	77.210	- 96.584	- 105.623	13.578
1800	15.604	90.850	77.946	- 96.974	- 106.146	12.897
1900	15.609	91.704	78.610	- 97.259	- 106.646	12.297
2000	15.612	92.504	79.319	- 101.399	- 106.739	11.663
2100	15.613	93.266	79.965	- 101.828	- 106.996	11.135
2200	15.613	93.993	80.587	- 102.264	- 107.234	10.652
2300	15.613	94.693	81.186	- 102.604	- 107.454	10.202
2400	15.608	95.351	81.761	- 102.856	- 107.659	9.782
2500	15.603	95.988	82.318	- 103.611	- 107.823	9.425
2600	15.597	96.600	82.855	- 104.074	- 107.984	9.076
2700	15.590	97.188	83.375	- 104.544	- 108.124	8.752
2800	15.582	97.753	83.879	- 104.966	- 108.246	8.449
2900	15.573	98.302	84.367	- 105.350	- 108.356	8.166
3000	15.563	98.830	84.840	- 105.996	- 108.447	7.900
3100	15.553	99.340	85.300	- 106.495	- 108.519	7.650
3200	15.542	99.833	85.746	- 106.426	- 107.130	7.316
3300	15.530	100.307	86.180	- 106.536	- 106.528	6.922
3400	15.519	100.775	86.600	- 106.585	- 105.826	6.566
3500	15.507	101.225	87.014	- 106.611	- 99.317	6.201
3600	15.495	101.661	87.415	- 106.694	- 96.702	5.870
3700	15.482	102.086	87.806	- 106.790	- 94.094	5.558
3800	15.469	102.500	88.187	- 106.897	- 91.478	5.261
3900	15.456	102.900	88.559	- 106.980	- 88.860	4.987
4000	15.446	103.291	88.923	- 107.045	- 86.239	4.712
4100	15.434	103.672	89.278	- 107.099	- 83.612	4.457
4200	15.422	104.044	89.625	- 107.146	- 80.986	4.214
4300	15.410	104.407	89.957	- 107.178	- 78.352	3.982
4400	15.399	104.761	90.277	- 107.200	- 75.704	3.760
4500	15.388	105.107	90.622	- 107.214	- 73.081	3.549
4600	15.377	105.445	90.941	- 107.221	- 70.433	3.346
4700	15.366	105.776	91.253	- 107.225	- 67.786	3.152
4800	15.355	106.100	91.559	- 107.226	- 65.126	2.965
4900	15.345	106.416	91.856	- 107.226	- 62.456	2.786
5000	15.335	106.726	92.153	- 107.226	- 59.809	2.614
5100	15.325	107.029	92.442	- 107.226	- 57.140	2.448
5200	15.316	107.327	92.725	- 107.226	- 54.463	2.289
5300	15.307	107.618	93.003	- 107.226	- 51.778	2.135
5400	15.297	107.906	93.277	- 107.226	- 49.087	1.987
5500	15.288	108.185	93.545	- 107.226	- 46.393	1.844
5600	15.280	108.460	93.809	- 107.226	- 43.702	1.705
5700	15.271	108.731	94.068	- 107.226	- 41.001	1.572
5800	15.263	108.996	94.324	- 107.226	- 38.284	1.443
5900	15.255	109.258	94.577	- 107.226	- 35.573	1.318
6000	15.247	109.513	94.821	- 107.226	- 32.844	1.196

Point group [D_{∞h}]
S°_{298.15} = [63.4] cal. deg.⁻¹ mole⁻¹
ΔH_f° 0 = -92.9 ± 3.4 kcal. mole⁻¹
ΔH_f° 298.15 = -93.1 ± 3.4 kcal. mole⁻¹

Electronic Levels and Quantum Weights

ε ₁ , cm. ⁻¹	g ₁
0	[5]
[1000]	[10]
[4000]	[5]
[6000]	[5]

Vibrational Frequencies and Degeneracies

ω _j , cm. ⁻¹
[550] (1)
[190] (2)
[714] (1)

Bond Distances: Fe-F = [1.8] Å
Bond Angle: F-Fe-F = [180]°
Rotational Constant: B₀ = 0.13692 cm.⁻¹
σ⁻ = 2

Heat of Formation.

The rate of sublimation of FeF₂(c) was measured between 965 and 1149°K. by the Knudsen technique employing the high temperature magnetic mass spectrometer by John L. Margrave, "Research in Fluorine Chemistry", Progress Report No. 7, 1 January to 31 March 1965, William March Rice University, Houston, Texas. The only vapor species of importance is FeF₂(g). From the vapor pressure data the third law heat of sublimation (ΔH_f° 298.15) was reported as 75.6 ± 2.0 kcal. mole⁻¹. The sum of the values of ΔH_f° 298.15 and ΔH_f° 298.15 for FeF₂(c) is the ΔH_f° 298.15 (FeF₂ g).

Heat Capacity and Entropy.

The molecular structure was assumed to be linear. The Fe-F bond distance was estimated from that in FeF₂(c) reported by W. H. Baur, Acta Cryst. 11, 488 (1955). The vibrational frequencies, ω_j, and ω_j, were estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. 63, 111 (1963). The values of ω_j, electronic levels and quantum weights were estimated by comparison with those for FeCl₂(g). See FeCl₂(g) table for details. The moment of inertia is 2.04404 X 10⁻³⁹ g. cm.²

Potassium Bifluoride (KHF₂)
(Crystal) Mol. Wt. = 78.108

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _f
0	∞	∞	∞	∞	∞	∞	∞
100	11.680	8.458	39.618	-3.654	-220.744	-220.744	INFINITE
200	16.010	18.154	26.619	-1.116	-216.401	-216.401	472.920
298	18.361	23.960	23.000	0.000	-211.695	-211.695	230.566
300	18.400	25.114	25.000	0.034	-211.905	-205.553	150.741
400	20.603	30.705	25.748	1.963	-222.387	-200.004	149.738
500	23.960	41.322	27.579	6.871	-219.398	-194.610	109.272
600	23.960	45.691	30.265	9.267	-218.910	-189.697	95.060
700	23.960	49.384	32.722	11.663	-218.432	-184.866	69.094
800	23.960	52.584	35.005	14.059	-217.967	-180.104	57.715
900	23.960	55.406	37.122	16.455	-217.515	-175.398	49.200
1000	23.960	57.930	39.079	18.951	-217.084	-170.743	42.590
1100	23.960	60.214	40.898	21.247	-235.580	-165.105	37.314
1200	23.960	62.299	42.506	23.643	-234.945	-158.724	32.602
1300	23.960	64.216	44.186	26.039	-234.321	-152.390	28.006
1400	23.960	65.992	45.681	28.435	-233.706	-146.119	25.619
1500	23.960	67.645	47.091	30.831	-233.101	-139.883	22.809
1600	23.960	69.191	48.424	33.227	-232.506	-133.689	20.380
1700	23.960	70.644	49.689	35.623	-231.919	-127.531	18.260
1800	23.960	72.013	50.892	38.019	-231.342	-121.409	16.394
1900	23.960	73.309	52.036	40.415	-230.773	-115.317	14.740
2000	23.960	74.538	53.132	42.811	-230.211	-109.253	13.264
							11.938

POTASSIUM BIFLUORIDE (KHF₂)

(CRYSTAL)

MOL. WT. = 78.108

$\Delta H_f^o = -220.74 \pm 0.35$ kcal. mole⁻¹
 ΔH_f^o 298.15 = -221.90 ± 0.35 kcal. mole⁻¹
 $\Delta H_c^o = 2.671 \pm 0.01$ kcal. mole⁻¹
 $\Delta H_m^o = 1.582 \pm 0.003$ kcal. mole⁻¹
 $S_{298.15}^o = 25.0 \pm 0.1$ cal. deg. mole⁻¹
 $T_c = 469.8^\circ K.$
 $T_m = 511.8^\circ K.$

Heat of Formation.

The heat of formation was obtained from the enthalpy of decomposition measurements of M. L. Davis and E. F. Westrum, J. Phys. Chem. 65, 339 (1961) who gave $\Delta H_d^{500} = 18.82 \pm 0.05$ kcal. mole⁻¹ and the heats of formation of HF(g) and KF(c) in conjunction with enthalpies at 500°K. from E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949). A third law analysis of the decomposition vapor pressure by Westrum and Pitzer, loc. cit. did not agree with enthalpy of decomposition measurements, giving $\Delta H_d^{298} = 21.274 \pm 0.2$ kcal. mole⁻¹ as compared to Davis and Westrum's value at 298°K. of 21.505 ± 0.05 kcal. mole⁻¹. As the liquid vapor pressure data, which were not used, have a large trend in the third law heat of vaporization with temperature it was suspected that the pressure measurements were in error. This is borne out somewhat by a small trend in the values over the solid in the range 480-500°K.

Heat Capacity and Entropy.

Westrum and Pitzer, loc. cit., have measured the heat capacity from 16°K. to the melting point. Their data has been used to calculate the entropy at 298° using a T³ law extrapolation below 16°K., giving $S_{16}^o = 0.103$ e.u.

Melting and Transition Data.

The temperatures of melting and transition and the heats of melting and transition were taken from Davis and Westrum, loc. cit.

F₂HK

F₂HK

Potassium Bifluoride (KHF₂)
(Liquid) Mol. Wt. = 78.108

F₂HK

T. °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0							
100	18.344	32.300	32.100	0.000	-218.243	-204.168	149.652
200							
298	18.344	32.300	32.100	0.000	-218.243	-204.168	149.652
300	18.400	32.414	32.200	0.034	-218.243	-204.081	148.646
400	25.000	36.817	33.112	2.282	-218.426	-199.287	108.880
500	25.000	44.306	34.632	6.782	-217.825	-194.574	85.044
600	25.000	48.954	36.617	7.282	-217.233	-189.979	69.196
700	25.000	52.808	38.633	9.782	-216.651	-185.482	57.907
800	25.000	56.000	40.714	12.782	-216.072	-181.000	49.464
900	25.000	58.690	42.765	14.782	-215.492	-176.520	42.864
1000	25.000	61.725	44.843	17.282	-214.901	-172.045	37.686
1100	25.000	64.107	46.9124	19.782	-213.383	-167.101	31.216
1200	25.000	66.283	47.714	22.282	-212.644	-161.204	26.358
1300	25.000	68.200	48.400	24.782	-211.883	-155.283	21.104
1400	25.000	70.136	49.249	27.282	-211.197	-149.343	15.513
1500	25.000	71.861	50.006	29.782	-210.488	-143.595	20.621
1600	25.000	73.475	53.298	32.282	-228.789	-137.826	18.625
1700	25.000	74.990	54.530	34.782	-228.099	-132.099	16.982
1800	25.000	76.400	55.717	37.282	-227.417	-126.415	15.348
1900	25.000	77.711	56.893	39.782	-226.747	-120.747	13.714
2000	25.000	79.053	57.612	42.282	-226.079	-115.151	12.982

June 30, 1962; Dec. 31, 1963

POTASSIUM BIFLUORIDE (KHF₂)

(LIQUID)

MOL. WT. = 78.108

S°_{298.15} = 32.3 cal. deg. mole⁻¹ ΔH_f^o 298.15 = -218.24 ± 0.35 kcal. mole⁻¹

T_m = 511.8°K. ΔH_m^o = 1.582 ± 0.003 kcal. mole⁻¹

T_{decomp.} = [751]°K.

Heat of Formation.

This was calculated from the heat of formation of the crystal, the heat of melting and H°_{511.8} - H°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The entropy was determined from that of the crystal in a manner analogous to the heat of formation. The heat capacity just above the melting point was measured by E. F. Westrum and K. S. Pitzer, J. Am. Chem. Soc. 71, 1940 (1949) and was assumed constant above the melting point. A glass type transition was assumed at 341°K. below which the heat capacity is that of the solid.

Melting.

See table for crystal.

Decomposition.

The temperature of decomposition was estimated from the free energy cross-over and is the point where the HF(g) reaches 1 atm. It should be noted that the vapor pressures over the liquid of Westrum and Pitzer, loc. cit. are apparently in error, being high by roughly 12%. A 3rd law analysis at each vapor pressure point gave an almost constant heat of reaction in the solid region but in the liquid region the value changed abruptly with temperature. The only factors which were variable were the pressure and the liquid heat capacity, a trial change of 20% in the heat capacity produced an almost negligible change in the heat of reaction. Thus the vapor pressures over the liquid appear to be in error and the decomposition point of 702°K. obtained by extrapolating to 1 atmosphere is also in error.

F₂HK

Difluorosilane (SiH₂F₂)
 (Ideal Gas) Mol. Wt. = 68.106

INTERIM TABLE

T. °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	5.366	51.702	51.702	2.788	191.898	191.898	191.898	INFINITE
200	5.881	57.023	57.023	1.985	181.184	181.184	181.184	41.7, 81.1
300	6.262	62.262	62.262	1.079	180.506	180.506	180.506	207.073
400	6.571	66.412	66.412	0.623	180.000	180.000	180.000	137.434
500	6.830	69.597	69.597	0.368	180.013	180.013	180.013	101.171
600	7.066	72.066	72.066	0.242	180.041	180.041	180.041	85.649
700	7.289	74.289	74.289	0.176	180.053	180.053	180.053	75.079
800	7.498	76.427	76.427	0.131	180.059	180.059	180.059	67.827
900	7.681	78.481	78.481	0.103	180.063	180.063	180.063	61.878
1000	7.831	80.451	80.451	0.081	180.064	180.064	180.064	56.639
1100	7.956	82.346	82.346	0.066	180.066	180.066	180.066	51.916
1200	8.066	84.166	84.166	0.056	180.068	180.068	180.068	47.572
1300	8.161	85.911	85.911	0.048	180.070	180.070	180.070	43.569
1400	8.241	87.581	87.581	0.041	180.072	180.072	180.072	39.869
1500	8.306	89.181	89.181	0.036	180.074	180.074	180.074	36.439
1600	8.356	90.711	90.711	0.031	180.076	180.076	180.076	33.259
1700	8.396	92.181	92.181	0.027	180.078	180.078	180.078	30.289
1800	8.426	93.591	93.591	0.024	180.080	180.080	180.080	27.489
1900	8.446	94.951	94.951	0.021	180.082	180.082	180.082	24.839
2000	8.456	96.261	96.261	0.019	180.084	180.084	180.084	22.329
2100	8.456	97.521	97.521	0.017	180.086	180.086	180.086	20.029
2200	8.446	98.731	98.731	0.016	180.088	180.088	180.088	17.929
2300	8.426	99.891	99.891	0.015	180.090	180.090	180.090	16.029
2400	8.396	100.991	100.991	0.014	180.092	180.092	180.092	14.329
2500	8.356	102.041	102.041	0.013	180.094	180.094	180.094	12.829
2600	8.306	103.041	103.041	0.012	180.096	180.096	180.096	11.529
2700	8.246	103.991	103.991	0.011	180.098	180.098	180.098	10.429
2800	8.176	104.891	104.891	0.010	180.100	180.100	180.100	9.529
2900	8.096	105.741	105.741	0.009	180.102	180.102	180.102	8.829
3000	8.006	106.541	106.541	0.008	180.104	180.104	180.104	8.329
3100	7.906	107.291	107.291	0.007	180.106	180.106	180.106	7.929
3200	7.796	108.001	108.001	0.006	180.108	180.108	180.108	7.629
3300	7.676	108.661	108.661	0.005	180.110	180.110	180.110	7.429
3400	7.546	109.281	109.281	0.004	180.112	180.112	180.112	7.329
3500	7.406	109.861	109.861	0.003	180.114	180.114	180.114	7.329
3600	7.256	110.401	110.401	0.002	180.116	180.116	180.116	7.429
3700	7.096	110.901	110.901	0.001	180.118	180.118	180.118	7.629
3800	6.926	111.361	111.361	0.000	180.120	180.120	180.120	7.929
3900	6.746	111.781	111.781	0.000	180.122	180.122	180.122	8.329
4000	6.556	112.161	112.161	0.000	180.124	180.124	180.124	8.829
4100	6.356	112.501	112.501	0.000	180.126	180.126	180.126	9.429
4200	6.146	112.801	112.801	0.000	180.128	180.128	180.128	10.129
4300	5.926	113.061	113.061	0.000	180.130	180.130	180.130	10.929
4400	5.696	113.281	113.281	0.000	180.132	180.132	180.132	11.829
4500	5.456	113.461	113.461	0.000	180.134	180.134	180.134	12.829
4600	5.206	113.601	113.601	0.000	180.136	180.136	180.136	13.929
4700	4.946	113.701	113.701	0.000	180.138	180.138	180.138	15.129
4800	4.676	113.761	113.761	0.000	180.140	180.140	180.140	16.429
4900	4.396	113.781	113.781	0.000	180.142	180.142	180.142	17.829
5000	4.106	113.761	113.761	0.000	180.144	180.144	180.144	19.329
5100	3.806	113.691	113.691	0.000	180.146	180.146	180.146	20.929
5200	3.496	113.581	113.581	0.000	180.148	180.148	180.148	22.629
5300	3.176	113.431	113.431	0.000	180.150	180.150	180.150	24.429
5400	2.846	113.241	113.241	0.000	180.152	180.152	180.152	26.329
5500	2.506	113.011	113.011	0.000	180.154	180.154	180.154	28.329
5600	2.156	112.741	112.741	0.000	180.156	180.156	180.156	30.429
5700	1.796	112.431	112.431	0.000	180.158	180.158	180.158	32.629
5800	1.426	112.081	112.081	0.000	180.160	180.160	180.160	34.929
5900	1.046	111.691	111.691	0.000	180.162	180.162	180.162	37.329
6000	0.656	111.261	111.261	0.000	180.164	180.164	180.164	39.829

December 31, 1960.



Difluorosilane (SiH₂F₂) (Ideal Gas)

Mol. Wt. = 68.106

ΔH_f^o 298.15 = [-194 ± 15] kcal. mole⁻¹

S_{298.15}^o = [62.576] cal. deg⁻¹ mole⁻¹

Point Group C_{2v}

Ground State Multiplicity = 1

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹
2245 (1)	321.7 (1)	728.2 (1)
870 (1)	2250 (1)	[905] (1)
984.8 (1)	[978] (1)	[785] (1)

Moments of Inertia: I_A = 3.40 X 10⁻³⁹ g. cm.²
I_B = 10.76 X 10⁻³⁹ g. cm.²
I_C = 13.16 X 10⁻³⁹ g. cm.²

Heat of Formation. ΔH_f^o 298.15 was estimated in C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were taken from G. Janz and Y. Mikawa, Bull. Chem. Soc. Japan 34, 1485 (1961). Moments of inertia were found in Henderson and Scheffer, op. cit.

T. °K.	C _p ^a	S ^b	cal. mole ⁻¹ deg. ⁻¹	(F° - H ₂₉₈)/T	H° - H ₂₉₈	cal. mole ⁻¹	ΔH _f ^c	ΔF _f ^c	Log K _p
0									
100	17.491	27.400	27.400	4.000	0.000	101.000	- 89.426	- 89.426	65.548
200	17.900	27.911	27.900	4.033	0.033	100.983	- 89.355	- 89.355	65.092
300	18.400	28.428	28.400	4.066	0.066	100.966	- 89.284	- 89.284	64.636
400	18.900	28.945	28.900	4.099	0.099	100.949	- 89.213	- 89.213	64.180
500	19.400	29.462	29.400	4.132	0.132	100.932	- 89.142	- 89.142	63.724
600	19.900	29.979	29.900	4.165	0.165	100.915	- 89.071	- 89.071	63.268
700	20.400	30.496	30.400	4.198	0.198	100.898	- 89.000	- 89.000	62.812
800	20.900	31.013	30.900	4.231	0.231	100.881	- 88.929	- 88.929	62.356
900	21.400	31.530	31.400	4.264	0.264	100.864	- 88.858	- 88.858	61.900
1000	21.900	32.047	31.900	4.297	0.297	100.847	- 88.787	- 88.787	61.444
1100	22.400	32.564	32.400	4.330	0.330	100.830	- 88.716	- 88.716	60.988
1200	22.900	33.081	32.900	4.363	0.363	100.813	- 88.645	- 88.645	60.532
1300	23.400	33.598	33.400	4.396	0.396	100.796	- 88.574	- 88.574	60.076
1400	23.900	34.115	33.900	4.429	0.429	100.779	- 88.503	- 88.503	59.620
1500	24.400	34.632	34.400	4.462	0.462	100.762	- 88.432	- 88.432	59.164
1600	24.900	35.149	34.900	4.495	0.495	100.745	- 88.361	- 88.361	58.708
1700	25.400	35.666	35.400	4.528	0.528	100.728	- 88.290	- 88.290	58.252
1800	25.900	36.183	35.900	4.561	0.561	100.711	- 88.219	- 88.219	57.796
1900	26.400	36.700	36.400	4.594	0.594	100.694	- 88.148	- 88.148	57.340
2000	26.900	37.217	36.900	4.627	0.627	100.677	- 88.077	- 88.077	56.884

March 31, 1962

MERCURY DIFLUORIDE (HgF₂) (Crystal)

Mol. Wt. = 238.61

 $\Delta H_f^\circ 298.15 = [-101.0 \pm 10.0] \text{ kcal. mole}^{-1}$ $\Delta G_f^\circ 298.15 = [27.800 \pm 2.0] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_m = 918^\circ \text{K}$ $\Delta H_m = [5.5 \pm 1.0] \text{ kcal. mole}^{-1}$

Heat of Formation. Estimated by comparison of the mercurous and mercuric halides.

Heat Capacity and Entropy. The heat capacity was assumed to be a linear function of temperature and was estimated to be 7.0 cal. deg.⁻¹ per atom at the melting point. The entropy was estimated by comparison with the other mercuric and mercurous halides and use of additive entropy constants for the halogens from K. K. Kelley (Private Communication, 1960).

Melting. T_m was given by O. Ruff and G. Behlau, Ber. 51, 1752 (1918). The heat of melting was from L. Brewer, paper 7, National Nuclear Energy Series A-198 "Thermodynamics" McGraw-Hill (1950).

Mercury Difluoride (HgF₂)
(Liquid) Mol. Wt. = 238.61

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100	17.891	32.083	32.083	.000	- 86.475	63.305
200						
298	17.900	32.194	32.083	.033	- 86.412	62.948
300	16.400	37.411	32.791	1.426	- 83.017	45.356
400	10.900	41.571	34.145	3.713	- 79.723	34.645
600	19.400	45.061	35.681	5.428	- 76.513	27.849
700	24.400	44.715	37.282	8.003	- 71.935	22.427
800	24.400	51.974	38.920	10.443	- 66.644	18.205
900	24.400	54.658	40.533	12.493	- 61.266	14.954
1000	24.400	57.414	42.095	15.323	- 56.848	12.380
1100	24.400	59.744	43.595	17.743	- 51.815	10.204
1200	24.400	61.867	45.031	20.203	- 47.077	8.253
1300	24.400	63.880	46.402	22.443	- 42.426	7.132
1400	24.400	65.628	47.712	25.083	- 37.854	5.909
1500	24.400	67.312	48.963	27.523	- 33.357	4.660
1600	24.400	68.986	50.159	29.943	- 28.955	3.422
1700	24.400	70.366	51.305	32.403	- 24.565	2.400
1800	24.400	71.740	52.403	34.843	- 20.265	1.642
1900	24.400	73.060	53.457	37.283	- 16.189	1.182
2000	24.400	74.331	54.469	39.723	- 11.921	1.292

MERCURY DIFLUORIDE (HgF₂)
(Liquid)

Mol. Wt. = 238.61
ΔH_f^o 298.15 = [-96.772 ± 10.0] kcal. mole⁻¹
S_{298.15}^o = [32.083 ± 2.0] cal. deg.⁻¹ mole⁻¹
T_m = 918°K
ΔH_m = [5.5 ± 1.0] kcal. mole⁻¹
T_b = 920°K
ΔH_v = [22.0 ± 4.0] kcal. mole⁻¹

Heat of Formation. Calculated from ΔH_f^o (crystal).

Heat Capacity and Entropy. C_p was estimated by analogy with mercuric iodide and bromide. A glass type transition was assumed at 613°K below which the heat capacity was that of HgF₂(crystal). The entropy was calculated from S°(crystal) and the estimated ΔH_m and heat capacities of crystal and liquid.

Fusion and Vaporization. T_m was given by O. Ruff and G. Bahian, Ber. 51, 1752 (1918). T_b, ΔH_m, and ΔH_v were all taken from L. Brewer, paper 7, National Nuclear Energy Series 4-19B "Thermodynamics" McGraw-Hill (1950).



MOL. WT. = 238.61

(IDEAL GAS)

MERCURY DIFLUORIDE (HgF₂)

Point Group D_{∞h}

ΔH_f⁰ 298.15 = [-70.2 ± 10.0] kcal mole⁻¹ S_{298.15} = 63.545 cal deg⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm⁻¹
[600] (1)
[120] (2)
[593] (1)

Hg-F distance = [1.96] Å

Moment of Inertia = [12.118 × 10⁻³⁹] g cm² σ = 2

Heat of Formation

Estimated by comparison with the other gaseous mercuric halides and with the crystalline mercurous mercuric fluorides.

Heat Capacity and Entropy

Vibrational constants were estimated by analogy with the other mercuric halides and the mercurous halides. The bond length was estimated by assuming the mercurous bond to be 0.965 of the mercuric bond by analogy with the mercury chlorides.

INTERIM TABLE

Mercury Difluoride (HgF₂)

(Ideal Gas) Mol. Wt. = 238.61

T, °K.	C _p ⁰	S ⁰ - (F ⁰ -H ₂₉₈ ^{0)/T}	H ⁰ -H ₂₉₈ ⁰	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	3.152	68.994	68.994	INFINITE
100	10.129	51.105	2.307	69.252	69.404	151.674
200	11.722	58.627	1.213	69.475	69.671	75.901
300	12.499	63.545	0.000	70.185	69.269	50.773
400	12.916	63.626	-0.024	70.187	69.263	50.456
500	13.618	67.443	1.354	70.288	68.938	37.668
600	14.263	73.110	4.152	70.430	68.231	24.652
700	14.852	75.321	5.587	68.521	66.266	20.695
800	15.400	76.670	6.492	68.351	63.101	16.837
900	15.608	76.970	6.955	68.270	58.523	12.790
1000	15.659	80.512	7.526	68.191	55.952	11.116
1100	14.701	81.911	12.423	68.113	53.386	9.723
1200	14.132	81.912	12.495	68.113	53.386	9.723
1300	13.777	85.866	15.866	68.066	50.778	8.536
1400	13.793	86.486	17.325	68.066	45.730	6.663
1500	14.807	87.441	18.405	68.066	43.190	5.699
1600	14.835	89.989	20.268	68.066	42.258	4.726
1700	14.835	90.989	21.251	68.066	41.634	4.063
1800	14.842	90.750	24.735	68.066	41.634	3.612
1900	14.847	91.474	26.219	68.066	41.634	3.178
2000	14.852	92.185	27.704	68.066	41.634	2.763
2100	14.857	92.874	29.188	68.066	41.634	2.363
2200	14.861	93.547	30.671	68.066	41.634	1.978
2300	14.864	94.204	32.152	68.066	41.634	1.608
2400	14.867	94.847	33.629	68.066	41.634	1.253
2500	14.869	95.477	35.105	68.066	41.634	0.913
2600	14.870	96.094	36.578	68.066	41.634	0.588
2700	14.871	96.697	38.047	68.066	41.634	0.278
2800	14.872	97.286	39.512	68.066	41.634	0.000
2900	14.873	97.860	40.973	68.066	41.634	-0.287
3000	14.874	98.419	42.430	68.066	41.634	-0.577
3100	14.876	97.263	43.881	68.066	41.634	-0.872
3200	14.876	97.736	45.327	68.066	41.634	-1.172
3300	14.877	98.193	46.768	68.066	41.634	-1.477
3400	14.878	98.636	48.204	68.066	41.634	-1.787
3500	14.881	99.069	49.636	68.066	41.634	-2.097
3600	14.885	99.489	51.064	68.066	41.634	-2.407
3700	14.886	100.896	52.487	68.066	41.634	-2.717
3800	14.887	102.291	53.906	68.066	41.634	-3.027
3900	14.888	103.674	55.320	68.066	41.634	-3.337
4000	14.889	105.044	56.729	68.066	41.634	-3.647
4100	14.889	101.425	58.133	68.066	41.634	-3.957
4200	14.890	101.783	59.533	68.066	41.634	-4.267
4300	14.891	102.127	60.928	68.066	41.634	-4.577
4400	14.891	102.457	62.318	68.066	41.634	-4.887
4500	14.892	102.771	63.703	68.066	41.634	-5.197
4600	14.892	103.138	65.083	68.066	41.634	-5.507
4700	14.893	103.459	66.458	68.066	41.634	-5.817
4800	14.893	103.724	67.828	68.066	41.634	-6.127
4900	14.893	104.021	69.193	68.066	41.634	-6.437
5000	14.894	104.340	70.553	68.066	41.634	-6.747
5100	14.895	104.675	71.908	68.066	41.634	-7.057
5200	14.895	104.964	73.258	68.066	41.634	-7.367
5300	14.895	105.248	74.603	68.066	41.634	-7.677
5400	14.896	105.528	75.943	68.066	41.634	-7.987
5500	14.896	105.800	77.278	68.066	41.634	-8.297
5600	14.896	106.068	78.608	68.066	41.634	-8.607
5700	14.897	106.332	79.933	68.066	41.634	-8.917
5800	14.897	106.591	81.253	68.066	41.634	-9.227
5900	14.897	106.843	82.568	68.066	41.634	-9.537
6000	14.897	107.096	83.878	68.066	41.634	-9.847

December 31, 1961



Mercury Monofluoride, Dimeric (Hg_2F_2)

(Crystal) Mol. Wt. = 439.22 INTERIM TABLE

T. °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
100							
200							
298	24.000	38.400		.000	-116.000	-102.169	74.888
300	24.020	38.549		.044	-115.994	-102.083	74.364
400	25.020	45.599		2.898	-115.632	-97.487	53.267
500	25.910	51.280		5.045	-115.196	-93.013	40.654
600	26.690	56.075		7.676	-114.695	-88.624	32.280
700	27.370	60.241		10.380	-114.192	-84.180	25.344
800	27.950	63.935		13.147	-113.685	-79.525	19.812
900	28.430	67.255		15.966	-113.176	-74.695	15.537
1000	28.860	70.273		18.831	-112.664	-69.695	12.151
1100	29.250	73.062		21.736	-112.149	-64.526	9.382
1200	29.607	75.601		24.677	-111.629	-59.190	7.101
1300	29.935	77.979		27.648	-111.106	-53.692	5.185
1400	30.240	80.199		30.644	-110.580	-48.037	3.556
1500	30.520	82.260		33.661	-110.050	-42.226	2.155



MERCURY MONOFLUORIDE, DIMERIC (Hg_2F_2) (Crystall)

Mol. Wt. = 439.22
 $\Delta H_f^{298.15} = [-116.0 \pm 3.0]$ kcal. mole⁻¹
 $S_{298.15}^{298.15} = [38.4 \pm 2.0]$ cal. deg.⁻¹ mole⁻¹
 $T_{\text{sub}} = [848]^\circ\text{K}$ (decomp.)

Heat of Formation. A value of $\Delta H_f^{298.15}$ was obtained from the cell measurements of G. G. Koerber and T. de Vries, J. Amer. Chem. Soc. 71, 5000 (1949). This was combined with ΔS_f^{298} from the estimated entropy.

Heat Capacity and Entropy. The heat capacity was estimated by comparison with mercurous chloride. The entropy was estimated by comparison with the other mercurous and mercuric halides and use of additive entropy constants for the halogens from K. K. Kelley (Private Communication, 1960).

Sublimation. Sublimation with decomposition to $\text{Hg}(g)$ and $\text{HgF}_2(g)$ was assumed at 848°K from the free energy change of the reaction.



Potassium Difluoride Uninegative Ion (KF₂⁻)
(Ideal Gas) GFW = 77.09935

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ²⁹⁸)/T	H ^o -H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0							
100	13.627	42.561	42.561	.000	-166.000	-164.112	120.298
200		42.561	42.561	.025	-166.011	-164.100	119.547
300	13.640	42.645	43.103	2.684	-167.200	-163.263	99.203
400	14.130	46.645	48.103	2.684	-167.820	-162.208	70.901
500	14.386	49.828	49.828				
600	14.537	52.466	53.315	4.291	-168.428	-161.028	56.656
700	14.693	54.714	55.501	5.749	-169.033	-159.745	49.878
800	14.833	56.672	57.652	7.216	-169.641	-158.379	43.267
900	14.973	58.405	59.753	8.687	-170.253	-156.934	36.109
1000	14.767	59.960	60.997	10.162	-170.863	-155.421	33.967
1100		61.366	70.786	11.640	-190.431	-152.421	30.363
1200	14.608	62.656	71.722	13.120	-190.842	-149.383	27.206
1300	14.622	63.842	72.609	14.602	-191.256	-145.910	24.530
1400	14.633	64.941	73.451	16.085	-191.674	-142.406	22.231
1500	14.642	65.964	74.252	17.568	-192.095	-138.871	20.234
1600	14.650	66.922	75.014	19.053	-192.520	-135.309	18.482
1700	14.656	67.823	75.741	20.538	-192.946	-131.722	16.934
1800	14.661	68.672	76.436	22.024	-193.376	-128.108	15.554
1900	14.665	69.476	77.102	23.511	-193.812	-124.471	14.317
2000	14.669	70.236	77.740	25.000	-194.250	-120.808	13.201
2100	14.672	70.944	78.352	26.484	-194.692	-117.126	12.189
2200	14.675	71.606	78.937	27.972	-195.139	-113.422	11.267
2300	14.678	72.231	79.501	29.459	-195.590	-109.694	10.424
2400	14.680	72.820	80.056	30.947	-196.047	-105.954	9.648
2500	14.682	73.384	80.594	32.435	-196.512	-102.191	8.934
2600	14.683	73.922	81.094	33.922	-196.981	-98.406	8.272
2700	14.684	74.436	81.566	35.410	-197.459	-94.608	7.656
2800	14.686	74.925	82.006	36.901	-197.945	-90.791	7.087
2900	14.687	75.389	82.419	38.389	-198.440	-86.952	6.563
3000	14.688	75.827	82.799	39.878	-198.945	-83.102	6.084
3100	14.689	76.240	83.146	41.367	-199.461	-79.230	5.586
3200	14.690	76.623	83.460	42.856	-199.989	-75.345	5.146
3300	14.691	76.991	83.753	44.345	-200.530	-71.443	4.731
3400	14.692	77.335	84.025	45.834	-201.085	-67.524	4.340
3500	14.692	77.657	84.286	47.323	-201.657	-63.585	3.970
3600	14.693	77.959	84.528	48.812	-202.244	-59.630	3.620
3700	14.693	78.245	84.750	50.302	-202.854	-55.659	3.288
3800	14.694	78.517	84.953	51.791	-203.485	-51.674	2.972
3900	14.695	78.775	85.137	53.281	-204.139	-47.674	2.672
4000	14.695	79.020	85.301	54.770	-204.818	-43.649	2.385
4100	14.695	79.253	85.446	56.260	-205.527	-39.611	2.111
4200	14.696	79.475	85.573	57.749	-206.269	-35.556	1.850
4300	14.696	79.687	85.687	59.239	-207.042	-31.482	1.600
4400	14.697	79.889	85.788	60.728	-207.857	-27.393	1.361
4500	14.697	80.081	85.874	62.218	-208.709	-23.279	1.131
4600	14.697	80.263	85.947	63.708	-209.604	-19.151	.910
4700	14.697	80.436	86.006	65.198	-210.551	-14.999	.697
4800	14.698	80.599	86.055	66.687	-211.546	-10.823	.493
4900	14.698	80.753	86.096	68.177	-212.595	-6.633	.296
5000	14.698	80.899	86.129	69.667	-213.698	-2.423	.106
5100	14.698	81.035	86.157	71.157	-214.861	1.818	-.078
5200	14.699	81.163	86.176	72.647	-216.085	6.078	-.255
5300	14.699	81.283	86.188	74.136	-217.372	10.364	-.427
5400	14.699	81.397	86.194	75.626	-218.723	14.626	-.594
5500	14.699	81.500	86.194	77.116	-220.138	18.863	-.755
5600	14.699	81.593	86.188	78.606	-221.617	23.070	-.912
5700	14.699	81.676	86.176	80.096	-223.161	27.252	-1.070
5800	14.699	81.750	86.157	81.586	-224.768	31.411	-1.212
5900	14.699	81.815	86.133	83.076	-226.437	35.545	-1.356
6000	14.699	81.872	86.106	84.566	-228.166	39.655	-1.497

Dec. 31, 1968

POTASSIUM DIFLUORIDE UNINEGATIVE ION (KF₂⁻) (IDEAL GAS)

Point Group [D_{∞h}]
S_{298.15} = {63 ± 21 gibbs/mol
Ground State Quantum Weight = {1}
Bond Distance: K-F = {2.17} Å
Bond Angle: F-K-F = {180°}
Rotational Constant: B₀ = {0.094} cm⁻¹
σ = 2

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
{350} (1)
{130} (2)
{500} (1)

The heat of formation is estimated from three calculated values. The methods of calculation are described as follows. In a manner analogous to LiF₂(g), the first reaction considered is KF(g) + F⁻(g) = KF₂⁻(g) and the ΔH_f^o298(KF₂⁻, g) is evaluated to be between 0 and 1/2(-50) = -25 kcal/mol (see LiF₂⁻(g) table for details), yielding from JANAF Tables. The ΔH_f^o298 values for the other species involved are taken

The second reaction employed for estimation is K₂F₂(g) = KF₂⁻(g) + K⁺(g). The enthalpy change of this reaction is calculated as ΔH_r^o298 = 1/2(50.0) + 138.8 = 163.8 kcal/mol where the KF₂⁻ ion is considered to be converted from K₂F₂(g) by breaking one of the two dimer association bonds (ΔH_r^o298 = 50.0 kcal/mol) and one K⁺-F⁻ ionic bond (ΔH_r^o298 = 138.8 kcal/mol). Using ΔH_f^o298 = -206.2 and 122.9 kcal/mol for K₂F₂(g) and K⁺(g), we obtain the heat of formation for KF₂⁻(g) as -165 kcal/mol.

Based on an assumption that the electron affinity of KF₂⁻(g) is similar to that of F (see LiF₂⁻(g) table for details), i.e. ΔH_r^o = 83.5 kcal/mol (1) for the reaction KF₂⁻(g) = KF₂(g) + e⁻(g), we derive ΔH_f^o298(KF₂⁻, g) = -167.7 kcal/mol. The ΔH_f^o298 for KF₂(g) is calculated as -84.2 kcal/mol from the value ΔH_r^o298 = 143.3 kcal/mol for the reaction K₂F₂(g) = KF₂(g) + K(g) where the ΔH_r^o298 value is calculated as the sum of two enthalpy changes, i.e. half of the heat of dimer dissociation into two monomers or 1/2(50.0) = 25.0 kcal/mol, and the heat of dissociation of KF(g) or 118.3 kcal/mol. The value of ΔH_f^o298 for KF₂⁻(g) is tentatively adopted as -166 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion given by Walsh (2) that molecules with not more than 16 valency electrons are linear in their ground states. The K-F bond distance is taken to be the same as that of KF(g) reported by Veazey and Gordy (3). The vibrational frequencies are estimated from the vibrational frequency of KF(g) using the method suggested by Herzberg (4). The moment of inertia is 2.971 × 10⁻³⁸ g cm². The enthalpy at 0°K is -3.293 kcal/mol.

References

1. H. O. Pritchard, Chem. Rev. 52, 528 (1953).
2. A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953).
3. S. E. Veazey and W. Gordy, Phys. Rev. 138, A1303 (1965).
4. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, p. 172.

F₂K⁻

GFW = 116.2008

(IDEAL GAS)

POTASSIUM FLUORIDE, DIMERIC (K₂F₂)

Potassium Fluoride, Dimeric (K₂F₂) (Ideal Gas) GFW = 116.2008

Point Group D_{2h} $\Delta H_f^\circ = -205.1 \pm 2 \text{ kcal/mol}$ $S_{298.15}^\circ = 176.8 \pm 2.3 \text{ gibbs/mol}$ $\Delta H_f^\circ = -206.2 \pm 2 \text{ kcal/mol}$

Ground State Quantum Weight = [1]

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	Log Kp
0	1.000	INFINITE	INFINITE	4.381	-205.085	INFINITE
100	13.560	58.214	58.214	3.397	-205.624	499.500
200	17.815	68.185	68.185	1.815	-206.451	150.511
298	18.768	76.444	76.444	1.000	-206.200	
300	18.780	76.560	76.560	1.035	-206.205	149.579
400	19.240	82.035	82.035	1.939	-207.699	111.878
500	19.462	86.354	86.354	3.675	-208.056	80.164
600	19.585	89.914	89.914	5.626	-208.387	73.995
700	19.680	92.940	92.940	7.790	-208.704	63.144
800	19.759	95.568	95.568	9.759	-209.026	54.903
900	19.763	97.492	97.492	11.732	-209.356	48.463
1000	19.767	99.973	99.973	13.707	-209.708	43.456
1100	19.785	101.958	101.958	15.685	-209.894	38.979
1200	19.789	103.580	103.580	17.664	-209.860	34.877
1300	19.810	105.165	105.165	19.645	-209.724	31.404
1400	19.818	106.634	106.634	21.626	-209.444	28.429
1500	19.825	108.001	108.001	23.608	-209.567	25.452
1600	19.831	109.281	109.281	25.591	-209.493	23.598
1700	19.835	110.483	110.483	27.574	-209.424	21.610
1800	19.839	111.617	111.617	29.558	-209.356	19.643
1900	19.843	112.690	112.690	31.542	-209.288	18.263
2000	19.845	113.708	113.708	33.527	-209.249	16.480
2100	19.848	114.676	114.676	35.511	-209.170	15.454
2200	19.850	115.600	115.600	37.496	-209.144	14.385
2300	19.852	116.482	116.482	39.481	-209.112	13.318
2400	19.853	117.327	117.327	41.467	-209.084	12.339
2500	19.855	118.137	118.137	43.452	-209.070	11.439
2600	19.856	118.916	118.916	45.434	-209.063	10.608
2700	19.857	119.666	119.666	47.423	-209.071	9.830
2800	19.858	120.388	120.388	49.409	-209.094	9.125
2900	19.859	121.085	121.085	51.391	-209.132	8.460
3000	19.860	121.758	121.758	53.368	-209.187	7.839
3100	19.861	122.409	122.409	55.347	-209.263	7.258
3200	19.861	123.040	123.040	57.325	-209.360	6.713
3300	19.862	123.651	123.651	59.300	-209.481	6.201
3400	19.863	124.244	124.244	61.275	-209.630	5.719
3500	19.863	124.820	124.820	63.252	-209.807	5.264
3600	19.864	125.379	125.379	65.229	-209.018	4.834
3700	19.864	125.923	125.923	67.204	-208.264	4.427
3800	19.864	126.453	126.453	69.171	-208.555	4.041
3900	19.865	126.969	126.969	71.125	-208.890	3.674
4000	19.865	127.472	127.472	73.074	-209.273	3.325
4100	19.865	127.963	127.963	75.020	-209.714	2.993
4200	19.866	128.441	128.441	76.961	-210.216	2.675
4300	19.866	128.909	128.909	78.903	-210.782	2.372
4400	19.866	129.365	129.365	80.841	-211.424	2.082
4500	19.866	129.812	129.812	82.775	-212.144	1.804
4600	19.867	130.249	130.249	84.705	-212.952	1.538
4700	19.867	130.676	130.676	86.630	-213.851	1.281
4800	19.867	131.094	131.094	88.551	-214.847	1.035
4900	19.867	131.504	131.504	90.467	-215.951	0.798
5000	19.867	131.905	131.905	92.378	-217.162	0.569
5100	19.868	132.299	132.299	94.283	-218.489	0.348
5200	19.868	132.684	132.684	96.184	-219.936	0.134
5300	19.868	133.063	133.063	98.080	-221.504	0.072
5400	19.868	133.434	133.434	100.000	-223.202	0.073
5500	19.868	133.799	133.799	101.944	-225.025	0.067
5600	19.868	134.157	134.157	103.931	-226.975	0.065
5700	19.868	134.508	134.508	105.973	-229.051	0.069
5800	19.869	134.854	134.854	108.005	-231.292	0.018
5900	19.869	135.195	135.195	110.091	-233.705	0.015
6000	19.869	135.527	135.527	112.246	-236.301	0.012

June 30, 1981; Mar. 31, 1984; June 30, 1989

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}
[273] (1)	[150] (1)
[150] (1)	[255] (1)
[235] (1)	[258] (1)

Bond Distance: K-F = 2.2 Å
 Bond Angles: F-K-F = [90°] K-F-K = [90°]
 Product of the Moments of Inertia: $I_A I_B I_C = [2.240 \times 10^{-113}] \text{ g cm}^6$

Heat of Formation

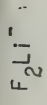
The equilibrium constants (K_c) for the reaction $K_2F_2(g) = 2KF(g)$, in the temperature range 978-1052°K, were determined by Eisenstadt, Rothberg, and Kusch (2). Although the reported absolute values of the vapor pressures of $KF(g)$ are not adopted for evaluation, the reported K_c values are used to calculate the enthalpy change (ΔH_{298}°) for the above reaction. The second law and third law values of ΔH_{298}° are derived as 51.0 ± 1.6 and 50.0 kcal/mol , respectively. Based on the third law ΔH_{298}° and $\Delta H_{298}^\circ(KF, g) = -78.1 \text{ kcal/mol}$, we obtain $\Delta H_{298}^\circ = -206.2 \text{ kcal/mol}$ for $K_2F_2(g)$ which is tentatively adopted.

Heat Capacity and Enthalpy

The molecular structure and K-F bond distance were determined by Akishin and Rambidi (2), using electron diffraction with sector microphotometry. The bond angles are estimated by comparison with other alkali halide dimers. The vibrational frequencies are taken from Berkowitz (3) which were calculated based on an ionic model. The three principal moments of inertia are: $I_A = 3.1423 \times 10^{-38}$, $I_B = 1.5267 \times 10^{-38}$, and $I_C = 4.6690 \times 10^{-38} \text{ g cm}^2$.

References

1. H. Eisenstadt, G. H. Rothberg, and P. Kusch, J. Chem. Phys. **29**, 797 (1958).
2. P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. **213**, 111 (1960).
3. J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).



LITHIUM DIFLUORIDE UNINEGATIVE ION (LiF_2^-) (IDEAL GAS)

GFW = 44.93635

$\Delta H_F^0 = (-169 \pm 15) \text{ kcal/mol}$

$\Delta H_F^{298.15} = [-170 \pm 16] \text{ kcal/mol}$

Point Group $[D_{\infty h}]$

$S_{298.15} = [55 \pm 2] \text{ gibbs/mol}$

Ground State Quantum Weight = {1}

Vibrational Frequencies and Degeneracies	
ω, cm^{-1}	
[1300] (1)	
[350] (2)	
[550] (1)	

Bond Distance: $Li-F = [1.57] \text{ \AA}$

Bond Angle: $F-Li-F = [180^\circ]$

Rotational Constant: $B_0 = [0.180] \text{ cm}^{-1}$

Heat of Formation

Due to lack of thermal data, the heat of formation for $LiF_2^-(g)$ is arbitrarily selected from the following three estimated values. For the reaction (1) $LiF(g) + F^-(g) = LiF_2^-(g)$, we expect the enthalpy change would be between 0 to -31 kcal/mol. Comparison with the other molecules like CO_2 , BO_2 , BeF_2 , etc. having 16 valence electrons leads us to assume that the isoelectronic molecule LiF_2^- should also be quite stable. This indicates that reaction (1) is favorable or ΔH_{298}^0 is negative. However, the $Li-F$ bond strength is expected to be weaker than half of the two ionic bonds between Li^+ and F^- in LiF_2 molecule (see LiF_2 (g) table for the molecular structure). In other words, the ΔH_{298}^0 value of reaction (1) is less negative than half of the heat of dimerization (-62.4 kcal/mol). Incorporating $\Delta H_{298}^0 = 0$ and -31 kcal/mol , respectively, for reaction (1), with $\Delta H_{298}^0 = -81.45$ and -62.2 kcal/mol for $LiF(g)$ and $F^-(g)$, we derived the corresponding values for $\Delta H_{298}^0(LiF_2^-, g)$ as -144 and -175 kcal/mol , which are the upper and lower limits.

The electron affinities of Li and F atoms are reported as 0.7 and 3.448 eV, respectively, by Beckett and Cassidy (1). From this data we estimate that the electron affinity of $LiF_2(g)$ should be closer to that of F atom than to that of Li. Assuming ΔH_{298}^0 = electron affinity of F atom = 83.5 kcal/mol for the reaction $LiF_2^-(g) = LiF_2(g) + e^-(g)$, we obtain the heat of formation for $LiF_2^-(g)$ as -177.3 kcal/mol . The $\Delta H_{298}^0(LiF_2, g)$ used for calculation is derived from an estimated $\Delta H_{298}^0 = 169.9 \text{ kcal/mol}$ for the decomposition of LiF dimer or $Li_2F_2(g) = LiF_2(g) + Li(g)$ as the sum of two enthalpy changes, namely, half of the heat of dissociation of the dimer and the heat of dissociation of the monomer.

The third estimated value for the heat of formation of $LiF_2^-(g)$ is calculated as follows. Based on the two heats of reaction, i.e. $\Delta H_{298}^0 = 62.4 \text{ kcal/mol}$ for $Li_2F_2(g) = LiF(g) + LiF(g)$, and $\Delta H_{298}^0 = 183.5 \text{ kcal/mol}$ for $LiF(g) + F^-(g) = LiF_2^-(g)$, we assume the enthalpy change of the reaction $Li_2F_2(g) = LiF_2(g) + Li^+(g) + F^-(g)$ to be $1/2(62.4) + 183.5 = 714.7 \text{ kcal/mol}$. In other words, we consider the $LiF_2^-(g)$ molecule is formed by breaking half of the dimer dissociation bonds and one monomer dissociation bond to produce two ions. Using $\Delta H_{298}^0 = -225.33$ and 164.24 kcal/mol for $Li_2F_2(g)$ and $Li^+(g)$, we evaluate $\Delta H_{298}^0(LiF_2^-, g) = -174.9 \text{ kcal/mol}$.

From the above three estimated values, we tentatively choose $\Delta H_{298}^0(LiF_2^-, g)$ as $-170 \pm 15 \text{ kcal/mol}$.

Heat Capacity and Entropy

According to A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953), molecules with not more than 16 valence electrons are linear in their ground states. Since $LiF_2^-(g)$ has 16 valence electrons, we assume its molecular structure is linear. The $Li-F$ bond distance is estimated by comparison with that of $LiF(g)$ reported by Wharton et al. (2). The vibrational frequencies are estimated from those of the isoelectronic gaseous molecules, CO_2 and BeF_2 . The moment of inertia is $1.555 \times 10^{-38} \text{ g cm}^2$. The enthalpy at 0°K is -2.653 kcal/mol .

References

1. C. W. Beckett and E. C. Cassidy, U. S. Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. L. Wharton, W. Klumperer, L. P. Gold, R. Strauch, J. J. Gallagher, and V. E. Derr, J. Chem. Phys. 38, 1203 (1963).

Lithium Difluoride Uninegative Ion (LiF_2^-) (Ideal Gas)

GFW = 44.93635

T, °K	C_p^0	$S^0 - (G^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_F^0	ΔG_F^0	Log Kp
0						
100						
200						
298	11.393	54.653	-0.000	-170.000	-169.349	123.403
300						
400	11.413	54.984	0.021	-170.013	-169.339	122.635
500	12.005	56.336	0.113	-170.015	-169.337	121.890
600	12.922	61.154	0.249	-170.017	-169.339	121.180
700	13.363	63.551	3.760	-172.890	-165.607	120.322
800	13.682	65.636	58.291	-173.591	-164.337	119.408
900	13.918	67.479	59.326	-174.266	-162.970	118.521
1000	14.095	69.129	60.325	-174.929	-161.516	117.666
1100	14.230	70.621	61.282	-175.584	-159.993	116.836
1200	14.335	71.983	62.193	-176.233	-158.403	116.022
1300	14.418	73.234	63.062	-176.877	-156.754	115.226
1400	14.484	74.390	63.869	-177.517	-155.059	114.456
1500	14.536	75.466	64.616	-178.155	-153.324	113.711
1600	14.583	76.470	65.331	-178.790	-151.559	113.000
1700	14.619	77.413	66.011	-179.422	-149.659	112.322
1800	14.650	78.300	66.640	-180.048	-147.631	111.676
1900	14.677	79.138	67.220	-180.668	-145.481	111.056
2000	14.699	79.932	67.764	-181.283	-143.213	110.460
2100	14.718	80.687	68.273	-181.893	-140.833	109.888
2200	14.735	81.405	68.749	-182.497	-138.353	109.338
2300	14.750	82.081	69.189	-183.095	-135.783	108.808
2400	14.762	82.747	69.593	-183.687	-133.133	108.298
2500	14.774	83.376	69.964	-184.273	-130.413	107.808
2600	14.784	83.979	70.309	-184.853	-127.633	107.338
2700	14.793	84.559	70.625	-185.427	-124.803	106.888
2800	14.800	85.117	70.913	-186.000	-121.923	106.458
2900	14.808	85.656	71.173	-186.573	-118.993	106.048
3000	14.814	86.175	71.409	-187.147	-116.023	105.658
3100	14.820	86.678	71.625	-187.720	-113.013	105.288
3200	14.825	87.164	71.825	-188.293	-110.003	104.938
3300	14.830	87.635	72.024	-188.867	-107.003	104.608
3400	14.834	88.091	72.224	-189.440	-104.013	104.298
3500	14.838	88.534	72.416	-190.013	-101.023	104.008
3600	14.842	88.964	72.597	-190.587	-98.033	103.738
3700	14.845	89.382	72.769	-191.160	-95.043	103.488
3800	14.848	89.789	72.932	-191.733	-92.053	103.258
3900	14.851	90.185	73.088	-192.307	-89.063	103.048
4000	14.854	90.571	73.232	-192.880	-86.073	102.858
4100	14.856	90.947	73.370	-193.453	-83.083	102.688
4200	14.858	91.314	73.501	-194.027	-80.093	102.538
4300	14.861	91.672	73.624	-194.600	-77.103	102.408
4400	14.863	92.021	73.741	-195.173	-74.113	102.298
4500	14.864	92.363	73.851	-195.747	-71.123	102.208
4600	14.866	92.697	73.955	-196.320	-68.133	102.138
4700	14.868	93.024	74.053	-196.893	-65.143	102.088
4800	14.869	93.344	74.145	-197.467	-62.153	102.058
4900	14.871	93.657	74.232	-198.040	-59.163	102.048
5000	14.872	93.963	74.313	-198.613	-56.173	102.058
5100	14.873	94.264	74.388	-199.187	-53.183	102.088
5200	14.874	94.558	74.458	-199.760	-50.193	102.138
5300	14.876	94.847	74.524	-200.333	-47.203	102.208
5400	14.877	95.131	74.586	-200.907	-44.213	102.298
5500	14.878	95.409	74.645	-201.480	-41.223	102.408
5600	14.879	95.682	74.701	-202.053	-38.233	102.538
5700	14.880	95.950	74.753	-202.627	-35.243	102.688
5800	14.881	96.213	74.801	-203.200	-32.253	102.858
5900	14.881	96.472	74.845	-203.773	-29.263	103.048
6000	14.882	96.726	74.885	-204.347	-26.273	103.258
6100	14.883	96.977	74.921	-204.920	-23.283	103.488

Dec. 31, 1968

Magnesium Difluoride (MgF₂)

(Crystal)

Mol. Wt. = 62.3033

F₂Mg

MAGNESIUM DIFLUORIDE (MgF₂)

MOL. WT. = 62.3088

(CRYSTAL)

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	-	2.370	-267.764	-267.764	INFINITE
100	5.193	2.552	24.676	-	2.462	-268.435	-268.435	26.805
200	11.420	6.483	13.683	-	1.464	-268.435	-268.435	26.805
298	14.720	13.683	13.683	-	0.000	-268.700	-256.005	187.848
300	14.790	13.775	13.684	0.027	-268.698	-255.927	186.434	
400	16.390	18.265	14.285	1.592	-268.517	-251.695	137.513	
500	17.310	22.028	15.468	3.280	-268.278	-247.516	108.184	
600	17.830	25.232	16.895	5.038	-268.021	-243.388	88.650	
700	18.250	28.013	18.237	6.843	-267.760	-239.302	74.710	
800	18.600	30.473	19.616	8.685	-267.509	-235.256	64.266	
900	18.930	32.683	20.947	10.562	-267.269	-231.238	56.150	
1000	19.230	34.693	22.223	12.470	-267.045	-227.266	49.023	
1100	19.520	36.536	23.441	14.408	-266.821	-223.369	42.878	
1200	19.800	38.250	24.605	16.374	-266.679	-219.537	39.828	
1300	20.080	39.846	25.717	18.368	-266.441	-215.853	36.065	
1400	20.350	41.344	26.780	20.389	-266.211	-212.309	32.768	
1500	20.610	42.757	27.799	22.437	-265.971	-208.920	29.904	
1600	20.880	44.096	28.774	24.512	-265.728	-205.659	27.468	
1700	21.140	45.369	29.715	26.613	-265.482	-202.518	25.459	
1800	21.400	46.585	30.618	28.740	-265.236	-199.496	23.863	
1900	21.660	47.749	31.489	30.893	-264.991	-196.591	22.553	
2000	21.920	48.867	32.331	33.072	-264.746	-193.797	21.489	
2100	22.175	49.942	33.144	35.277	-264.501	-191.118	20.659	
2200	22.430	50.980	33.931	37.507	-264.256	-188.553	19.940	
2300	22.686	51.982	34.694	39.763	-264.011	-186.099	19.323	
2400	22.943	52.953	35.435	42.044	-263.766	-183.757	18.796	
2500	23.200	53.895	36.155	44.351	-263.521	-181.526	18.357	

Dec. 31, 1960; June 30, 1964; Mar. 31, 1966

S_{298.15} = 13.68 ± 0.07 cal. deg.⁻¹ mole⁻¹
T_m = 1536°K.
ΔH_f^o 0 = -267.8 ± 0.3 kcal. mole⁻¹
ΔH_f^o 298.15 = -268.7 ± 0.3 kcal. mole⁻¹
ΔH_m^o = 13.90 kcal. mole⁻¹
ΔH_m^o 298.15 = 95.5 ± 1.5 kcal. mole⁻¹

Heat of Formation.

The value of ΔH_f^o 298.15 for MgF₂(c) was obtained from E. Rudzitis and W. N. Hubbard, Argonne National Laboratory, Argonne, Illinois, private communication, dated June 18, 1964. This value was determined by fluorine bomb calorimetry which is considered as comparatively the best method available at the present time. The heats of reaction involving MgF₂(c) were measured by many early investigators. However, the ΔH_f^o 298.15(MgF₂, c) values derived are in reasonable agreement. The results are presented as follows.

Investigator	Chemical Reaction	ΔH _f ^o 298.15, kcal. mole ⁻¹	ΔH _f ^o 298.15, kcal. mole ⁻¹
Domange (1)	MgF ₂ (c) + H ₂ O(g) → 2HF(g) + MgO(c)	+51.76 ± 1.2 (1)	-267.3 ± 1.3
Wartenberg (2)	Mg(c) + 2(HF·80H ₂ O) → MgF ₂ (c) + H ₂ (g) + 160H ₂ O(l)	-109.5 ± 0.7	-262.1 ± 0.8
Torgeson, et al. (3)	Mg(OH) ₂ (c) + 2HF(sol.) → MgF ₂ (c) + 2H ₂ O(l)	-29.09	-266.5 ± 0.8
Gross, et al. (4)	Mg(c) + PbF ₂ (c) → MgF ₂ (c) + Pb(c)	-109.5 ± 1.5	-269.1 ± 1.8
(1) L. Domange, Ann. chim. phys. 7(11)225 (1937). The ΔH _f ^o value was calculated by the third law method.			
(2) H. V. Wartenberg, Z. anorg. allgem. Chem. 249, 100 (1942).			
(3) D. R. Torgeson and T. G. Sahan, J. Am. Chem. Soc. 70, 2156 (1948).			
(4) P. Gross, C. Hayman and D. L. Levi, Trans. Faraday Soc. 50, 477 (1954).			

Heat Capacity and Entropy.

The low temperature heat capacities, 54.22-296.5°K., were measured by S. S. Todd, J. Am. Chem. Soc. 71, 4115 (1949). The high temperature heat capacities, 298-1536°K., were obtained from the heat content measurements determined by E. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). These two sets of data were joined smoothly at 298°K. S_{298.15} was obtained from C_p data reported by S. S. Todd, loc. cit., using S_{298.15} (extrap.) = 0.537 cal. deg.⁻¹ mole⁻¹.

Melting Data.

T_m and ΔH_m^o were taken from E. F. Naylor, loc. cit.

Heat of Sublimation.

The vapor pressure of MgF₂(c) has been measured by seven investigators. Using the reported data, the respective ΔH_m^o 298.15 for MgF₂(c) were calculated (see MgF₂(c) table for detail). The adopted value was selected to be 95.5 ± 1.5 kcal. mole⁻¹.

F₂Mg

Magnesium Difluoride (MgF₂)

(Liquid) Mol. Wt. = 62.3088

F₂Mg

MOL. WT. = 62.3088

(LIQUID)

MAGNESIUM DIFLUORIDE (MgF₂)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
100						
200						
298						
2250	15.290	15.290	-	-0.000	-247.341	181.297
22570	15.430	15.290	0.042	-259.540	-247.266	180.124
22570	21.923	16.176	2.299	-258.667	-243.308	132.931
22570	26.959	17.847	4.556	-257.859	-239.563	104.708
22570	31.074	19.719	6.813	-257.103	-235.976	85.950
22570	34.553	21.596	9.070	-256.390	-232.550	72.590
22570	37.567	23.408	11.327	-255.724	-229.147	62.597
22570	40.225	25.132	13.584	-255.104	-225.862	54.844
22570	42.603	26.763	15.841	-254.651	-222.463	48.617
22570	44.754	28.302	18.098	-254.088	-219.073	43.524
22570	46.718	29.756	20.355	-253.555	-215.731	39.288
22570	48.525	31.131	22.612	-253.054	-212.432	35.711
22570	50.197	32.434	24.869	-252.548	-209.174	32.577
22570	51.755	33.671	27.126	-252.099	-205.954	29.616
22570	53.211	34.847	29.383	-251.654	-202.774	26.833
22570	54.560	35.968	31.640	-251.212	-199.626	24.260
22570	55.870	37.038	33.897	-250.774	-196.512	21.796
22570	57.090	38.062	36.154	-250.337	-193.426	19.437
22570	58.248	39.042	38.411	-249.904	-190.374	17.183
22570	59.349	39.983	40.668	-249.474	-187.354	15.033
22570	60.399	40.888	42.925	-249.047	-184.365	12.983
22570	61.402	41.758	45.182	-248.622	-181.405	11.033
22570	62.363	42.596	47.439	-248.200	-178.474	9.183
22570	63.284	43.406	49.696	-247.782	-175.572	7.433
22570	64.169	44.187	51.953	-247.366	-172.696	5.783
22570	65.021	44.943	54.210	-246.953	-169.844	4.233
22570	65.842	45.675	56.467	-246.542	-167.016	2.783
22570	66.634	46.384	58.724	-246.132	-164.212	1.333
22570	67.399	47.072	60.981	-245.724	-161.426	-0.117
22570	68.139	47.740	63.238	-245.319	-158.656	-1.567
22570	68.856	48.388	65.495	-244.916	-155.900	-3.017
22570	69.550	49.019	67.752	-244.514	-153.158	-4.467
22570	70.224	49.633	70.009	-244.114	-150.430	-5.917
22570	70.878	50.231	72.266	-243.716	-147.714	-7.367
22570	71.514	50.813	74.523	-243.319	-145.012	-8.817
22570	72.132	51.381	76.780	-242.924	-142.322	-10.267
22570	72.734	51.935	79.037	-242.530	-139.644	-11.717
22570	73.321	52.476	81.294	-242.137	-136.978	-13.167
22570	73.892	53.004	83.551	-241.746	-134.324	-14.617

Heat of Formation.

ΔH_f° 298.15(l) was obtained from ΔH_f° 298.15(c) by adding ΔH_m° and the difference between H_m°-H_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

Heat capacity (169-1800°K.) was reported by B. F. Naylor, J. Am. Chem. Soc. 67, 150 (1945). The same value was used for other temperatures. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m and ΔH_m° were obtained from B. F. Naylor, Loc. Cit.

Vaporization Data.

T_b was obtained from equilibrium calculation between the species MgF₂(l), MgF₂(g), and (MgF₂)₂(g), i.e., the temperature at which the sum of the partial pressures of MgF₂(g) and (MgF₂)₂(g) equals one atmosphere.

From the difference between the heats of formation of MgF₂(l) and MgF₂(g) at the boiling point, the heat of vaporization was calculated. At the boiling point the amount of dimeric species is negligible in comparison with that of the monomeric species.

F₂Mg

Magnesium Difluoride (MgF₂)

(Ideal Gas) Mol. Wt. = 62.3088

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	8.442	50.459	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
200	10.468	67.319	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
298	11.621	71.734	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
300	11.638	71.734	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
400	12.364	85.252	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
500	12.615	95.102	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
600	13.103	104.37	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
700	13.295	112.472	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
800	13.427	119.256	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
900	13.522	125.044	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1000	13.592	130.012	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1100	13.644	134.270	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1200	13.685	137.759	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1300	13.717	140.496	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1400	13.743	142.445	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1500	13.764	143.782	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1600	13.782	144.511	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1700	13.796	144.677	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1800	13.808	144.785	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
1900	13.818	144.835	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2000	13.827	144.867	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2100	13.835	144.887	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2200	13.841	144.898	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2300	13.846	144.902	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2400	13.850	144.906	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2500	13.853	144.909	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2600	13.856	144.912	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2700	13.858	144.914	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2800	13.860	144.916	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
2900	13.861	144.917	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3000	13.862	144.918	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3100	13.863	144.919	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3200	13.864	144.920	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3300	13.865	144.921	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3400	13.866	144.922	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3500	13.867	144.923	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3600	13.868	144.924	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3700	13.869	144.925	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3800	13.870	144.926	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
3900	13.871	144.927	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4000	13.872	144.928	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4100	13.873	144.929	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4200	13.874	144.930	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4300	13.875	144.931	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4400	13.876	144.932	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4500	13.877	144.933	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4600	13.878	144.934	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4700	13.879	144.935	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4800	13.880	144.936	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
4900	13.881	144.937	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5000	13.882	144.938	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5100	13.883	144.939	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5200	13.884	144.940	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5300	13.885	144.941	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5400	13.886	144.942	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5500	13.887	144.943	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5600	13.888	144.944	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5700	13.889	144.945	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5800	13.890	144.946	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
5900	13.891	144.947	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE
6000	13.892	144.948	172.773	-2.409	-172.773	-172.773	-172.773	INFINITE

Dec. 51, 1960; June 30, 1964; Mar. 31, 1966

MAGNESIUM DIFLUORIDE (MgF₂)

(IDEAL GAS)

Point Group C_{2v}
 $S_{298.15}^0 = 61.734 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]

$\Delta H_f^0 = -172.0 \pm 1.5 \text{ kcal. mole}^{-1}$
 $\Delta F_f^0 = -173.2 \pm 1.5 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹
478 (1)
241 (1)
834 (1)

Bond Distances: Mg-F = $1.77 \pm 0.02 \text{ \AA}$
 Bond Angle: F-Mg-F = $150 \pm 5^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 1.80532 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$

 $\sigma^* = 2$

Heat of Formation.

The vapor pressure of MgF₂(g) over MgF₂(c) and MgF₂(l) has been measured by many investigators using different methods. Based on the reported vapor pressure data, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K.	Method*	Second Law Value	Third Law Value	Drift
Ruff and Boucher ¹	1934 - 2129	a	99.49 ± 2.56	96.19	-1.66 ± 1.31
Quentner ²	1284 - 1550	b	95.06 ± 0.50	95.64	0.45 ± 0.53
Hammer ³	1451 - 1533	b	93.68 ± 2.67	96.21	1.62 ± 1.79
	1568 - 1613	b	94.17 ± 6.40	96.21	1.26 ± 4.16
	1413 - 1518	c	96.75 ± 2.99	96.19	0.22 ± 2.08
	1539 - 1614	c	96.81 ± 4.35	96.09	-0.51 ± 2.74
Berkowitz and Marquart ⁴	1450	c	80.72 ± 1.11	91.58	7.75 ± 0.80
Farber, et al. ⁵	1275 - 1513	c	91.80 ± 1.11	93.40	1.12 ± 0.78
Hildenbrand, et al. ⁶	1544 - 1604	c	94.49 ± 5.00	95.95	-0.39 ± 3.17
	1425 - 1533	c	104.79 ± 1.00	95.75	-6.14 ± 0.65
	1540 - 1608	c	102.81	95.49	-4.65
Margrave, et al. ⁷	1200 - 1550	-	94.0	95.07	1.69 ± 0.08
	1241 - 1492	b	95.77 ± 2.5	95.07	1.69 ± 0.08

*a = Manometric method; b = Knudsen effusion method; and c = Torsion effusion method

1 O. Ruff and L. LeBoucher, Z. anorg. allgem. Chem. 219, 376 (1934).

2 K. O. Quentner, Unstet. Ber. 31, 9 (1956).

3 R. R. Hammer, Ph.D. Thesis, University of California, 1961. Also see R. R. Hammer and J. A. Pask, J. Am. Chem. Soc. 83, 264 (1961).

4 J. Berkowitz and J. R. Marquart, J. Chem. Phys. 37, 1853 (1962). The value, 91.36 kcal. mole⁻¹, was converted from the reported value 86 kcal. mole⁻¹ at 1350°K.5 H. A. Greenbaum, H. C. Ho, R. Kong and M. Farber, J. Phys. Chem. 69, 985 (1964), whose reported ΔH_f 238.15 kcal. mole⁻¹ was derived using different values of free energy functions for MgF₂(c) and MgF₂(g) from those used here.

6 Values of data were obtained from D. L. Hildenbrand, et al., J. Phys. Chem. 68, 1155 (1964), and D. L. Hildenbrand, et al., J. Phys. Chem. 68, 1155 (1964).

7 J. W. Green, G. D. Blue, T. C. Ehler and J. L. Margrave, J. Chem. Phys. 41, 2245 (1964).

When vapor pressure data were determined above melting point, 1530°K., the heat of sublimation was derived from the heat of vaporization obtained incorporating heat of melting. All data were carefully examined and some inconsistent vapor pressure points were discarded. The heat value of ΔH_f 238.15 for MgF₂(c) was selected as 95.5 ± 1.5 kcal. mole⁻¹. The heat of formation for MgF₂(g) was calculated from the heats of formation and sublimation for MgF₂(c).

Heat Capacity and Entropy.

The molecular structure of MgF₂(g) has been reported to be linear by A. Büchler, J. L. Stauffer and W. Klemperer, Interim Technical Report No. 7, June 30, 1964, A. D. Little, Inc., and bent by M. J. Linevsky, First Quarterly Report, Nov. 1, 1963 - Jan. 31, 1964, General Electric Company. An intensive investigation of the matrix spectrum of MgF₂(g) has been made recently by D. E. Mann and O. V. Calder, National Bureau of Standards Report 8919, July 1, 1965. The final results were presented by D. E. Mann at the ICRG Working Group on Thermochemistry meeting on Mar. 17, 1966.The vibrational frequencies, bent structure and bond angle were confirmed by use of isotopic substitution, and were adopted here. The Mg-F bond distance was reported by P. A. Aikshin, V. P. Spiridonov, O. A. Sobolev and V. A. Naumov, Zh. Fiz. Khim. 31, 463 (1957). The three principal moments of inertia are: I_A = 5.1660 × 10⁻⁴⁰, I_B = 1.8442 × 10⁻⁵⁸ and I_C = 1.8959 × 10⁻⁵⁹ g. cm.²F₂Mg

MOL. WT. = 62.3088

F₂Mg

T, °K.	C _p	S° - (S° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f ⁰	Log K _p
0	7.985	0.000	INFINITE	10.718	INFINITE
100	7.985	50.345	10.718	10.718	10.718
200	8.077	56.044	10.751	10.751	13.604
298	8.801	59.715	10.100	13.564	9.962
300	8.822	59.775	10.098	13.585	9.896
400	10.851	62.748	10.113	14.762	8.095
500	11.617	65.256	10.015	15.953	6.973
600	12.159	67.425	9.884	17.148	6.246
700	12.546	69.248	9.716	18.348	5.755
800	12.820	71.024	9.516	19.548	5.429
900	13.024	72.546	9.282	20.743	5.209
1000	13.177	73.927	8.997	21.932	5.029
1100	13.295	75.189	8.667	23.118	4.874
1200	13.387	76.342	8.298	24.300	4.739
1300	13.460	77.424	7.892	25.478	4.619
1400	13.519	78.442	7.454	26.652	4.509
1500	13.568	79.398	6.997	27.822	4.404
1600	13.608	80.295	6.528	28.987	4.304
1700	13.640	81.132	6.054	29.147	4.209
1800	13.670	81.902	5.576	30.302	4.119
1900	13.694	82.584	5.094	31.452	4.034
2000	13.714	83.184	4.609	32.597	3.954
2100	13.732	83.724	4.122	33.737	3.879
2200	13.748	84.214	3.632	34.872	3.809
2300	13.761	84.654	3.139	35.992	3.744
2400	13.773	85.054	2.644	37.107	3.684
2500	13.784	85.414	2.149	38.217	3.629
2600	13.793	85.734	1.654	39.322	3.579
2700	13.802	86.014	1.159	40.422	3.534
2800	13.809	86.254	0.664	41.517	3.494
2900	13.816	86.454	0.169	42.607	3.459
3000	13.822	86.614	0.000	43.692	3.429
3100	13.828	86.734	-0.405	44.772	3.404
3200	13.833	86.814	-0.810	45.847	3.384
3300	13.838	86.854	-1.215	46.917	3.369
3400	13.842	86.864	-1.620	47.982	3.359
3500	13.846	86.844	-2.025	49.042	3.354
3600	13.849	86.794	-2.430	50.097	3.354
3700	13.852	86.714	-2.835	51.147	3.359
3800	13.855	86.594	-3.240	52.192	3.369
3900	13.858	86.434	-3.645	53.232	3.379
4000	13.861	86.234	-4.050	54.267	3.394
4100	13.863	85.994	-4.455	55.297	3.414
4200	13.865	85.714	-4.860	56.322	3.439
4300	13.867	85.384	-5.265	57.347	3.469
4400	13.869	84.994	-5.670	58.367	3.504
4500	13.871	84.544	-6.075	59.382	3.544
4600	13.873	84.034	-6.480	60.392	3.589
4700	13.875	83.464	-6.885	61.397	3.639
4800	13.876	82.834	-7.290	62.397	3.694
4900	13.877	82.144	-7.695	63.392	3.754
5000	13.879	81.394	-8.100	64.382	3.819
5100	13.880	80.584	-8.505	65.367	3.889
5200	13.881	79.714	-8.910	66.347	3.964
5300	13.882	78.784	-9.315	67.322	4.044
5400	13.883	77.794	-9.720	68.292	4.129
5500	13.884	76.744	-10.125	69.257	4.219
5600	13.885	75.634	-10.530	70.217	4.314
5700	13.886	74.464	-10.935	71.172	4.414
5800	13.887	73.234	-11.340	72.122	4.519
5900	13.888	71.944	-11.745	73.067	4.629
6000	13.889	70.594	-12.150	74.007	4.744

Dec. 31, 1962; Mar. 31, 1964

C. B. Colburn and P. A. Johnson, J. Chem. Phys. **33**, 1869 (1960), report the study of the dissociation reaction N₂F₄(g) = 2NF₂(g) by two independent methods: (a) measurement of the pressure variation with temperature at constant volume and (b) a spectrophotometric method based on the temperature dependence of the ultraviolet absorption of the NF₂ radical. The authors give a more detailed account of their data in J. Am. Chem. Soc. **83**, 3043 (1961). The contents of these articles indicate that 2NF₂(g) should read 2NF₂(g) in the above reaction. The first method gave a value of 19.85 kcal. mole⁻¹ for the heat of dissociation in the temperature range 373 to 423°K, which corresponds to 19.87 kcal. mole⁻¹ at 298°K. From their ΔH and ΔS data, ΔP was calculated and used in a third law evaluation of the heat of dissociation. The ΔH₂₉₈ so calculated showed an increasing trend with increasing temperature; the average value was 22.87 kcal. mole⁻¹ which is not in agreement with their value of 19.87 kcal. mole⁻¹. The spectrophotometric value of 21.7 kcal. mole⁻¹ at 298°K. was obtained from the integrated Van't Hoff equation.

L. H. Piette, P. A. Johnson, K. A. Boomer and C. B. Colburn, J. Chem. Phys. **35**, 1481 (1961), studied the temperature dependence of the EPR spectrum of the NF₂ radical. They obtained a second law value of 19.3 kcal. mole⁻¹ for the heat of dissociation. This value, however, depends upon the degree of dissociation of N₂F₄ which they calculated from the (dP/dT) measurements of Colburn and Johnson. Any error in the (dP/dT) measurements would manifest itself in like manner here.

H. E. Doornbos and B. R. Loy, J. Chem. Phys. **39**, 2393 (1963), investigated the ESR spectrum of the N₂F₄-NF₂ equilibrium from which they calculated a second law value of 19.8 kcal. mole⁻¹ for the heat of dissociation. They report that at 25°C. and 13 atm. N₂F₄ is 0.02% dissociated in the vapor phase. A third law calculation using this datum and the relationship $K_p = (4\alpha^2/\lambda - \alpha^2)P_0$, where α is the degree of dissociation of N₂F₄ and P₀ is the total pressure, gave a heat of dissociation of 21.79 kcal. mole⁻¹ at 298°K.; this is not in agreement with their second law value.

J. T. Herron and V. H. Dibel, J. Research Natl. Bur. Standards **65A**, 405 (1961), report thermal dissociation data for N₂F₄. From their data they calculate a second law value of 21.5 kcal. mole⁻¹ for the heat of dissociation of N₂F₄. A second and third law evaluation of their data was performed in the Dow Thermal Laboratory. It was found that if the k factor, relating their measured ion abundances to partial pressures, was taken as 4.72 X 10⁻⁹, a third law value was obtained that showed slight scatter but no temperature dependence. Excluding those points that showed scatter, the third law heat of dissociation at 298°K. was 22.27 kcal. mole⁻¹. A second law plot gave a heat value of 22.23 kcal. mole⁻¹ at an average temperature of 400°K. or 22.25 kcal. mole⁻¹ at 298°K. Those points that deviated from the chosen straight line in the second law plot showed corresponding deviations in the third law calculation. Those points lying on the second law slope gave a constant third law value.

The heat of dissociation for N₂F₄(g) = 2NF₂(g) was taken to be 22.26 kcal. mole⁻¹. Utilizing the heat of formation of N₂F₄(g) (see N₂F₄ table), the heat of formation of the difluoramine radical becomes 10.1 ± 2.0 kcal. mole⁻¹. All values for the heat of dissociation fall within the limits of error assigned to the heat of formation of NF₂.

Heat Capacity and Entropy.

See table on tetrafluorohydrazine (N₂F₄) (ideal gas) for writup.

DIFLUORODIAZINE, Cis-(N₂F₂)

(IDEAL GAS)

MOL. WT. = 66.0102

Point Group C_{2v}

$\Delta H_f^\circ = 17.9 \pm 1.2$ kcal. mole⁻¹

$\Delta H_f^\circ = 16.4 \pm 1.2$ kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
896 (1)	952 (1)
1524 (1)	573 (1)
552 (1)	737 (1)

Bond Distance: N-F = 1.384 Å N-N = 1.214 Å

Bond Angle: F-N-F = 114.5 ± 0.5°

Product of the Moments of Inertia: I_AI_BI_C = 6.585821 X 10⁻¹¹⁵ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation was derived from the heat of reaction $N_2F_2(g) + 8/3 NH_3(g) = 2NH_4F(c) + 4/3 N_2(g)$ which was measured calorimetrically by G. T. Armstrong and S. Marantz¹. There are two isomers, the trans and the active form of difluorodiazine. The heats of formation were determined to be 19.4 and 16.4 kcal. mole⁻¹ for the trans and the active isomers respectively. The active form of N₂F₂ has been interpreted here as the cis isomer which will be discussed later. The heat of isomerization has also been reported as 3.0 kcal. mole⁻¹ by Armstrong and Marantz. The value, ΔH_f° 298 (cis N₂F₂, g) = 16.4 kcal. mole⁻¹, is adopted in the tabulation.

A. V. Pankratov et al.² have measured the enthalpy of reaction $N_2F_2(g) + 3KI = 2KF + N_2 + KI_3$ in acidic solution (pH = 3), and reported ΔH_f° 298 (active N₂F₂, g) = 25.3 ± 2.0 kcal. mole⁻¹.

The "heat of isomerization" has been reported as 27.5 ± 5.0 kcal. mole⁻¹ by C. B. Colburn et al.⁹. The derivation of this value is unknown. The authors observed three values of the equilibrium constant for the isomerization reaction. Third law analysis of their data gives ΔH_f° 298 = 2.52 ± 0.05 kcal. mole⁻¹ for the reaction cis N₂F₂(g) → trans N₂F₂(g) which is in good agreement with Armstrong and Sidney's data.

Heat Capacity and Entropy.

Although the infrared spectrum^{7,8} of the active form of N₂F₂(g) has been interpreted as favoring the 1,1-difluorodiazine over the cis-configuration^{3,4}, n.m.r.⁵ and microwave studies definitely indicate the latter. The vibrational frequencies⁷ previously assigned to the 1,1-difluorodiazine have been adopted here for the cis isomer. The selected bond distances and angle were taken from the isotopic nitrogen microwave studies⁶. The principal moments of inertia were: I_A = 4.2438 X 10⁻³⁹, I_B = 10.5129 X 10⁻³⁹ and I_C = 14.7567 X 10⁻³⁹ g. cm.². See the trans N₂F₂(g) table for the comparison of the different physical properties between trans and cis isomers.

References:

- (1) G. T. Armstrong and S. Marantz, *J. Chem. Phys.* **35**, 169 (1963).
- (2) A. V. Pankratov, A. N. Zereninov, O. G. Talakin, O. M. Sokolov, and N. A. Knyazeva, *Zh. Fiz. Khim.* **37**, 1399 (1963).
- (3) R. Ettinger, F. A. Johnson, and C. B. Colburn, *J. Chem. Phys.* **34**, 2187 (1961).
- (4) J. T. Herron and V. H. Dibelor, *J. Res. Natl. Bur. Std.* **55A**, 405 (1961).
- (5) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.* **37**, 182 (1962).
- (6) R. L. Kuzkowski and E. B. Wilson, Jr., *J. Chem. Phys.* **39**, 1050 (1963).
- (7) R. H. Sanborn, *J. Chem. Phys.* **33**, 1855 (1960).
- (8) R. H. Sanborn, *J. Chem. Phys.* **35**, 2188 (1961).
- (9) C. B. Colburn, F. A. Johnson, K. Kennedy, K. McCallum, L. C. Metzger and C. O. Parker, *J. Am. Chem. Soc.* **81**, 6397 (1959).

Dec. 31, 1965

T. °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(H ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	2.725	17.857	17.857	INFINITE	INFINITE
100	8.454	51.781	17.857	1.000	16.739	22.887	-25.000	-25.000
200	9.644	71.787	17.857	1.000	16.739	22.887	-25.000	-25.000
298	11.941	82.071	17.857	1.000	16.739	22.887	-25.000	-25.000
300	12.145	82.071	17.857	1.022	16.739	26.043	-18.972	-18.972
400	13.980	85.867	17.857	1.321	16.227	26.290	-16.003	-16.003
500	15.306	88.124	17.857	1.785	16.181	32.562	-14.232	-14.232
600	16.318	89.214	17.857	2.436	16.221	35.837	-13.053	-13.053
700	17.053	90.060	17.857	3.039	16.312	39.100	-12.207	-12.207
800	17.595	90.702	17.857	3.513	16.437	42.345	-11.568	-11.568
900	18.002	91.183	17.857	3.883	16.583	45.576	-11.067	-11.067
1000	18.313	91.542	17.857	4.170	16.740	48.786	-10.662	-10.662
1100	18.555	91.809	17.857	4.392	16.904	51.985	-10.328	-10.328
1200	18.746	92.000	17.857	4.562	17.072	55.168	-10.047	-10.047
1300	18.900	92.150	17.857	4.692	17.240	58.336	-9.807	-9.807
1400	19.025	92.275	17.857	4.789	17.409	61.489	-9.598	-9.598
1500	19.127	92.381	17.857	4.856	17.576	64.633	-9.417	-9.417
1600	19.213	92.468	17.857	4.901	17.743	67.765	-9.256	-9.256
1700	19.284	92.539	17.857	4.930	17.906	70.887	-9.113	-9.113
1800	19.345	92.595	17.857	4.948	18.067	73.997	-8.984	-8.984
1900	19.397	92.638	17.857	4.958	18.227	77.103	-8.868	-8.868
2000	19.442	92.670	17.857	4.963	18.384	80.198	-8.763	-8.763
2100	19.481	92.692	17.857	4.965	18.538	83.281	-8.667	-8.667
2200	19.514	92.707	17.857	4.965	18.689	86.361	-8.579	-8.579
2300	19.542	92.717	17.857	4.965	18.838	89.434	-8.498	-8.498
2400	19.566	92.723	17.857	4.965	18.985	92.499	-8.423	-8.423
2500	19.585	92.726	17.857	4.965	19.127	95.560	-8.353	-8.353
2600	19.614	92.726	17.857	4.965	19.268	98.614	-8.289	-8.289
2700	19.632	92.723	17.857	4.965	19.406	101.667	-8.229	-8.229
2800	19.652	92.717	17.857	4.965	19.542	104.707	-8.172	-8.172
2900	19.664	92.709	17.857	4.965	19.676	107.752	-8.120	-8.120
3000	19.677	92.699	17.857	4.965	19.805	110.783	-8.070	-8.070
3100	19.690	92.685	17.857	4.965	19.933	113.810	-8.023	-8.023
3200	19.701	92.668	17.857	4.965	20.058	116.838	-7.979	-7.979
3300	19.711	92.648	17.857	4.965	20.179	119.862	-7.938	-7.938
3400	19.720	92.625	17.857	4.965	20.300	122.881	-7.898	-7.898
3500	19.729	92.600	17.857	4.965	20.416	125.896	-7.861	-7.861
3600	19.736	92.573	17.857	4.965	20.530	128.908	-7.825	-7.825
3700	19.744	92.544	17.857	4.965	20.642	131.920	-7.792	-7.792
3800	19.750	92.513	17.857	4.965	20.751	134.926	-7.760	-7.760
3900	19.756	92.480	17.857	4.965	20.857	137.928	-7.729	-7.729
4000	19.762	92.445	17.857	4.965	20.961	140.929	-7.700	-7.700
4100	19.767	92.409	17.857	4.965	21.062	143.926	-7.672	-7.672
4200	19.772	92.372	17.857	4.965	21.160	146.920	-7.645	-7.645
4300	19.777	92.334	17.857	4.965	21.257	149.918	-7.619	-7.619
4400	19.781	92.295	17.857	4.965	21.350	152.905	-7.594	-7.594
4500	19.785	92.255	17.857	4.965	21.439	155.885	-7.571	-7.571
4600	19.789	92.214	17.857	4.965	21.528	158.864	-7.548	-7.548
4700	19.792	92.172	17.857	4.965	21.613	161.844	-7.526	-7.526
4800	19.796	92.129	17.857	4.965	21.696	164.821	-7.505	-7.505
4900	19.799	92.085	17.857	4.965	21.775	167.800	-7.485	-7.485
5000	19.802	92.040	17.857	4.965	21.852	170.812	-7.466	-7.466
5100	19.804	92.000	17.857	4.965	21.927	173.784	-7.447	-7.447
5200	19.807	91.958	17.857	4.965	22.000	176.767	-7.429	-7.429
5300	19.809	91.915	17.857	4.965	22.068	179.743	-7.411	-7.411
5400	19.812	91.872	17.857	4.965	22.134	182.714	-7.394	-7.394
5500	19.814	91.830	17.857	4.965	22.197	185.680	-7.378	-7.378
5600	19.816	91.787	17.857	4.965	22.258	188.662	-7.363	-7.363
5700	19.818	91.744	17.857	4.965	22.315	191.634	-7.347	-7.347
5800	19.820	91.700	17.857	4.965	22.371	194.608	-7.333	-7.333
5900	19.822	91.656	17.857	4.965	22.423	197.571	-7.318	-7.318
6000	19.823	91.612	17.857	4.965	22.473	200.541	-7.304	-7.304

Di fluorodiazine, Trans-(N₂F₂)

(Ideal Gas) Mol. wt. = 66.0102

F₂N₂

MOL. WT. = 66.0102

(IDEAL GAS)

DI FLUORODIAZINE, Trans-(N₂F₂)

Point Group C_{2h}

$\Delta H_f^\circ = 20.7 \pm 1.2$ kcal. mole⁻¹

$\Delta H_f^\circ = 62.75$ cal. mole⁻¹ deg.⁻¹

$\Delta H_f^\circ = 298.15 = 19.4 \pm 1.2$ kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
1010 (1)	989 (1)
1686 (1)	421 (1)
592 (1)	360 (1)

Bond Distance: N-P = 1.44 Å N-N = 1.25 Å

Bond Angle: P-N-N = 115°

Product of the Moments of Inertia: $I_A I_B I_C = 432.6784 \times 10^{-117}$ g.³ cm.⁶

$\sigma = 2$

Heat of Formation.

G. T. Armstrong and S. Marentz, J. Chem. Phys. **39**, 169 (1963) have measured calorimetrically the enthalpy of reaction $N_2F_2(g) + 8/5 NH_3(g) = 2NH_4^+(c) + 4/5 N_2(g)$, and reported ΔH_f° 298 (trans N₂F₂, g) = 19.4 ± 1.2 kcal. mole⁻¹ which is adopted in this tabulation.

Heat Capacity and Entropy.

The bond distances and bond angle were obtained from S. H. Bauer, J. Am. Chem. Soc. **69**, 3104 (1947), by electron diffraction. The fundamental vibrational frequencies were obtained from R. H. Sanborn, J. Chem. Phys. **33**, 1855 (1960) by infrared spectroscopy. The three principal moments of inertia are $I_A = 0.919 \times 10^{-39}$, $I_B = 21.2433 \times 10^{-39}$ and $I_C = 22.1623 \times 10^{-39}$ g. cm.²

As pointed out by R. Ettinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. **34**, 2187 (1961), the trans N₂F₂ is the less active isomer which is different from the active isomer by its (1) vapor pressure (2) boiling point (3) heat of vaporization (4) critical temperature (5) melting point (6) mass spectral cracking pattern (7) NMR spectrum (8) infrared spectrum (9) heat of isomerization (10) reactivity with mercury and glass.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	20.659	∞	∞
100	8.453	51.506	2.423	20.659	22.813	∞
200	10.774	58.062	6.860	20.659	25.733	-49.856
298	12.779	62.752	11.660	20.659	28.118	-28.118
300	12.832	62.832	11.660	20.659	28.118	-28.118
400	14.392	66.744	13.87	20.659	32.006	-21.096
500	15.583	70.090	16.289	20.659	35.186	-15.379
600	16.473	73.014	18.494	20.659	38.362	-13.973
700	17.139	75.428	20.494	20.659	41.538	-12.569
800	17.661	77.428	22.216	20.659	44.714	-11.165
900	18.026	79.029	23.661	20.659	47.890	-9.761
1000	18.323	81.945	25.846	20.659	51.066	-8.357
1100	18.568	85.702	28.763	20.659	54.242	-6.953
1200	18.724	89.932	32.416	20.659	57.418	-5.549
1300	18.895	94.661	36.806	20.659	60.594	-4.145
1400	19.019	99.912	41.941	20.659	63.770	-2.741
1500	19.121	105.683	47.836	20.659	66.946	-1.337
1600	19.206	111.976	54.491	20.659	70.122	0.067
1700	19.277	118.792	61.906	20.659	73.298	1.471
1800	19.338	126.040	70.081	20.659	76.474	2.875
1900	19.390	133.728	79.016	20.659	79.650	4.279
2000	19.435	141.865	88.721	20.659	82.826	5.683
2100	19.474	150.461	99.296	20.659	86.002	7.087
2200	19.508	159.517	110.741	20.659	89.178	8.491
2300	19.538	169.034	123.066	20.659	92.354	9.895
2400	19.565	179.011	136.281	20.659	95.530	11.299
2500	19.588	189.447	150.496	20.659	98.706	12.703
2600	19.609	200.343	165.711	20.659	101.882	14.107
2700	19.628	211.699	182.026	20.659	105.058	15.511
2800	19.645	223.516	199.441	20.659	108.234	16.915
2900	19.660	235.792	217.956	20.659	111.410	18.319
3000	19.673	248.528	237.571	20.659	114.586	19.723
3100	19.686	261.724	258.286	20.659	117.762	21.127
3200	19.697	275.380	279.101	20.659	120.938	22.531
3300	19.707	289.495	300.016	20.659	124.114	23.935
3400	19.717	304.069	321.031	20.659	127.290	25.339
3500	19.726	319.104	342.146	20.659	130.466	26.743
3600	19.733	334.609	363.361	20.659	133.642	28.147
3700	19.741	350.584	384.676	20.659	136.818	29.551
3800	19.748	366.929	406.091	20.659	140.000	30.955
3900	19.754	383.644	427.606	20.659	143.182	32.359
4000	19.760	400.729	449.221	20.659	146.364	33.763
4100	19.765	418.184	470.936	20.659	149.546	35.167
4200	19.770	436.009	492.751	20.659	152.728	36.571
4300	19.775	454.194	514.666	20.659	155.910	37.975
4400	19.779	472.739	536.681	20.659	159.092	39.379
4500	19.783	491.644	558.796	20.659	162.274	40.783
4600	19.787	510.909	580.911	20.659	165.456	42.187
4700	19.791	530.534	603.026	20.659	168.638	43.591
4800	19.794	550.519	625.141	20.659	171.820	44.995
4900	19.797	570.854	647.256	20.659	175.002	46.399
5000	19.800	591.539	669.371	20.659	178.184	47.803
5100	19.803	612.574	691.486	20.659	181.366	49.207
5200	19.805	633.969	713.601	20.659	184.548	50.611
5300	19.808	655.714	735.716	20.659	187.730	52.015
5400	19.810	677.809	757.831	20.659	190.912	53.419
5500	19.813	699.254	779.946	20.659	194.094	54.823
5600	19.815	721.049	802.061	20.659	197.276	56.227
5700	19.817	743.194	824.176	20.659	200.458	57.631
5800	19.819	765.689	846.291	20.659	203.640	59.035
5900	19.820	788.534	868.406	20.659	206.822	60.439
6000	19.822	811.729	890.521	20.659	210.004	61.843

F₂N₂

Sodium Difluoride Uninegative Ion (NaF₂⁻)

(Ideal Gas) GFW = 60.98715

T, °K	C _p ^o	S ^o	-(G ^o -H ^o)/T	H ^o -H ²⁹⁸	kcal/mol ΔH ^o	Log Kp
0	13.112	59.095	59.095	.000	-160.000	116.005
100	13.126	59.066	59.065	.024	-156.245	115.281
200	13.140	59.040	59.040	.137	-151.713	114.601
300	13.154	59.014	59.014	.269	-146.405	113.960
400	13.168	58.988	58.988	.419	-140.324	113.356
500	13.182	58.962	58.962	.586	-133.467	112.786
600	13.196	58.936	58.936	.769	-125.736	112.246
700	13.210	58.910	58.910	.966	-117.126	111.736
800	13.224	58.884	58.884	1.177	-107.636	111.256
900	13.238	58.858	58.858	1.400	-97.266	110.806
1000	13.252	58.832	58.832	1.644	-86.006	110.386
1100	13.266	58.806	58.806	1.908	-73.846	109.996
1200	13.280	58.780	58.780	2.192	-60.786	109.636
1300	13.294	58.754	58.754	2.496	-46.826	109.306
1400	13.308	58.728	58.728	2.819	-31.866	108.996
1500	13.322	58.702	58.702	3.161	-15.906	108.706
1600	13.336	58.676	58.676	3.522	0.054	108.436
1700	13.350	58.650	58.650	3.902	16.094	108.186
1800	13.364	58.624	58.624	4.301	32.234	107.956
1900	13.378	58.598	58.598	4.719	48.464	107.746
2000	13.392	58.572	58.572	5.156	64.784	107.556
2100	13.406	58.546	58.546	5.612	81.184	107.386
2200	13.420	58.520	58.520	6.087	97.654	107.236
2300	13.434	58.494	58.494	6.581	114.184	107.106
2400	13.448	58.468	58.468	7.094	130.764	106.996
2500	13.462	58.442	58.442	7.626	147.384	106.906
2600	13.476	58.416	58.416	8.177	164.034	106.836
2700	13.490	58.390	58.390	8.747	180.704	106.786
2800	13.504	58.364	58.364	9.336	197.384	106.756
2900	13.518	58.338	58.338	9.944	214.064	106.736
3000	13.532	58.312	58.312	10.571	230.734	106.726
3100	13.546	58.286	58.286	11.217	247.384	106.726
3200	13.560	58.260	58.260	11.881	264.004	106.736
3300	13.574	58.234	58.234	12.563	280.584	106.756
3400	13.588	58.208	58.208	13.264	297.114	106.786
3500	13.602	58.182	58.182	13.984	313.584	106.836
3600	13.616	58.156	58.156	14.723	330.004	106.906
3700	13.630	58.130	58.130	15.481	346.364	106.996
3800	13.644	58.104	58.104	16.258	362.664	107.106
3900	13.658	58.078	58.078	17.054	378.894	107.236
4000	13.672	58.052	58.052	17.869	395.044	107.386
4100	13.686	58.026	58.026	18.703	411.104	107.556
4200	13.700	57.999	57.999	19.556	427.064	107.746
4300	13.714	57.973	57.973	20.428	442.924	107.956
4400	13.728	57.947	57.947	21.319	458.674	108.186
4500	13.742	57.921	57.921	22.229	474.304	108.436
4600	13.756	57.895	57.895	23.158	489.804	108.706
4700	13.770	57.869	57.869	24.106	505.164	108.996
4800	13.784	57.843	57.843	25.073	520.384	109.306
4900	13.798	57.817	57.817	26.058	535.454	109.636
5000	13.812	57.791	57.791	27.061	550.374	109.996
5100	13.826	57.765	57.765	28.082	565.134	110.386
5200	13.840	57.739	57.739	29.121	579.734	110.806
5300	13.854	57.713	57.713	30.178	594.174	111.256
5400	13.868	57.687	57.687	31.252	608.444	111.736
5500	13.882	57.661	57.661	32.343	622.534	112.246
5600	13.896	57.635	57.635	33.451	636.444	112.786
5700	13.910	57.609	57.609	34.576	650.164	113.356
5800	13.924	57.583	57.583	35.718	663.694	113.960
5900	13.938	57.557	57.557	36.877	677.024	114.601
6000	13.952	57.531	57.531	38.052	690.154	115.281

Dec. 31, 1968

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
[400] (1)
[170] (2)
[650] (1)

σ = [2]

Bond Distance: Na-F = [1.93] Å

Bond Angle: F-Na-F = [180°]

Rotational Constant: B₀ = [0.119] cm⁻¹

Heat of Formation

The heat of formation for NaF₂⁻(g) is estimated from three calculated values. The methods of calculation are described as follows. The first reaction we take into consideration is NaF(g) + F⁻(g) + Na₂⁻(g). In a manner analogous to LiF₂⁻(g) molecule (see LiF₂⁻(g) table for details), we assume NaF₂⁻(g) is stable and ΔH_F²⁹⁸ for the reaction NaF(g) + F⁻(g) = NaF₂⁻(g) is somewhere between 0 to 1/2(-64) = -32 kcal/mol where the value -56 kcal/mol is the heat of dimerization. Based on ΔH_F²⁹⁸ = 0 and -28 kcal/mol, respectively, with JANAF ΔH_F²⁹⁸ values for the species involved, we obtain ΔH_F²⁹⁸(NaF₂⁻, g) = -132 and -164 kcal/mol as the upper and lower limits.

The heat of formation, calculated based on the reaction NaF₂⁻(g) = NaF₂(g) + e⁻(g), is -165.8 kcal/mol, using ΔH_F²⁹⁸ and ΔH_F²⁹⁸(NaF₂, g) estimated as 83.5 and -82.3 kcal/mol, respectively. The ΔH_F²⁹⁸ value is obtained from an assumption that the enthalpy change for removing an electron from NaF₂⁻(g) is comparable to that from F⁻(g). Due to the fact that the Na atom has smaller electronegativity (0.9) than that of the F atom (4.0), we expect that there is less possibility that the electron will associate with Na atom in the NaF₂⁻ molecule. Therefore we adopt the electron affinity of F(g) reported by H. O. Pritchard, Chem. Rev. 52, 529 (1953), or ΔH_F²⁹⁸ = 83.5 kcal/mol for the reaction F⁻(g) = F(g) + e⁻(g) as the ΔH_F²⁹⁸ for NaF₂⁻(g) = NaF₂(g) + e⁻(g). The value of ΔH_F²⁹⁸ for NaF₂(g) is calculated using the enthalpy change for the reaction NaF₂(g) = NaF₂⁻(g) + Na(g) as 145.8 kcal/mol which is derived from the sum of two enthalpy changes, namely, half of the ΔH_F²⁹⁸ value for the dimer dissociation reaction Na₂F₂(g) = 2NaF(g), and the ΔH_F²⁹⁸ for the monomer dissociation reaction NaF(g) = Na(g) + F(g).

Employing ΔH_F²⁹⁸ = 83.5 kcal/mol for NaF₂(g) and 153.0 kcal/mol for NaF₂⁻(g) = Na⁺(g) + F⁻(g), we estimate ΔH_F²⁹⁸ = 1/2(83.5) + 153.0 = 184.7 kcal/mol for the reaction Na₂F₂(g) = NaF₂(g) + Na⁺(g), which leads to ΔH_F²⁹⁸ = 183.4 kcal/mol for NaF₂⁻(g). For all calculations the ΔH_F²⁹⁸ values of the chemical species involved are taken from JANAF Thermochemical Tables.

The value of ΔH_F²⁹⁸ for NaF₂⁻(g) is tentatively adopted as -160 ± 10 kcal/mol.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion by A. D. Walsh, J. Chem. Soc. 1953, 2266 (1953) that molecules with not more than 16 valence electrons are linear in their ground state. The Na-F bond distance is estimated by comparison with that of NaF(g) reported by S. E. Veazy and W. Gordy, Phys. Rev. 138, A1303 (1965). The vibrational frequencies are estimated from those for the isoelectronic molecule SiO₂(g). The moment of inertia is 2.380 × 10⁻³⁸ gm². The enthalpy at 0°K is -3.117 kcal/mol.

Sodium Fluoride, Dimeric (Na₂F₂)
(Ideal Gas)

GFW = 83.9764

SODIUM FLUORIDE, DIMERIC (Na₂F₂)

(IDEAL GAS)

GFW = 83.9764

Point Group [D_{2h}] $\Delta H_f^\circ = [-200.8 \pm 3] \text{ kcal/mol}$ $S_{298.15}^\circ = [68.7 \pm 4] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-202.3 \pm 3] \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies
 $\frac{\omega_e}{\text{cm}^{-1}}$

$\frac{\omega_e}{\text{cm}^{-1}}$	Degeneracy
[420] (1)	[200] (1)
[400] (1)	[425] (1)
[350] (1)	[500] (1)

Bond Distance: Na-F = 2.02 Å

Bond Angle: Na-F-Na = [85°]

Product of the Moments of Inertia: $I_{A,B,C} = [5.6135 \times 10^{-114}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

Although the absolute values of the vapor pressure measurements are not used for evaluation, the ratios of the numbers of dimeric and monomeric NaF molecules that effuse from the oven at the temperatures 1115 - 1191°K determined by Eisenstadt, Rothberg, and Kusch (1) by use of the electron-beam velocity-selector method are used. Based on the reported equilibrium data we evaluate the enthalpy change of the reaction $(A) \text{ Na}_2\text{F}_2(g) = 2\text{NaF}(g)$ by the second and third law methods. The results are presented in the table below.

Porter and Schoonmaker (2) analyzed the vapor effusing from a Knudsen cell at 1121°K mass spectrometrically and derived the partial pressures of NaF(g) and Na₂F₂(g) at that temperature. Using these reported partial pressures we calculate, by the third law method, the value $\Delta H_{298}^\circ = 64.1 \text{ kcal/mol}$ for reaction (A).

Sidorov et al. (3) studied the NaF - ZrF₄ system by the mass spectrometric method and derived the partial pressures of NaF(g) and Na₂F₂(g) as a function of composition and temperature. Employing the data points reported at 1074° and 1167°K we obtain the third law value $\Delta H_{298}^\circ = 62.0 \pm 1.6 \text{ kcal/mol}$ for the same reaction.

The ΔH_{298}° (Na₂F₂, g) is calculated based on the adopted third law value $\Delta H_{298}^\circ = 63.5 \text{ kcal/mol}$ for the reaction $\text{Na}_2\text{F}_2(g) = 2\text{NaF}(g)$, using ΔH_{298}° (NaF, g) = -69.5 kcal/mol. Brewer and Brackett (3) reported $\Delta H_{1000}^\circ = 56.9 \text{ kcal/mol}$ for the above reaction. According to our tables the ΔH_{1000}° value is 62.5 kcal/mol.

Investigator	Temperature, °K	No. of Points	ΔH_{298}° , kcal/mol	Drift, kcal/mol	ΔH_{298}° , kcal/mol
1. Eisenstadt et al. (1958)	1115 - 1191	6	58.1 ± 2.9	4.7 ± 2.5	-202.4
2. Porter and Schoonmaker (1958)	1121	1	64.1	—	-203.0
3. Sidorov et al. (1964)	1074 - 1167	8	62.0 ± 1.6	—	-200.9

Heat Capacity and Entropy

The Na₂F₂ molecule is assumed to have a rhombic structure with D_{2h} (h) symmetry (4, 5). The Na-F bond distance is reported by Akishin and Rambidi (5), who studied the molecular structure of alkali halide vapors by electron diffraction with sector microphotometry. The bond angle is estimated by comparison with those of the other alkali halides. Berkowitz (4, 6) has calculated the vibration frequencies of Na₂F₂ based on an ionic model. By comparison of the calculated frequencies of Li₂F₂ (g) with those of the observed ones (see Li₂F₂(g) table for details) we reestimate the vibrational frequencies for Na₂F₂(g) to be higher than the ones reported by Berkowitz (5). Bauer et al. (7) used a pseudo-electrostatic model, similar to the one suggested by O'Konski and Higuchi (8), to calculate the entropies of dimerization for a number of gaseous alkali halides and estimated the six vibrational frequencies as 477, 318, 291, 477, 291, and 291 cm⁻¹. Bauer et al. calculated $\Delta S_{1146}^\circ = -32.5 \text{ eu}$ for the reaction $2\text{NaF}(g) = \text{Na}_2\text{F}_2(g)$, in reasonable agreement with the value -33.5 eu which is derived using JANAF Silus values for NaF(g) and Na₂F₂(g).

The three principal moments of inertia are: $I_A = 1.399 \times 10^{-38}$, $I_B = 1.422 \times 10^{-38}$, and $I_C = 2.821 \times 10^{-38} \text{ g cm}^2$.

References

1. M. Eisenstadt, G. M. Rothberg, and P. Kusch, J. Chem. Phys. **28**, 787 (1958).
2. R. F. Porter and R. C. Schoonmaker, J. Chem. Phys. **28**, 1070 (1958).
3. L. N. Sidorov, P. A. Akishin, V. I. Balousov, and V. V. Shol'ts, Russ. J. Phys. Chem. (English Transl.) **38**, 641 (1964).
4. J. Berkowitz, J. Chem. Phys. **29**, 1306 (1958).
5. P. A. Akishin and N. G. Rambidi, Z. Physik. Chem. **213**, 111 (1960).
6. J. Berkowitz, J. Chem. Phys. **32**, 1513 (1960).
7. S. H. Bauer, R. M. Diner, and R. F. Porter, J. Chem. Phys. **29**, 991 (1958).
8. C. T. O'Konski and W. I. Higuchi, J. Chem. Phys. **23**, 1175 (1955).
9. L. Brewer and E. Brackett, Chem. Rev. **53**, 425 (1961).

June 30, 1964; Dec. 31, 1968

GTW = 53.9962

(IDEAL GAS)

OXYGEN DIFLUORIDE (F₂O)Point Group C_{2v} $\Delta H_f^\circ = 6.40 \pm 0.38$ kcal/mol $\Delta H_f^\circ = 59.12 \pm 0.1$ gibbs/mol

Ground State Quantum Weight = [1]

Oxygen Difluoride (F₂O)

GTW = 53.9962

(Ideal Gas)

T, °K	C _p ^a	gibbs/mol S ^b - (C _p ^a - H ^o)/T	H ^o - H ³⁰⁰ kcal/mol ΔH_f°	ΔG_f°	Log K _p
0	0.000	INFINITE	4.404	7.359	INFINITE
100	4.066	40.343	4.457	7.359	16.083
200	9.095	55.249	6.025	8.643	9.445
298	10.349	59.118	7.318	9.984	7.318
300	10.371	59.182	7.320	10.000	7.292
400	12.037	62.327	8.536	11.400	6.229
500	12.661	64.928	9.631	12.794	5.592
600	12.824	67.170	10.614	14.166	5.167
700	12.861	69.293	11.483	15.575	4.863
800	12.885	71.298	12.264	16.937	4.623
900	12.900	73.205	12.982	18.261	4.438
1000	12.908	75.000	13.642	19.552	4.308
1100	12.913	76.692	14.254	20.815	4.199
1200	12.916	78.284	14.820	22.056	4.090
1300	12.918	79.789	15.348	23.282	3.985
1400	12.919	81.210	15.835	24.496	3.885
1500	12.920	82.558	16.281	25.698	3.790
1600	12.921	83.834	16.693	26.888	3.701
1700	12.922	85.040	17.070	28.067	3.618
1800	12.923	86.180	17.414	29.237	3.541
1900	12.924	87.256	17.725	30.398	3.469
2000	12.925	88.270	18.013	31.552	3.402
2100	12.926	89.224	18.278	32.699	3.340
2200	12.927	90.120	18.521	33.840	3.282
2300	12.928	90.958	18.744	34.976	3.228
2400	12.929	91.739	18.948	36.108	3.179
2500	12.930	92.464	19.134	37.237	3.134
2600	12.931	93.134	19.302	38.363	3.093
2700	12.932	93.749	19.454	39.486	3.055
2800	12.933	94.310	19.592	40.607	3.021
2900	12.934	94.818	19.717	41.725	2.990
3000	12.935	95.274	19.830	42.840	2.962
3100	12.936	95.679	19.931	43.952	2.938
3200	12.937	96.034	20.021	45.061	2.918
3300	12.938	96.340	20.100	46.167	2.899
3400	12.939	96.598	20.169	47.271	2.882
3500	12.940	96.809	20.228	48.373	2.867
3600	12.941	96.974	20.278	49.473	2.853
3700	12.942	97.095	20.319	50.571	2.840
3800	12.943	97.173	20.352	51.667	2.828
3900	12.944	97.208	20.378	52.761	2.817
4000	12.945	97.200	20.397	53.853	2.807
4100	12.946	97.158	20.410	54.944	2.798
4200	12.947	97.084	20.418	56.034	2.790
4300	12.948	96.979	20.421	57.123	2.783
4400	12.949	96.845	20.420	58.211	2.777
4500	12.950	96.682	20.415	59.299	2.772
4600	12.951	96.491	20.407	60.387	2.768
4700	12.952	96.274	20.396	61.474	2.764
4800	12.953	96.034	20.382	62.561	2.761
4900	12.954	95.772	20.365	63.648	2.758
5000	12.955	95.491	20.346	64.735	2.756
5100	12.956	95.191	20.315	65.822	2.754
5200	12.957	94.874	20.273	66.909	2.753
5300	12.958	94.542	20.221	67.996	2.752
5400	12.959	94.196	20.160	69.083	2.751
5500	12.960	93.837	20.090	70.170	2.750
5600	12.961	93.466	20.012	71.257	2.750
5700	12.962	93.084	19.927	72.344	2.750
5800	12.963	92.692	19.835	73.431	2.750
5900	12.964	92.291	19.737	74.518	2.750
6000	12.965	91.881	19.633	75.605	2.750

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1964; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

 ω_e, cm^{-1}

928 (1)

461 (1)

831 (1)

Bond Distance: F-O = 1.412 Å

Bond Angle: F-O-F = 103°10'

Product of the Moments of Inertia: $I_A I_B I_C = 1.01936 \times 10^{-115} \text{ g cm}^2$ $\sigma = 2$

Heat of Formation

King and Armstrong (1) have established the heat of formation with a series of reactions in a flame calorimeter. They burned F₂O in hydrogen to give HF aqueous, in addition they burned F₂ in hydrogen so that the heat of formation, 5.86 kcal/mol, is directly obtainable. This value is in good agreement with the recalculated values (1) from Wartenberg and Klinkott (2), 5.7 ± 2 kcal/mol, and Ruff and Menzel (3), 4.7 ± 2 kcal/mol but differs from that of Bisbee et al. (4), -4.06 ± 2.2 kcal/mol. There were several factors in the experiments of Bisbee that might cause a too negative heat of formation and we choose to adopt the definitive value of 5.86 kcal/mol reported by King and Armstrong.

Heat Capacity and Entropy

The structural parameters are those reported by Pierce et al. (5) for the average ground state molecule from the microwave spectrum. Earlier measurements of Hilton et al. (6) disagree but according to Pierce et al. (7) the line assignments used by Hilton are incorrect. The vibrational frequencies were reported by Jones et al. (8), several other investigators report similar values (9, 10, 11). Nebgen et al. (12) have obtained the anharmonic constants for the three vibrations. Individual moments of inertia are $I_A = 1.4396 \times 10^{-39}$, $I_B = 7.7255 \times 10^{-39}$ and $I_C = 9.1651 \times 10^{-39} \text{ g cm}^2$.

References

1. R. C. King and G. T. Armstrong, J. Research. Natl. Bur. Std. 72A, 113 (1968).
2. H. Wartenberg and G. Z. Klinkott, Z. Anorg. Chem. 193, 409 (1930).
3. O. Ruff and W. Menzel, Z. Anorg. Chem. 190, 257 (1930).
4. W. R. Bisbee, J. V. Hamilton, R. Rushworth, T. J. Houser, and J. M. Gerhauser, Advan. Chem. Ser. 54, 215 (1965).
5. L. Pierce, N. DiGianni and R. H. Jackson, J. Chem. Phys. 38, 730 (1963).
6. A. R. Hilton, A. W. Jache, J. B. Beal, W. D. Henderson and R. J. Robinson, J. Chem. Phys. 24, 1137 (1956).
7. L. Pierce, R. H. Jackson and N. DiGianni, J. Chem. Phys. 35, 2240 (1961).
8. E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielsen, J. Chem. Phys. 18, 685 (1950).
9. H. J. Bernstein and J. P. Fowling, J. Chem. Phys. 18, 685 (1950).
10. G. Hettner, R. Pohlman, and H. J. Schumacher, Z. Physik. 95, 203 (1935).
11. G. B. M. Sutherland and W. G. Penney, Proc. Roy. Soc. (London) 158A, 678 (1936).
12. J. W. Nebgen, F. I. Metz and W. B. Rose, J. Mol. Spectry. 21, 99 (1966).

Thionyl Difluoride (SO₂F₂)

(Ideal Gas) Mol. Wt. = 86.0602

T. °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	0.000	INFINITE	-3.063	-133.862	-133.862	INFINITE
100	8.650	55.063	77.606	-2.254	-134.269	-133.334	-133.334	201.386
200	11.515	61.114	86.160	-1.246	-134.697	-132.224	-132.224	144.480
298	14.833	66.985	90.985	0.000	-135.000	-130.941	-130.941	95.976
300	13.870	67.051	66.965	0.26	-135.005	-130.916	-130.916	95.367
400	15.508	71.280	67.531	1.500	-135.755	-129.497	-129.497	70.750
500	16.622	74.868	68.649	3.110	-136.256	-127.873	-127.873	55.890
600	17.389	77.971	69.980	4.813	-136.619	-126.160	-126.160	45.951
700	17.928	80.694	71.294	6.580	-136.892	-124.369	-124.369	38.828
800	18.317	83.115	72.623	8.393	-137.109	-122.535	-122.535	33.828
900	18.605	85.290	73.912	10.240	-137.283	-120.650	-120.650	29.272
1000	18.821	87.262	75.150	12.112	-137.420	-118.720	-118.720	25.630
1100	18.989	89.064	76.334	14.003	-137.526	-116.754	-116.754	22.654
1200	19.120	90.722	77.445	15.908	-137.604	-114.759	-114.759	20.175
1300	19.224	92.257	78.544	17.826	-137.658	-112.746	-112.746	18.079
1400	19.309	93.684	79.575	19.753	-137.692	-110.724	-110.724	16.285
1500	19.378	95.019	80.561	21.687	-137.702	-108.698	-108.698	14.732
1600	19.435	96.271	81.504	23.628	-137.698	-106.668	-106.668	13.373
1700	19.483	97.451	82.408	25.574	-137.682	-104.635	-104.635	12.176
1800	19.524	98.566	83.275	27.524	-137.654	-102.601	-102.601	11.113
1900	19.559	99.623	84.108	29.478	-137.616	-100.568	-100.568	10.163
2000	19.588	100.627	84.909	31.436	-137.568	-98.536	-98.536	9.308
2100	19.614	101.580	85.680	33.396	-137.513	-96.502	-96.502	8.536
2200	19.637	102.496	86.424	35.358	-137.452	-94.468	-94.468	7.834
2300	19.656	103.369	87.142	37.323	-137.386	-92.435	-92.435	7.194
2400	19.674	104.206	87.836	39.290	-137.316	-90.402	-90.402	6.607
2500	19.690	105.010	88.507	41.258	-137.242	-88.370	-88.370	6.068
2600	19.703	105.782	89.156	43.227	-137.164	-86.337	-86.337	5.571
2700	19.715	106.526	89.786	45.198	-137.082	-84.304	-84.304	5.111
2800	19.726	107.243	90.397	47.170	-137.000	-82.272	-82.272	4.684
2900	19.735	107.935	90.980	49.143	-136.918	-80.240	-80.240	4.286
3000	19.744	108.605	91.566	51.117	-136.836	-78.208	-78.208	3.916
3100	19.752	109.252	92.126	53.092	-136.754	-76.176	-76.176	3.570
3200	19.760	109.879	92.671	55.068	-136.672	-74.144	-74.144	3.245
3300	19.766	110.488	93.202	57.044	-136.590	-72.112	-72.112	2.941
3400	19.772	111.078	93.719	59.021	-136.508	-70.080	-70.080	2.654
3500	19.778	111.651	94.223	60.998	-136.426	-68.048	-68.048	2.384
3600	19.783	112.208	94.715	62.977	-136.344	-66.016	-66.016	2.128
3700	19.788	112.750	95.195	64.955	-136.262	-63.984	-63.984	1.887
3800	19.792	113.278	95.664	66.934	-136.180	-61.952	-61.952	1.659
3900	19.796	113.797	96.122	68.914	-136.100	-59.920	-59.920	1.443
4000	19.800	114.294	96.570	70.893	-136.020	-57.888	-57.888	1.237
4100	19.804	114.782	97.008	72.874	-135.940	-55.856	-55.856	1.041
4200	19.807	115.260	97.437	74.854	-135.860	-53.824	-53.824	0.855
4300	19.810	115.726	97.857	76.835	-135.780	-51.792	-51.792	0.678
4400	19.813	116.181	98.269	78.816	-135.700	-49.760	-49.760	0.508
4500	19.815	116.627	98.672	80.797	-135.620	-47.728	-47.728	0.347
4600	19.818	117.062	99.067	82.779	-135.540	-45.696	-45.696	0.192
4700	19.820	117.488	99.454	84.761	-135.460	-43.664	-43.664	0.044
4800	19.822	117.906	99.834	86.743	-135.380	-41.632	-41.632	0.000
4900	19.824	118.314	100.207	88.725	-135.300	-39.600	-39.600	0.000
5000	19.826	118.715	100.573	90.708	-135.220	-37.568	-37.568	0.000
5100	19.828	119.108	100.933	92.691	-135.140	-35.536	-35.536	0.000
5200	19.830	119.493	101.286	94.673	-135.060	-33.504	-33.504	0.000
5300	19.831	119.870	101.633	96.656	-134.980	-31.472	-31.472	0.000
5400	19.833	120.241	101.974	98.640	-134.900	-29.440	-29.440	0.000
5500	19.834	120.605	102.310	100.623	-134.820	-27.408	-27.408	0.000
5600	19.835	120.962	102.640	102.606	-134.740	-25.376	-25.376	0.000
5700	19.837	121.313	102.964	104.590	-134.660	-23.344	-23.344	0.000
5800	19.838	121.658	103.284	106.574	-134.580	-21.312	-21.312	0.000
5900	19.839	121.998	103.598	108.558	-134.500	-19.280	-19.280	0.000
6000	19.840	122.331	103.907	110.542	-134.420	-17.248	-17.248	0.000

Dec. 31, 1960, Sept. 30, 1965

Thionyl Difluoride (SO₂F₂)

(Ideal Gas) MOL. WT. = 86.0602

Point Group C_{2v}
 $\Delta H_f^o = 66.965 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = [-134 \pm 10] \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = [-135 \pm 10] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies	ω , cm. ⁻¹	ω , cm. ⁻¹
	1308 (1)	395 (1)
	801 (1)	721 (1)
	526 (1)	326 (1)

Bond Distances: O-S = 1.412 Å S-F = 1.585 Å
 Bond Angle: O-S-F = 106° 49' F-S-F = 92° 49'
 Product of the Moments of Inertia: I_AI_BI_C = 1.65545 X 10⁻¹¹⁴ g.³ cm.⁶
 $\sigma = 1$

Heat of Formation.

From the enthalpy change, $\Delta H_f^o = 131.03 \text{ kcal. mole}^{-1}$, for the reaction $\text{SO}_2(\text{g}) + \text{O}(\text{g})$, the value of ΔH_f^o for $\text{SO}_2(\text{g})$ was calculated to be -133.5 kcal. mole⁻¹, using $\Delta H_f^o = -203.0$ and 59.56 kcal. mole⁻¹ for $\text{SO}_2(\text{g})$ and $\text{O}(\text{g})$, respectively. The value of ΔH_f^o for $\text{SO}_2(\text{g})$ was assumed to be the same as that for the reaction $\text{SO}_2(\text{g}) = \text{SO}(\text{g}) + \text{O}(\text{g})$ which was calculated based on $\Delta H_f^o = -70.95$, 0.52 and 59.56 kcal. mole⁻¹ for $\text{SO}_2(\text{g})$, $\text{SO}(\text{g})$ and $\text{O}(\text{g})$, respectively. Using $\Delta H_f^o = 127.86 \text{ kcal. mole}^{-1}$ for the reaction $\text{SO}_2(\text{g}) = \text{SO}_2(\text{g}) + \text{O}(\text{g})$, the value of ΔH_f^o for $\text{SO}_2(\text{g})$ was calculated to be -136.7 kcal. mole⁻¹ where the ΔH_f^o for $\text{SO}_2(\text{g})$ was assumed to be the same as the S-O bond energy in $\text{SO}_2(\text{g})$. The value of ΔH_f^o for $\text{SO}_2(\text{g})$ adopted is -135 ± 10 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond distances and angles were obtained from R. C. Ferguson, J. Am. Chem. Soc. 76, 850 (1954). The vibrational frequencies were taken from R. J. Gillespie and E. A. Robinson, Can. J. Chem. 39, 2171 (1961). The assignment of these vibrational frequencies was based on the previous measurements of the infrared and Raman spectra reported by J. K. O'Loane and M. K. Wilson, J. Chem. Phys. 23, 1313 (1955), P. Bender and J. M. Wood, J. Chem. Phys. 23, 1316 (1955) and D. M. Vost, Proc. Indian Acad. Sci. B, 333 (1958). The fundamental assignment reported by J. K. O'Loane and M. K. Wilson, loc. cit., was 1333, 808, 530, (410), 748 and 390 cm.⁻¹. The three principal moments of inertia are: I_A = 1.0034 X 10⁻³⁸, I_B = 9.7421 X 10⁻³⁹ and I_C = 1.6935 X 10⁻³⁸ g. cm.².

The heat capacities of thionyl fluoride (SO_2F_2) have been measured, from 12° to 230°K., by E. L. Pace and B. P. Turnbull, J. Chem. Phys. 43, 1953 (1965), for a sample of 99.97% mole % purity. Incorporating them with the measured ΔH_f^o of 1.506 kcal. mole⁻¹ at T₀ = 143.25°K. and ΔH_f^o of 5.091 kcal. mole⁻¹ at T₀ = 228.84°K., which was derived from the measured vapor pressure of SO_2F_2 (l), the entropy of SO_2F_2 (g) at 228.84°K. was evaluated as 63.56 e.u. This value is in excellent agreement with the corresponding value, 63.522 e.u., calculated using the adopted molecular constants. This indicates the fact that the molecular constants used for the calculation of the tabulated thermodynamic functions are adequate. Hence the new vibrational frequencies suggested by Pace and Turnbull, loc. cit., were not used.

Silicon Oxide Difluoride (SiOF₂)F₂Osi

(Ideal Gas)

Mol. Wt. = 82.09

SILICON OXIDE DIFLUORIDE (SiOF₂)

(IDEAL GAS)

MOL. WT. = 82.09

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-2.4069	-429.953	-429.953	INFINITE
100	8.205	53.862	-2.071	-230.270	-230.270	501.370
200	10.471	60.167	-1.148	-230.668	-228.412	249.585
298	12.832	64.806	0.000	-231.000	-227.231	166.257
300	12.871	64.885	0.024	-231.006	-227.208	165.513
400	14.656	68.847	1.405	-231.258	-225.902	123.421
500	15.922	72.261	2.938	-231.448	-224.540	98.142
600	16.818	75.248	4.377	-231.501	-223.145	81.276
700	17.462	77.891	5.723	-231.705	-221.727	69.223
800	17.932	80.255	7.0176	-231.801	-220.296	60.179
900	18.284	82.389	8.261	-231.887	-218.852	53.142
1000	18.551	84.330	9.4612	-231.968	-217.399	47.510
1100	18.758	86.108	10.618	-232.045	-215.940	42.901
1200	18.921	87.747	11.747	-232.120	-214.471	38.959
1300	19.052	89.267	12.846	-232.195	-212.997	35.806
1400	19.158	90.683	13.927	-232.269	-211.518	33.018
1500	19.245	92.008	14.986	-232.344	-210.033	30.600
1600	19.317	93.252	16.026	-232.421	-208.543	28.484
1700	19.378	94.422	17.060	-232.491	-207.038	26.603
1800	19.429	95.534	18.081	-232.556	-205.526	24.856
1900	19.473	96.586	19.091	-232.617	-204.010	23.292
2000	19.511	97.586	20.086	-232.672	-202.486	21.885
2100	19.543	98.534	21.068	-232.723	-200.956	20.612
2200	19.571	99.431	22.039	-232.770	-199.420	19.466
2300	19.597	100.278	22.999	-232.813	-197.879	18.436
2400	19.619	101.074	23.949	-232.852	-196.334	17.512
2500	19.638	101.825	24.889	-232.888	-194.786	16.693
2600	19.656	102.535	25.821	-232.921	-193.235	15.971
2700	19.671	103.202	26.746	-232.951	-191.680	15.343
2800	19.685	103.833	27.666	-232.978	-190.121	14.800
2900	19.698	104.434	28.581	-232.999	-188.558	14.343
3000	19.709	105.004	29.491	-233.016	-187.000	13.971
3100	19.719	105.549	30.396	-233.030	-185.446	13.687
3200	19.728	106.074	31.296	-233.041	-183.896	13.490
3300	19.737	106.584	32.191	-233.049	-182.350	13.289
3400	19.745	107.074	33.081	-233.054	-180.808	13.084
3500	19.752	107.549	33.966	-233.057	-179.270	12.875
3600	19.758	108.004	34.846	-233.058	-177.736	12.662
3700	19.764	108.444	35.721	-233.057	-176.206	12.445
3800	19.770	108.874	36.591	-233.054	-174.680	12.224
3900	19.775	109.299	37.456	-233.049	-173.158	12.000
4000	19.780	110.723	38.316	-233.041	-171.640	11.773
4100	19.784	111.712	39.171	-233.030	-170.126	11.543
4200	19.789	112.684	40.021	-233.016	-168.616	11.310
4300	19.792	113.634	40.866	-233.000	-167.110	11.075
4400	19.796	114.564	41.706	-232.981	-165.608	10.839
4500	19.799	115.474	42.541	-232.959	-164.110	10.600
4600	19.802	116.364	43.371	-232.934	-162.616	10.359
4700	19.805	117.234	44.196	-232.907	-161.126	10.116
4800	19.808	118.084	45.016	-232.878	-159.640	9.871
4900	19.811	118.914	45.831	-232.847	-158.158	9.624
5000	19.813	119.724	46.641	-232.813	-156.680	9.375
5100	19.815	120.514	47.446	-232.777	-155.206	9.124
5200	19.818	121.284	48.246	-232.739	-153.736	8.871
5300	19.820	122.034	49.041	-232.699	-152.270	8.616
5400	19.822	122.764	49.831	-232.657	-150.808	8.359
5500	19.823	123.474	50.616	-232.613	-149.350	8.100
5600	19.825	124.164	51.396	-232.567	-147.896	7.839
5700	19.827	124.834	52.171	-232.519	-146.446	7.576
5800	19.829	125.484	52.941	-232.469	-144.999	7.311
5900	19.831	126.114	53.706	-232.417	-143.556	7.044
6000	19.833	126.724	54.466	-232.363	-142.116	6.775

Sept. 30, 1953

Point Group [C_{2v}] $\Delta H_f^o = [-230 \pm 6] \text{ kcal. mole}^{-1}$ $\Delta H_f^{298.15} = [-231 \pm 6] \text{ kcal. mole}^{-1}$ $S_{298.15}^o = [64.806] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Ground State Quantum Weight $\sigma(1)$

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[440] (1)	[760] (1)
[490] (1)	[980] (1)
[610] (1)	[1420] (1)

Bond Distance: Si-O = [1.60] Å Si-P = [1.54] Å $\sigma = 2$

Bond Angle: P-Si-O = [120]° P-Si-P = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = 2.56608 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

 $\Delta H_{298.15}^o$ was estimated by comparison with those for SiF₄(g) and SiO₂(g).

Heat Capacity and Entropy.

The vibrational frequencies were estimated by comparison with those for COF₂(g) and TiOF₂(g). The vibrational frequencies for COF₂(g) and TiOF₂(g) were obtained from R. J. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys. 22, 1953 (1954), and J. S. Gordon, private communication, May 12, 1953, respectively. The bond distances of Si-O and Si-P were assumed to be the same as those for SiO(g) and SiF₄(g), respectively. Point group, ground state multiplicity, and bond angles were estimated.

F₂Osi

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ keal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-	-210.996	-210.996	INFINITE
100	15.000	52.529	6.8116	-210.996	-210.996	24.345
200	15.000	68.016	4.028	-210.996	-210.996	24.345
298	15.005	68.016	4.000	-210.996	-210.996	24.345
300	15.042	68.109	4.028	-210.996	-210.996	159.345
400	16.625	72.672	1.618	-210.996	-210.996	159.345
500	17.368	76.474	3.532	-210.996	-210.996	159.345
600	18.195	79.758	5.124	-210.996	-210.996	77.773
700	18.997	82.595	6.965	-210.996	-210.996	66.251
800	19.775	85.097	8.859	-210.996	-210.996	57.605
900	20.530	87.332	10.737	-210.996	-210.996	50.877
1000	21.214	89.344	12.601	-210.996	-210.996	45.452
1100	21.824	91.186	14.578	-210.996	-210.996	41.084
1200	22.368	92.871	16.515	-210.996	-210.996	37.401
1300	22.857	94.427	18.459	-210.996	-210.996	34.274
1400	23.300	95.873	20.410	-210.996	-210.996	31.593
1500	23.721	97.221	22.365	-210.996	-210.996	29.267
1600	24.129	98.486	24.324	-210.996	-210.996	27.230
1700	24.523	99.675	26.286	-210.996	-210.996	25.430
1800	24.904	100.798	28.251	-210.996	-210.996	23.830
1900	25.273	101.862	30.218	-210.996	-210.996	22.396
2000	25.633	102.872	32.187	-210.996	-210.996	21.094
2100	25.984	103.834	34.158	-210.996	-210.996	19.905
2200	26.327	104.751	36.131	-210.996	-210.996	18.823
2300	26.663	105.629	38.104	-210.996	-210.996	17.834
2400	26.992	106.469	40.079	-210.996	-210.996	16.926
2500	27.315	107.276	42.055	-210.996	-210.996	16.090
2600	27.633	108.051	44.032	-210.996	-210.996	15.318
2700	27.946	108.797	46.009	-210.996	-210.996	14.603
2800	28.254	109.517	47.987	-210.996	-210.996	13.937
2900	28.557	110.211	49.966	-210.996	-210.996	13.317
3000	28.855	110.882	51.945	-210.996	-210.996	12.750
3100	29.148	111.531	53.925	-210.996	-210.996	12.195
3200	29.436	112.160	55.906	-210.996	-210.996	11.686
3300	29.719	112.770	57.886	-210.996	-210.996	11.207
3400	29.997	113.361	59.867	-210.996	-210.996	10.756
3500	30.270	113.935	61.844	-210.996	-210.996	10.330
3600	30.538	114.494	63.821	-210.996	-210.996	9.940
3700	30.801	115.037	65.813	-210.996	-210.996	9.590
3800	31.059	115.565	67.819	-210.996	-210.996	9.275
3900	31.312	116.080	69.849	-210.996	-210.996	8.975
4000	31.560	116.582	71.861	-210.996	-210.996	8.684
4100	31.803	117.072	73.844	-210.996	-210.996	8.396
4200	32.041	117.550	75.807	-210.996	-210.996	8.111
4300	32.274	118.017	77.771	-210.996	-210.996	7.829
4400	32.502	118.474	79.710	-210.996	-210.996	7.551
4500	32.725	118.918	81.629	-210.996	-210.996	7.275
4600	32.943	119.345	83.662	-210.996	-210.996	7.001
4700	33.156	119.761	85.666	-210.996	-210.996	6.725
4800	33.364	120.160	87.630	-210.996	-210.996	6.451
4900	33.568	120.548	89.564	-210.996	-210.996	6.175
5000	33.768	120.925	91.469	-210.996	-210.996	5.901
5100	33.964	121.292	93.353	-210.996	-210.996	5.625
5200	34.156	121.647	95.216	-210.996	-210.996	5.351
5300	34.344	121.991	97.059	-210.996	-210.996	5.075
5400	34.528	122.324	98.882	-210.996	-210.996	4.801
5500	34.708	122.647	100.685	-210.996	-210.996	4.525
5600	34.884	122.960	102.468	-210.996	-210.996	4.251
5700	35.056	123.264	104.231	-210.996	-210.996	3.975
5800	35.224	123.559	105.974	-210.996	-210.996	3.701
5900	35.388	123.845	107.697	-210.996	-210.996	3.425
6000	35.548	124.122	109.400	-210.996	-210.996	3.151

Point Group [C_{2v}]
 $\Delta H_f^0 = [-220]$ kcal. mole⁻¹
 $\Delta F_f^0 = [-221]$ kcal. mole⁻¹
 $S_{298.15}^0 = [68.016]$ cal. deg⁻¹ mole⁻¹
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[553] (1)	[718] (1)	[300] (1)
[888] (1)	[452] (1)	[350] (1)

Bond Distances: Ti-O = [1.62] Å Ti-F = [1.74] Å
 Bond Angle: O-Ti-F = [120°]
 Product of Moments of Inertia: I_AI_BI_C = [4.34 X 10⁻¹¹⁴] g.³ cm.⁶
 $\epsilon = 2$

Heat of Formation.
 ΔH_f^0 was estimated as -220 kcal. mole⁻¹ by J. S. Gordon, AstroSystems, Inc., Caldwell Twp., N. J., private communication, January 10, 1963. ΔH_f^0 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. The principal moments of inertia are:
 $I_A = 14.3274 \times 10^{-39}$ g. cm.², $I_B = 11.6632 \times 10^{-39}$ g. cm.², and $I_C = 25.9907 \times 10^{-39}$ g. cm.²

Sulfuryl Difluoride (SO₂F₂)

(Ideal Gas) Mol. Wt. = 102.066

F₂O₂S

MOL. WT. = 102.066

SULFURYL DIFLUORIDE (SO₂F₂)

(IDEAL GAS)

Point Group C_{2v} $\Delta H_f^\circ 0 = -203 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = 69.883 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^\circ 298.15 = -205 \text{ kcal. mole}^{-1}$

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
1269 (1)	274 (1)	539 (1)
846 (1)	360 (1)	885 (1)
553 (1)	1502 (1)	386 (1)

Bond Distance: S-O = $1.405 \pm 0.003 \text{ \AA}$ S-F = $1.530 \pm 0.003 \text{ \AA}$ Bond Angle: O-S-O = $123^\circ 58' \pm 12'$ F-S-F = $98^\circ 7' \pm 10'$ Product of the Moments of Inertia: $I_A I_B I_C = 4.4873 \times 10^{-114} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation was reported by R. M. Reese, V. H. Dibeler and J. L. Franklin, J. Chem. Phys. 29, 880 (1958). The value was calculated from the appearance potential of the SO₂⁺ ion obtained from electron impact studies of SO₂ and SO₂P₂.

Heat Capacity and Entropy.

The vibrational frequencies were obtained from G. R. Hunt, and M. K. Wilson, Spectrochim. Acta, 16, 570 (1960). The bond distances and bond angles were reported by D. R. Lide, Jr., D. E. Mann, and R. M. Fristrom, J. Chem. Phys., 26, 734 (1957). The entropy of sulfuryl fluoride gas has been calculated from the calorimetric data and the third law of thermodynamics to be 62.66 cal. deg.⁻¹ mole⁻¹ at 217.78°K. by P. J. Bockhoff, R. V. Petrella, and E. L. Pace, J. Chem. Phys. 32, 799 (1960). The discrepancy between entropy value calculated from calorimetric data and that calculated from molecular and spectroscopic data (1 atm., 217.78°K) is attributed to randomness in the solid at 0°K by P. J. Bockhoff and E. L. Pace, J. Chem. Phys. 34, 3502 (1962). The vibrational frequencies reported by M. D. Perkins and M. Kent Wilson, J. Chem. Phys. 20, 1791 (1952) were 1269 (1), 846 (1), 544 (1), [500] (1), [385] (1), 1502 (1), 553 (1), 885 (1), and 539 (1) cm.⁻¹. The three principal moments of inertia are: 1.6567×10^{-38} , 1.6567×10^{-38} , and $1.6349 \times 10^{-38} \text{ g. cm.}^2$.

F₂O₂S

Dec. 31, 1960; Mar. 31, 1963

Phosphorus Difluoride (PF₂)

(Ideal Gas) Mol. Wt. = 68.975

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ cal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
0	8.000	INFINITE	-	2.658	-104.696	INFINITE
100	8.116	57.151	-	2.658	-104.696	10.453
200	9.437	58.201	-	0.989	-104.628	116.512
298	10.677	62.207	0.000	-	-107.478	78.779
300	10.698	62.273	0.020	-	-107.493	78.305
400	11.528	65.468	1.140	-	-105.186	59.166
500	12.269	68.158	2.337	-	-103.037	47.084
600	12.887	70.434	3.586	-	-101.551	39.982
700	12.970	72.412	4.870	-	-100.772	34.485
800	13.169	74.158	6.178	-	-100.459	31.803
900	13.318	75.718	7.502	-	-100.392	27.969
1000	13.415	77.126	8.839	-	-100.380	24.900
1100	13.499	78.409	10.185	-	-100.354	22.390
1200	13.562	79.586	11.538	-	-100.341	20.208
1300	13.612	80.674	12.897	-	-100.329	18.528
1400	13.652	81.689	14.260	-	-100.318	17.011
1500	13.684	82.627	15.627	-	-100.305	15.697
1600	13.711	83.511	16.988	-	-100.300	14.547
1700	13.733	84.343	18.359	-	-100.294	13.532
1800	13.752	85.129	19.743	-	-100.290	12.630
1900	13.768	85.867	21.131	-	-100.287	11.823
2000	13.782	86.579	22.527	-	-100.286	11.097
2100	13.793	87.252	23.936	-	-100.287	10.440
2200	13.804	87.894	25.355	-	-100.282	9.842
2300	13.813	88.508	26.786	-	-100.287	9.297
2400	13.821	89.096	28.227	-	-100.305	8.797
2500	13.828	89.660	29.680	-	-100.315	8.337
2600	13.834	90.202	31.143	-	-100.328	7.912
2700	13.839	90.725	32.617	-	-100.342	7.519
2800	13.844	91.228	34.101	-	-100.355	7.154
2900	13.848	91.714	35.596	-	-100.368	6.813
3000	13.853	92.184	37.101	-	-100.378	6.490
3100	13.856	92.638	38.617	-	-100.420	6.199
3200	13.860	93.078	40.143	-	-100.447	5.921
3300	13.863	93.504	41.688	-	-100.474	5.659
3400	13.866	93.916	43.253	-	-100.504	5.412
3500	13.868	94.320	44.832	-	-100.536	5.180
3600	13.870	94.711	46.429	-	-100.570	4.960
3700	13.873	95.091	48.042	-	-100.607	4.753
3800	13.875	95.461	49.672	-	-100.646	4.556
3900	13.877	95.822	51.320	-	-100.686	4.369
4000	13.878	96.173	52.986	-	-100.727	4.192
4100	13.880	96.515	54.669	-	-100.770	4.023
4200	13.881	96.850	56.368	-	-100.817	3.862
4300	13.882	97.177	58.083	-	-100.867	3.708
4400	13.883	97.498	59.812	-	-100.919	3.562
4500	13.885	97.808	61.556	-	-100.974	3.422
4600	13.886	98.113	63.316	-	-101.032	3.288
4700	13.887	98.412	65.090	-	-101.093	3.159
4800	13.888	98.704	66.878	-	-101.155	3.036
4900	13.889	98.991	68.680	-	-101.219	2.918
5000	13.890	99.271	70.496	-	-101.286	2.804
5100	13.891	99.546	72.326	-	-101.356	2.695
5200	13.891	99.816	74.170	-	-101.427	2.590
5300	13.892	100.080	76.028	-	-101.499	2.489
5400	13.892	100.339	77.900	-	-101.572	2.392
5500	13.893	100.595	79.786	-	-101.646	2.298
5600	13.894	100.845	81.686	-	-101.721	2.207
5700	13.895	101.091	83.600	-	-101.797	2.120
5800	13.895	101.333	85.528	-	-101.874	2.035
5900	13.895	101.571	87.470	-	-101.952	1.953
6000	13.896	101.804	89.426	-	-102.031	1.874

June 30, 1962

Phosphorus Difluoride (PF₂) (Ideal Gas)

Mol. Wt. = 68.975

ΔH°_f 298.15 = [-105 ± 15] kcal. mole⁻¹

S°_{298.15} = [62.2 ± 3] cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = 2

Point Group C_{2v}

Vibrational Levels and Multiplicities

U, cm.⁻¹

(376) (1)

(775) (1)

(890) (1)

I_AI_BI_C = [1.9059 × 10⁻¹¹⁵] g.³ cm.⁶

σ = 2

Heat of Formation. ΔH°_f 298.15 was estimated by C. B. Henderson

and R. S. Scheffer, *Atlantic Research Corp., Alexandria, Virginia*,

"Survey of Thermochemical Data," January, 1960. For their esti-

mation they assumed certain bond energies for the dissociation of

PF₃(g). Bond one was assumed 20% greater than bond two and three

which were assumed to be equal. ΔH°_f 298.15 was corrected for the

change in phosphorus reference state (white α → red γ).

Heat Capacity and Entropy. Molecular constants and vibrational

levels were estimated by J. S. Gordon, *Thiokol Chemical Corp.,*

Reaction Motors Division, *Denville, N. J., "Thermodynamic Data*

for Combustion Products," January, 1960.

Lead Difluoride (PbF₂)

GFW = 245.1868

T, °K	Cp	$\frac{\text{gibbs/mol}}{S}$	$-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	17,720	27,000	27,000	.000	-161.600	-150.789	110.531
300	17,750	27,110	27,000	.033	-161.793	-150.761	109.600
400	19,290	32,427	27,715	1.665	-161.845	-150.722	107.797
500	20,830	38,697	29,115	3.691	-160.837	-149.586	62.761
600	22,370	40,831	30,746	6.051	-160.199	-140.190	51.044
700	23,910	45,394	32,569	12.074	-159.093	-136.810	42.714
800	24,300	49,529	34,643	16.053	-158.504	-133.823	36.504
900	24,300	52,391	36,299	14.463	-157.665	-131.583	31.806
1000	24,300	54,955	38,000	12.513	-156.513	-129.594	27.806
1100	24,300	57,267	39,663	19.343	-155.987	-124.715	24.776
1200	24,300	59,382	41,238	21.773	-155.185	-121.907	22.202
1300	24,300	61,327	42,709	24.203	-154.304	-119.171	20.035
1400	24,300	63,126	44,104	26.633	-153.464	-116.511	18.167
1500	24,300	64,804	45,499	29.063	-152.631	-113.906	16.593
1600	24,300	66,372	46,669	31.493	-151.803	-111.333	15.207
1700	24,300	67,845	47,691	33.923	-150.980	-108.826	13.991
1800	24,300	69,234	49,038	36.353	-150.166	-106.375	12.916
1900	24,300	70,548	50,134	38.783	-149.358	-103.968	11.979
2000	24,300	71,795	51,166	41.213	-148.558	-101.598	11.102

Mar. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

S°_{298.15} = [27.0 ± 2] gibbs/molT_m = 613°KT₁ = 725°KT_m = 1099°KΔH°_{298.15} = 58.5 kcal/mol

The heats of formation at 298.15°K derived from the enthalpy changes of different chemical reactions are listed below. The adopted one is the average of the last three ΔH°_{298.15} values, which is also in reasonable agreement with the ΔH°_{298.15} values evaluated from (1) and (5).

Heat of Formation

Reference	Chemical Reaction	ΔH° _{298.15} Kcal/mol	ΔH° _{298.15} Kcal/mol
1	PbF ₂ (c) + H ₂ (g) = Pb(l) + 2 HF(g)	32.0 ± 0.58*	-161.3 ± 0.6
2	PbF ₂ (c) + H ₂ O(g) = PbO(c) + 2 HF(g)	29.6 ± 2.1**	-154.5 ± 4.0
3	Pb(c) + F ₂ (g) = PbF ₂ (c)	-159.7 ± 0.5	-159.7 ± 0.5
4	PbO(c) + 2 HF(40% aq) = PbF ₂ (c) + H ₂ O(l)	-22.9 ± 0.3	-159.0 ± 0.5
5	PbF ₂ (c) + 2 Na(c) = Pb(c) + 2 NaF(aq)	-112.2 ± 0.2	-162.2 ± 0.4
6	PbF ₂ (c) + Mg(c) = Pb(c) + MgF ₂ (c)	-109.5 ± 1.5	-159.2 ± 2.0
7	3/2 PbF ₂ (c) + Al(c) = 3/2 Pb(c) + AlF ₃ (c)	-118.5 ± 0.1	-161.5 ± 1.0
8	3/2 PbF ₂ (c) + Al(c) = 3/2 Pb(c) + AlF ₃ (c)	-117.7 ± 0.6	-162.1 ± 1.0
9	1/2 PbF ₂ (c) + 1/3 Al(c) = 1/2 Pb(c) + 1/3 AlF ₃ (c)	-38.3 ± 0.8	-161.8 ± 1.0

* This is the third law value. The second law value is 32.4 ± 0.9 kcal/mol. The entropy drift is -0.5 ± 1.2 eu.
 ** This is the third law value. The second law value is 39.6 ± 0.7 kcal/mol. The entropy drift is -10.9 ± 0.8 eu.

Heat Capacity and Entropy

Banashek, Patsukova, and Rassonskaya (10) measured the high temperature enthalpies (H° - H°_{298.15}) for PbF₂(c) in the temperature range 670-1165°K. Based on their enthalpy measurements the heat capacity of PbF₂(c) at temperatures 725-1099°K is derived as 24.3 ± 0.2 gibbs/mol by the least square method. The heat capacities below 725°K are estimated using their reported enthalpies at 670-725°K, which are based on a mixture of β and γ, as a guide.

The S°_{298.15} is estimated to be 25 eu by the method suggested by Kubaschewski and Evans (11), and adjusted to 27 eu so that the second and third law ΔH°_{298.15} values derived from the equilibrium data reported by Jellinek and Rudat (12) are in good agreement.

Transition Data

The transition temperatures are obtained from Banashek, Patsukova, and Rassonskaya (10). The β + γ transition at 613°K was reported as either slow or irreversible and the γ + β transition at 725°K was reversible. The polymorphism of PbF₂(c) has been studied by many other investigators. However, the relations between the temperature and the character of polymorphic transformation are not consistent (10).

The enthalpy difference at 725°K for PbF₂(γ) and PbF₂(β) is ΔH°₂. The value of ΔH°₂ is estimated such that the generated functions yield reasonable agreement among the derived ΔH°₂₉₈ values (see the above table).

Melting Data

See PbF₂(l) table.

Heat of Sublimation

The difference between ΔH°_{298.15} for PbF₂(g) and PbF₂(c) is ΔH°_{298.15}.

References

1. K. Jellinek and A. Rudat, Z. Anorg. Chem. 175, 281 (1928).
2. M. L. Domange, Compt. Rend. 200, 2180 (1935).
3. W. Jahn-Held and K. Jellinek, Z. Elektrochem. 42, 401 (1936).
4. H. Wartenberg, Z. Anorg. Allgem. Chem. 244, 337 (1940).
5. H. Wartenberg, D. Anorg. Chem. Soc. Trans. Faraday Soc. 50, 477 (1954).
6. P. Gross, C. Hayman, and D. L. Levi, Physical Chemistry of Process Metallurgy, Part 2, Interscience Publishers, Inc., New York, 1961.
7. V. P. Kolesov, A. M. Martynov, and S. M. Skuratov, Russ. J. Inorg. Chem. 5, 1326 (1961).
8. R. J. Heus and J. J. Egan, Z. Phys. Chem. 49, 5.38 (1966).
9. E. Z. Rassonskaya, A. M. Patsukova, and S. M. Rassonskaya, Invest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Meorg. Khim. Akad. Nauk SSSR 27, 23 (1956).
10. O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York, 1958.

$$S_{298.15}^{\circ} = [28.647] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} 298.15 = -158.722 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 2.98 \text{ kcal/mol}$$

$$T_m = 1099^{\circ}\text{K}$$

Heat of Formation

$\Delta H_f^{\circ} 298.15^{\circ}$ is obtained from $\Delta H_f^{\circ} 298.15^{\circ}$ (c) by adding ΔH_m° and the difference between $H_m^{\circ} - H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The enthalpies ($H^{\circ} - H_{298.15}^{\circ}$) of PbF₂(l) in the temperature range 1104-1165°K were determined by Banashek, Patukova, and Rassonskaya (1). Based on their reported results the heat capacity of PbF₂(l) is evaluated to be 24 ± 2 gibbs/mol by the least square method. This Cp value is adopted and extended to 298 and 2500°K, respectively.

The entropy ($S_{298.15}^{\circ}$) is calculated in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from Banashek, Patukova, and Rassonskaya (1). The enthalpy difference at T_m for PbF₂(l) and PbF₂(s) is ΔH_m° .

Other values of T_m (°K) reported are 1091 (2, 11), 1097 (3, 4, 5) and 1128 (6). Using the freezing point data of binary systems PbF₂-PbBr₂ (5), PbF₂-PbCl₂ (5, 7), PbF₂-PbI₂ (5, 8), PbF₂-PbO (9), and PbF₂-NaF (10), Kelley (3) evaluated the corresponding values of ΔH_m° (kcal/mol) as 1.70, 1.70, 1.96, 3.87, and 2.47. Other reported values of ΔH_m° are 3.00 (1) and 4.16 (2) kcal/mol.

Vaporization Data

From mass spectroscopic study on the vapor species in PbF₂, Zmbov, Hastie, and Margrave (4) have shown that molten PbF₂ vaporizes partly as molecular PbF₂. There is considerable disproportionation, and at 715°C the vapor composition is approximately 68% PbF₂, 25% PbF, 21% PbF, and 74% Pb (4, 12). T_b has been reported as 1565°K (11) where the vapor is expected to be a mixture of the above species.

References

1. E. I. Banashek, N. N. Patukova, and I. S. Rassonskaya, Izvest. Sektora Fiz. Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk SSSR 27, 223 (1956).
2. M. Blanc, Diplôme d'Études Supérieures, Paris, 1956, quoted by M. Blanc and G. Petit, Compt. Rend. 248, 1305 (1959).
3. K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936.
4. K. Zmbov, J. W. Hastie, and J. L. Margrave, Trans. Faraday Soc. 64, 861 (1968).
5. C. Sandonini, Gazz. Chim. Ital. 41, II 144 (1911).
6. Anadori, Gazz. Chim. Ital. 49, I 38 (1919).
7. C. Sandonini, Atti Acad. Lincei, Ser. 5, 20, I 172 (1911).
8. C. Sandonini, Atti Acad. Lincei, Ser. 5, 20, I 253 (1911).
9. C. Sandonini, Atti Acad. Lincei, Ser. 5, 23, I 959 (1914).
10. N. A. Puschin and A. B. Baskov, J. Russ. Phys. Chem. Soc. 45, 82 (1913); Z. Anorg. Chem. 81, 347 (1913).
11. H. V. Wartenberg and O. Bosse, Z. Elektrochem. 28, 384 (1922).
12. R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Phys. Chem. 72, 3510 (1968).

T, K	Cp°	S° gibbs/mol	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal/mol	ΔG°	Log Kp
100						
200						
298						
300	24.000	28.647	28.647	0.000	-148.202	108.635
400	24.000	28.786	28.648	0.044	-148.137	107.618
500	24.000	28.925	28.589	0.088	-148.073	106.605
600	24.000	29.064	28.536	0.132	-148.009	105.592
700	24.000	29.203	28.483	0.176	-147.945	104.579
800	24.000	29.342	28.430	0.220	-147.881	103.566
900	24.000	29.481	28.377	0.264	-147.817	102.553
1000	24.000	29.620	28.324	0.308	-147.753	101.540
1100	24.000	29.759	28.271	0.352	-147.689	100.527
1200	24.000	29.898	28.218	0.396	-147.625	99.514
1300	24.000	30.037	28.165	0.440	-147.561	98.501
1400	24.000	30.176	28.112	0.484	-147.497	97.488
1500	24.000	30.315	28.059	0.528	-147.433	96.475
1600	24.000	30.454	28.006	0.572	-147.369	95.462
1700	24.000	30.593	27.953	0.616	-147.305	94.449
1800	24.000	30.732	27.900	0.660	-147.241	93.436
1900	24.000	30.871	27.847	0.704	-147.177	92.423
2000	24.000	31.010	27.794	0.748	-147.113	91.410
2100	24.000	31.149	27.741	0.792	-147.049	90.397
2200	24.000	31.288	27.688	0.836	-146.985	89.384
2300	24.000	31.427	27.635	0.880	-146.921	88.371
2400	24.000	31.566	27.582	0.924	-146.857	87.358
2500	24.000	31.705	27.529	0.968	-146.793	86.345

Lead Difluoride (PbF₂)

(Ideal Gas)

Point Group C_{2v} $\Delta H_f^\circ = -102.7 \pm 1 \text{ kcal/mol}$ $\Delta H_{298.15}^\circ = -103.3 \pm 1 \text{ kcal/mol}$

Ground State Quantum Weight = {1}

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^d	Log Kp
0	0.000	0.000	INFINITE	3.138	102.684	102.684	INFINITE
100	9.766	56.829	11.449	2.765	103.862	103.862	276.991
200	11.549	66.186	12.152	1.993	103.160	104.405	114.405
298	12.603	71.027	12.603	0.000	103.160	105.416	77.272
300	12.616	71.105	12.616	0.023	103.103	105.429	76.805
400	13.115	74.811	13.115	1.713	103.435	106.117	57.940
500	13.379	77.768	13.379	2.639	103.569	106.772	46.670
600	13.512	80.222	13.512	3.085	103.745	107.391	39.117
700	13.562	82.316	13.562	3.383	103.928	107.789	33.653
800	13.622	84.140	13.622	3.579	104.115	108.155	29.597
900	13.737	85.756	13.737	3.681	104.367	108.493	26.366
1000	13.769	87.205	13.769	3.746	104.571	108.806	23.740
1100	13.793	88.518	13.793	3.785	104.735	109.095	21.474
1200	13.812	89.719	13.812	3.805	104.865	109.370	19.496
1300	13.826	90.826	13.826	3.816	104.961	109.626	17.630
1400	13.838	91.851	13.838	3.819	105.034	109.866	15.966
1500	13.847	92.806	13.847	3.816	105.087	110.089	14.500
1600	13.854	93.700	13.854	3.806	105.119	110.296	13.205
1700	13.859	94.540	13.859	3.785	105.129	110.485	12.065
1800	13.866	95.332	13.866	3.754	105.119	110.652	11.065
1900	13.871	96.082	13.871	3.714	105.087	110.797	10.181
2000	13.874	96.793	13.874	3.666	105.034	110.918	9.403
2100	13.876	97.470	13.876	3.611	104.961	109.603	8.727
2200	13.878	98.119	13.878	3.550	104.865	108.155	8.147
2300	13.881	98.733	13.881	3.484	104.745	106.666	7.647
2400	13.885	99.324	13.885	3.414	104.600	105.136	7.212
2500	13.887	99.891	13.887	3.340	104.431	103.566	6.832
2600	13.889	100.436	13.889	3.262	104.240	101.956	6.502
2700	13.892	100.957	13.892	3.180	104.029	100.306	6.212
2800	13.892	101.465	13.892	3.094	103.800	98.616	5.957
2900	13.893	101.953	13.893	3.004	103.557	96.886	5.732
3000	13.894	102.424	13.894	2.910	103.300	95.116	5.532
3100	13.895	102.876	13.895	2.812	103.029	93.306	5.352
3200	13.897	103.310	13.897	2.710	102.745	91.456	5.192
3300	13.898	103.726	13.898	2.604	102.449	89.566	5.052
3400	13.899	104.123	13.899	2.494	102.140	87.636	4.932
3500	13.898	104.506	13.898	2.380	101.819	85.666	4.832
3600	13.897	104.876	13.897	2.262	101.486	83.656	4.752
3700	13.895	105.237	13.895	2.140	101.140	81.606	4.692
3800	13.900	105.579	13.900	2.014	100.780	79.516	4.642
3900	13.901	105.900	13.901	1.884	100.406	77.386	4.602
4000	13.901	106.222	13.901	1.750	100.019	75.216	4.572
4100	13.902	106.535	13.902	1.612	99.620	73.006	4.552
4200	13.902	106.837	13.902	1.470	99.209	70.756	4.542
4300	13.903	107.127	13.903	1.324	98.786	68.466	4.542
4400	13.903	107.407	13.903	1.174	98.351	66.136	4.552
4500	13.903	107.677	13.903	1.020	97.904	63.766	4.572
4600	13.903	107.937	13.903	0.862	97.445	61.356	4.602
4700	13.903	108.187	13.903	0.700	96.970	58.906	4.642
4800	13.903	108.427	13.903	0.534	96.480	56.416	4.692
4900	13.904	108.657	13.904	0.364	95.975	53.886	4.752
5000	13.904	108.877	13.904	0.190	95.456	51.316	4.822
5100	13.905	109.087	13.905	0.014	94.921	48.706	4.902
5200	13.905	109.287	13.905	-0.164	94.370	46.056	4.992
5300	13.905	109.467	13.905	-0.334	93.804	43.366	5.092
5400	13.905	109.627	13.905	-0.504	93.224	40.636	5.202
5500	13.905	109.767	13.905	-0.674	92.630	37.866	5.322
5600	13.906	109.897	13.906	-0.844	92.021	35.056	5.452
5700	13.906	109.997	13.906	-1.014	91.396	32.206	5.592
5800	13.906	110.067	13.906	-1.184	90.756	29.316	5.742
5900	13.906	110.107	13.906	-1.354	90.101	26.386	5.902
6000	13.906	110.127	13.906	-1.524	89.431	23.416	6.072

Har. 31, 1962; Dec. 31, 1963; Dec. 31, 1965; June 30, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	Deg.
[450] (1)	1
[120] (1)	1
[450] (1)	1

Bond Distance: Pb-F = 2.13 ± 0.02 ÅBond Angle: F-Pb-F = 95° Product of the Moments of Inertia: $I_A I_B I_C = [4.5690 \times 10^{-114}] \text{ g cm}^6$

Heat of Formation

Vapor pressure data for PbF₂ have previously been interpreted on the assumption that PbF₂ was the only species present in the gas phase (1, 2). Zmbov, Hastie, and Margrave (3) have studied the vapor species over PbF₂(c, l) mass spectrometrically and shown that PbF₂ vaporizes only partly as molecular PbF₂ and there is considerable disproportionation. The vapor composition at 988°K is approximately 66% PbF₄, 25% PbF₂, 2% PbF, and 7% Pb (3, 4). From extrapolation of the ion intensity data from 1043 to 988°K to the temperature region in which Mesnayanov and Iofa (2) measured the saturated vapor pressures of PbF₂(c), 792-988°K, by Knudsen effusion method, the partial pressure of PbF₂(c), at 988°K was calculated to be 0.0435 ± 0.005 torr. Based on this calculated vapor pressure, the heat of sublimation (ΔH_{298}°) of PbF₂(c) is derived as 88.50 kcal/mol by the third law method, yielding ΔH_f° (PbF₂, g) = -103.3 ± 1 kcal/mol.

Due to lack of data on vapor compositions over PbF₂(c, l) at various temperatures, the partial pressure measurements reported by Wartenberg and Boses (1), using boiling point method, and those of Mesnayanov and Iofa (2) are not used for evaluation.

Heat Capacity and Entropy

The bond distance was determined by Akishin, Spiridonov and Khodchenkov (5). The bond angle is assumed to be the same as that in PbF₂(g) where X = Cl, Br or I (6). The vibrational frequencies are calculated by valence force method (10) using force constants estimated by comparison with those for PbF (7), CaF₂ (8), HgF₂ (9), and MgF₂ (9). The value of ν_2 is in fair agreement with the value, 145 cm^{-1} , estimated by (9). The three principal moments of inertia are: $I_A = 1.5559 \times 10^{-38}$, $I_B = 1.1040 \times 10^{-38}$, and $I_C = 2.6599 \times 10^{-38} \text{ g cm}^2$.

References

1. H. V. Wartenberg and O. Boses, Z. Elektrochem. 28, 384 (1922).
2. A. N. Mesnayanov and B. Z. Iofa, Zh. Neorg. Khim. 2, 486 (1955).
3. K. Zmbov, J. W. Hastie, and J. L. Margrave, Trans. Faraday Soc. 54, 861 (1958).
4. R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Phys. Chem. 72, 3510 (1968).
5. P. A. Akishin, V. P. Spiridonov, and A. N. Khodchenkov, Zh. Fiz. Khim. 32, 1678 (1958).
6. M. Lister and L. E. Sutton, Trans. Faraday Soc. 37, 406 (1941).
7. G. Herzberg, 'Spectra of Diatomic Molecules,' D. Van Nostrand Co., Inc., New York, 1950.
8. G. V. Calder, Matl. Bur. Std. Rept. 9389, July 1966.
9. JANAF HgF₂(g) table, Mar. 31, 1966.
10. G. Herzberg, 'Infrared and Raman Spectra,' D. Van Nostrand Co., Inc., New York, 1945.

Silicon Difluoride (SiF₂)

(Ideal Gas) GFW = 66.0828

SILICON DIFLUORIDE (SiF₂)

(IDEAL GAS)

GFW = 66.0828

Point Group [C_{2v}] $\Delta H_f^\circ = -140.3 \pm 3$ kcal/mol $S_{298.15}^\circ = 61.30 \pm 0.05$ gibbs/mol $\Delta H_f^\circ = -140.5 \pm 3$ kcal/mol

Electronic Levels and Quantum Weights

 $\epsilon_i, \text{ cm}^{-1}$ $\frac{g_i}{1}$

[20000]

44109

1

(3)

855 (1)

345 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

872 (1)

Heat of Formation

J. L. Margrave, A. S. Kanaan, and D. C. Pease, J. Phys. Chem. **66**, 1200 (1962), have reported some approximate equilibrium constants for the reaction $\text{Si}(g) + \text{SiF}_4(g) \rightleftharpoons 2\text{SiF}_2(g)$. These were calculated from yields of polymerized products and a knowledge of the total system pressure given in U. S. Patent No. 2,840,588 (1958). The data were subjected to third law analysis using the present JANAF functions and yielded $\Delta H_{298}^\circ = 92 \pm 10$ kcal/mol, which gives $\Delta H_f^\circ(\text{SiF}_2, g) = -147 \pm 5$ kcal/mol.T. C. Ehlert and J. L. Margrave, J. Chem. Phys. **41**, 1056 (1964), have reported equilibrium constants for three reactions determined mass spectrometrically.A. $\text{CaF}_2(c) + \text{Si}(g) + \text{Ca}(g) + \text{SiF}_2(g)$ B. $\text{CaF}_2(g) + \text{Si}(g) + \text{Ca}(g) + \text{SiF}_2(g)$ C. $2\text{CaF}(g) + \text{Si}(g) + 2\text{Ca}(g) + \text{SiF}_2(g)$

A 2nd and 3rd law analysis of the data is shown below.

We adopt $\Delta H_{298.15}^\circ(\text{SiF}_2, g) = -140.5 \pm 3$ kcal/mol.

Heat Capacity and Entropy

The microwave, ultraviolet and infrared spectra have all been extensively studied (1, 2, 3, 4, 5, 6, 7). We have adopted the vibrational frequencies and molecular structure from V. M. Khanna et al. (1). The electronic levels are from V. M. Khanna et al. (2) with an estimated triplet level by analogy with CF_2 .The individual moments of inertia are $I_A = 2.7482 \times 10^{-39}$ g cm², $I_B = 9.5100 \times 10^{-39}$ g cm², and $I_C = 12.2582 \times 10^{-39}$ g cm².

References

1. V. M. Khanna, R. Hauge, R. F. Curl, Jr., and J. L. Margrave, J. Chem. Phys. **47**, 5031 (1967).2. V. M. Khanna, G. Besenbruch, and J. L. Margrave, J. Chem. Phys. **46**, 2310 (1967).3. J. M. Bassler, P. L. Timms, and J. L. Margrave, Inorg. Chem. **5**, 729 (1966).4. V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, J. Chem. Phys. **43**, 2557 (1965).5. J. W. C. Johns, G. W. Chantry, and R. F. Barrow, Trans. Faraday Soc. **54**, 1589 (1958).6. D. R. Rao and P. Venkateswarlu, J. Mol. Spectry, **1**, 287 (1961).7. D. E. Milligan and M. E. Jacox, J. Chem. Phys. **49**, 4269 (1968).

T, K

Op°

S°

-(G°-H°₂₉₈)/TH°-H°₂₉₈

kcal/mol

ΔH°

ΔG°

Log Kp

INFINITE

2.476

140.299

140.299

141.214

141.214

142.141

142.141

142.990

142.990

143.006

143.006

143.815

143.815

143.577

143.577

143.168

143.168

143.322

143.322

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

143.532

Point Group {D_{2h}}

$$\Delta H_f^\circ = -164.1 \pm 10 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -164.5 \pm 10 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 61.1 \pm 1.5 \text{ gibbs/mol}$$

Ground State Quantum Weight = 3

Titanium Difluoride (TiF₂)

(Ideal Gas) GFW = 85.8968

T, K	Cp	S°	-(G°-H°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	INFINITE
100	8.236	49.695	71.156	-2.671	-164.109	-164.109	INFINITE
200	11.151	61.081	81.081	-1.335	-164.213	-164.213	360.864
298	12.638	61.081	81.081	-1.000	-164.213	-164.213	121.742
300	12.639	61.159	81.081	-0.923	-164.502	-164.502	120.999
400	13.466	68.927	81.569	1.335	-164.578	-166.610	91.032
500	13.942	67.990	82.573	2.708	-164.658	-167.111	73.044
600	14.211	70.857	83.693	4.117	-164.747	-167.591	61.046
700	14.367	72.762	84.637	5.544	-164.853	-168.059	52.470
800	14.504	74.692	85.951	6.993	-164.984	-168.540	46.035
900	14.590	76.405	87.019	8.444	-165.141	-169.030	41.024
1000	14.660	77.946	88.036	9.910	-165.328	-169.394	37.012
1100	14.722	79.346	89.001	11.379	-165.540	-169.745	33.725
1200	14.764	80.630	89.918	12.855	-165.713	-170.079	30.976
1300	14.805	81.816	90.786	14.336	-165.849	-170.394	28.639
1400	14.823	82.919	91.615	15.825	-165.996	-170.619	26.635
1500	15.002	83.951	92.404	17.321	-167.156	-170.872	24.496
1600	15.089	84.922	93.156	18.826	-167.329	-171.113	23.373
1700	15.181	85.840	93.875	20.339	-167.517	-171.345	22.026
1800	15.278	86.710	94.564	21.862	-167.721	-171.566	20.631
1900	15.378	87.539	95.226	23.395	-167.939	-171.773	19.196
2000	15.479	88.330	95.861	24.937	-172.622	-172.813	18.775
2100	15.579	89.088	96.473	26.480	-172.849	-173.768	17.876
2200	15.678	89.815	97.063	28.026	-173.049	-174.743	17.058
2300	15.775	90.514	97.633	29.574	-173.261	-175.735	16.310
2400	15.868	91.187	98.184	31.120	-173.487	-176.749	15.624
2500	15.956	91.837	98.717	32.709	-173.687	-177.786	14.991
2600	16.040	92.464	99.234	34.309	-173.894	-178.840	14.407
2700	16.120	93.071	99.735	36.007	-174.087	-179.924	13.865
2800	16.194	93.659	80.222	37.723	-174.264	-181.039	13.362
2900	16.264	94.228	80.695	39.443	-174.425	-182.182	12.892
3000	16.330	94.781	81.155	40.176	-174.564	-183.354	12.454
3100	16.391	95.317	81.604	42.912	-174.766	-184.554	12.044
3200	16.450	95.836	82.040	45.651	-175.031	-185.785	11.659
3300	16.503	96.345	82.466	48.399	-175.351	-187.049	11.296
3400	16.554	96.839	82.882	51.152	-175.725	-188.349	10.955
3500	16.602	97.319	83.287	53.909	-176.157	-189.684	10.633
3600	16.648	97.788	83.686	56.675	-176.647	-191.054	10.313
3700	16.692	98.244	84.071	59.442	-177.195	-192.459	9.999
3800	16.733	98.690	84.450	62.213	-177.802	-193.899	9.690
3900	16.773	99.125	84.821	64.984	-178.467	-195.374	9.386
4000	16.811	99.550	85.184	67.759	-179.191	-196.884	9.086
4100	16.848	99.964	85.539	70.539	-179.974	-198.429	8.790
4200	16.884	100.372	85.887	73.324	-180.817	-200.009	8.498
4300	16.918	100.770	86.229	76.113	-181.720	-201.624	8.210
4400	16.952	101.160	86.564	78.909	-182.684	-203.274	7.926
4500	16.984	101.541	86.892	81.713	-183.709	-204.969	7.646
4600	17.016	101.914	87.215	84.524	-184.794	-206.709	7.370
4700	17.046	102.281	87.532	87.341	-185.939	-208.494	7.100
4800	17.075	102.640	87.843	90.164	-187.144	-210.324	6.834
4900	17.104	102.992	88.148	92.991	-188.409	-212.209	6.572
5000	17.131	103.338	88.449	95.824	-189.734	-214.149	6.314
5100	17.157	103.678	88.744	98.661	-191.119	-216.144	6.060
5200	17.183	104.011	89.034	101.504	-192.564	-218.194	5.810
5300	17.207	104.339	89.320	104.354	-194.069	-220.309	5.564
5400	17.230	104.660	89.601	107.209	-195.634	-222.479	5.322
5500	17.251	104.977	89.878	110.069	-197.259	-224.704	5.084
5600	17.272	105.288	90.150	112.934	-198.944	-226.984	4.850
5700	17.291	105.594	90.418	115.804	-200.689	-229.324	4.620
5800	17.309	105.895	90.683	118.679	-202.494	-231.724	4.394
5900	17.325	106.191	90.943	121.549	-204.359	-234.174	4.172
6000	17.341	106.482	91.200	124.419	-206.284	-236.674	3.954

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968; Dec. 31, 1968

Heat of Formation
Zabov and Margrave (1) have reported ion intensities and the corresponding equilibrium constants for the reaction
 $\text{Ca(g)} + \text{TiF}_3(\text{g}) = \text{CaF(g)} + \text{TiF}_2(\text{g})$. Second and third law analyses of their data give a second law ΔH_{298}° of 7.0 kcal/mol, a third law ΔH_{298}° of 11.76 kcal/mol and a third law drift of 3.1 ± 3.8 eu. The heat of formation, ΔH_{298}° , of $\text{TiF}_2(\text{g})$ is calculated from the third law ΔH_{298}° , above, and the JANAF heat of formation of $\text{TiF}_3(\text{g})$, CaF(g) and Ca(g) .

Heat Capacity and Entropy

The interatomic distances are estimated from those of TiCl_2 , TiCl_4 , and TiF_4 . The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to be the same as $\text{TiCl}_2(\text{g})$. The levels of $\text{TiCl}_2(\text{g})$ are estimated by assuming they correspond to the inverted states of $\text{NiCl}_2(\text{g})$ (2). The linear configuration is assumed because experimental evidence (3) indicates that other transition metal difluorides, viz. those of Mn, Co, Ni, Cu, and Zn, are linear.

References

1. K. F. Zabov and J. L. Margrave, *J. Phys. Chem.*, **71**, 2893 (1967).
2. C. W. DeKock and D. H. Gruen, *J. Chem. Phys.*, **44**, 4387 (1966).
3. A. Buchler, J. L. Stauffer and W. Klemperer, *J. Chem. Phys.*, **40**, 3471 (1964).

GFW = 129.2168

(CRYSTAL)

ZIRCONIUM DIFLUORIDE (ZrF₂)Zirconium Difluoride (ZrF₂)

(Crystal) GFW = 129.2168

 $\Delta H_f^\circ = \text{Unknown}$ $\Delta H_f^\circ_{298.15} = [-230 \pm 15] \text{ kcal/mol}$ $\Delta H_m^\circ = [9 \pm 2] \text{ kcal/mol}$ $\Delta H_s^\circ_{298.15} = [96.6] \text{ kcal/mol}$ $S^\circ_{298.15} = [18 \pm 2] \text{ gibbs/mol}$ $T_m = [1175 \pm 150]^\circ \text{K}$

Heat of Formation

More recent thermal data related to the heat of formation of ZrF₂(c) is unavailable. The adopted $\Delta H_f^\circ_{298}(\text{ZrF}_2, \text{c})$ value is taken from (1) which was estimated by Brewer (2).

Heat Capacity and Entropy

The heat capacities in the temperature range 298-2000°K are estimated by comparison with those of ZrF₄(c) and Zr(c). The S°_{298} is calculated as 17.2 and 17.0 eu based on the assumptions that $S(\text{ZrF}_2) = 1/2[S(\text{ZrF}_4) + S(\text{Zr})]$ and $S(\text{ZrF}_2) = S(\text{ZrF}_2) - S(\text{Zr}) + S(\text{Zr})$. Using the additive entropy constants $S^\circ_{298} = 12.1$ and 4.7 eu for Zr and F suggested by Kubaschewski and Evans (3), we obtain $S^\circ_{298}(\text{ZrF}_2, \text{c}) = 12.1 + 2(4.7) = 21.5$ eu. Based on $S^\circ_{298} = 11.5$ and 3.9 eu for Zr* and F* recommended by Kelley (4), the value $S^\circ_{298}(\text{ZrF}_2, \text{c})$ is derived as 19.3 eu. The entropy at 298°K for ZrF₂(c) is tentatively adopted as 18 ± 2 eu.

Melting Data

Both T_m and ΔH_m° are estimated. The derived entropy of melting, 2.55 eu/atom, is the same as that of ZrF₄(c) which was obtained from experimental measurements (5). Therefore these estimated values are tentatively adopted.

Heat of Sublimation

The difference between $\Delta H_f^\circ_{298}$ for ZrF₂(g) and ZrF₂(c) is $\Delta H_s^\circ_{298}$.

References

1. U. S. Natl. Bur. Std. Circ. 500, 1952.
2. L. Brewer, unpublished data, University of California, Berkeley, California.
3. O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1958.
4. K. K. Kelley, private communication, June 1960.
5. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

T, °K	Cp*	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0							
100	15,760	18,000	18,000	0.000	-230.000	-216.145	159.905
200							
298	15,780	18,098	18,000	0.029	-229.996	-216.072	158.865
300	16,700	22,766	18,631	1.654	-229.764	-214.130	116.995
400	17,500	26,560	19,850	3.365	-229.511	-210.252	91.901
500							
600	18,000	29,638	21,050	5.151	-229.235	-206.426	75.190
700	18,400	32,687	22,684	7.002	-228.981	-202.687	63.749
800	19,270	35,228	24,096	8.906	-228.636	-198.912	54.340
900	19,700	37,523	25,462	10.655	-228.325	-195.215	47.405
1000	20,080	39,619	26,775	12.684	-228.010	-191.553	41.864
1100	20,380	41,587	28,031	15.068	-227.695	-187.923	37.337
1200	20,650	43,332	29,233	17,919	-227.377	-184.269	33.560
1300	20,890	44,995	30,382	18,987	-227.056	-180.624	30.366
1400	21,100	46,551	31,482	21,097	-226.734	-177.016	27.633
1500	21,230	48,011	32,536	23,213	-226.411	-173.443	25.271
1600	21,350	49,386	33,546	25,343	-226.082	-169.905	23.208
1700	21,420	50,682	34,517	27,481	-225.750	-166.394	21.391
1800	21,490	51,909	35,449	29,627	-225.416	-162.914	19.741
1900	21,500	53,071	36,346	31,777	-225.071	-159.459	18.342
2000	21,500	54,174	37,210	33,927	-224.720	-156.027	17.050

$$S_{298.15}^{\circ} = [24.103] \text{ gibbs/mol}$$

$$\Delta H_f^{\circ}{}_{298.15} = [-222.502] \text{ kcal/mol}$$

$$T_m = [1175 \pm 150]^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = [9 \pm 2] \text{ kcal/mol}$$

$$T_b = [2529]^{\circ}\text{K}$$

$$\Delta H_v^{\circ} = [69.0] \text{ kcal/mol}$$

Heat of Formation

The $\Delta H_f^{\circ}{}_{298}(l)$ is obtained from $\Delta H_f^{\circ}{}_{298}(c)$ by adding ΔH_m° and the difference between H_{1175}° - H_{298}° for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated from those of $ZrF_4(l)$, $CaF_2(l)$, and $Ca(l)$, and is assumed to be constant in the temperature range 800-3000°K. A glass transition temperature is assumed at 800°K. The Cp values below 800°K are adopted from the $ZrF_2(c)$ table.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

Both T_m and ΔH_m° are estimated. The derived entropy of melting, 2.55 eu/atom, is the same as that of $ZrF_4(c)$ which was obtained from experimental measurements (1). Therefore these estimated values are tentatively adopted.

Vaporization Data

T_b is the temperature at which the Gibbs energy change of the process $ZrF_2(l) = ZrF_2(g)$ approaches zero. The difference between ΔH_f° for $ZrF_2(l)$ and $ZrF_2(g)$ at T_b is ΔH_v° .

Reference

1. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Zirconium Difluoride (ZrF₂)

$$\text{GFW} = 129.2168$$

(Liquid)

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	15.740	24.103	24.103	.000	-222.502	-212.467	155.742
300	15.740	24.201	24.103	.029	-222.498	-212.485	154.737
400	16.750	25.683	25.683	1.076	-222.507	-205.876	149.522
500	17.500	26.683	26.683	3.365	-222.013	-205.806	140.958
600	18.200	27.353	27.353	5.151	-221.737	-202.559	133.783
700	18.800	27.790	27.790	6.421	-221.443	-199.421	127.622
800	19.400	28.132	28.132	7.002	-221.137	-196.294	122.262
900	19.900	28.388	28.388	7.807	-220.820	-193.166	117.656
1000	20.400	28.608	28.608	8.848	-220.494	-190.038	113.782
1100	20.900	28.795	28.795	10.107	-219.160	-186.910	110.622
1200	21.400	28.953	28.953	11.507	-217.826	-183.782	108.162
1300	21.900	29.083	29.083	13.007	-216.492	-180.654	106.402
1400	22.400	29.193	29.193	14.507	-215.158	-177.526	105.242
1500	22.900	29.283	29.283	16.007	-213.824	-174.398	104.682
1600	23.400	29.353	29.353	17.507	-212.490	-171.270	104.622
1700	23.900	29.403	29.403	19.007	-211.156	-168.142	105.062
1800	24.400	29.433	29.433	20.507	-209.822	-165.014	106.002
1900	24.900	29.453	29.453	22.007	-208.488	-161.886	107.442
2000	25.400	29.463	29.463	23.507	-207.154	-158.758	109.382
2100	25.900	29.463	29.463	25.007	-205.820	-155.630	111.822
2200	26.400	29.453	29.453	26.507	-204.486	-152.502	114.762
2300	26.900	29.433	29.433	28.007	-203.152	-149.374	118.202
2400	27.400	29.403	29.403	29.507	-201.818	-146.246	122.142
2500	27.900	29.363	29.363	31.007	-200.484	-143.118	126.582
2600	28.400	29.313	29.313	32.507	-199.150	-140.000	131.522
2700	28.900	29.253	29.253	34.007	-197.816	-136.872	136.962
2800	29.400	29.183	29.183	35.507	-196.482	-133.744	142.902
2900	29.900	29.103	29.103	37.007	-195.148	-130.616	149.342
3000	30.400	29.013	29.013	38.507	-193.814	-127.488	156.282

Dec. 31, 1960; June 30, 1961; June 30, 1969

GFV = 129.2168

(IDEAL GAS)

ZIRCONIUM DIFLUORIDE (ZrF₂)

Point Group C_{2v}

ΔH_{f0}⁰ = -132.8 ± 5 kcal/mol
ΔH_{f298.15}⁰ = -133.4 ± 5 kcal/mol

S_{298.15}⁰ = 167.7 ± 2.1 gibbs/mol

Ground State Quantum Weight = {3}

Zirconium Difluoride (ZrF₂)
(Ideal Gas)

GFV = 129.2168

T, °K	Cp ⁰	gibbs/mol S ⁰	-(G ⁰ -H ⁰ ₃₀₀)/T	H ⁰ -H ⁰ ₃₀₀	kcal/mol ΔH ⁰	ΔG ⁰	Log Kp
0	0.000	0.000	INFINITE	2.827	-132.796	-132.796	INFINITE
100	6.509	56.898	77.059	2.020	-132.866	-134.161	293.243
200	10.289	83.336	66.741	1.081	-133.161	-135.352	147.906
298	11.626	87.715	61.715	0.000	-133.400	-136.368	99.960
300	11.647	87.787	61.716	0.022	-133.403	-136.366	99.357
400	12.437	91.257	58.143	1.229	-133.569	-137.352	75.045
500	12.896	94.066	56.090	2.498	-133.778	-138.272	60.439
600	13.176	96.466	54.126	3.803	-133.983	-139.151	50.646
700	13.351	98.509	52.181	5.130	-134.213	-139.995	43.708
800	13.481	100.302	50.211	6.472	-134.470	-140.804	38.466
900	13.572	101.895	48.200	7.825	-134.755	-141.579	34.360
1000	13.646	103.329	46.143	9.186	-135.068	-142.321	31.104
1100	13.711	104.632	44.054	10.554	-135.409	-143.030	28.417
1200	13.766	105.828	41.928	11.928	-135.768	-143.655	26.163
1300	13.804	106.934	39.766	13.309	-136.144	-144.231	24.207
1400	13.818	107.962	37.566	14.697	-136.534	-144.791	22.603
1500	13.999	108.925	35.329	16.093	-137.999	-145.334	21.175
1600	14.086	109.831	33.066	17.497	-138.538	-145.863	19.924
1700	14.180	110.688	30.786	18.910	-139.080	-146.375	18.816
1800	14.277	111.501	28.495	20.333	-139.630	-146.875	17.833
1900	14.378	112.276	26.196	21.766	-140.186	-147.359	16.950
2000	14.479	113.016	23.890	23.209	-140.753	-147.859	16.154
2100	14.581	113.725	21.581	24.662	-141.328	-148.289	15.433
2200	14.680	114.406	19.261	26.125	-141.910	-148.658	14.776
2300	14.777	115.060	16.936	27.598	-142.496	-148.975	14.175
2400	14.870	115.691	14.606	29.080	-143.078	-149.243	13.633
2500	14.959	116.300	12.271	30.572	-143.657	-149.466	13.156
2600	15.043	116.888	9.936	32.072	-144.232	-149.646	12.749
2700	15.123	117.458	7.596	33.580	-144.802	-149.782	12.397
2800	15.198	118.009	5.261	35.096	-145.363	-149.882	12.097
2900	15.268	118.543	2.936	36.620	-145.919	-149.946	11.846
3000	15.334	119.062	0.616	38.150	-146.470	-149.986	11.646
3100	15.395	119.566	-1.704	39.684	-147.016	-149.992	11.496
3200	15.453	120.056	-4.031	41.222	-147.558	-149.970	11.292
3300	15.507	120.532	-6.356	42.777	-148.096	-149.922	11.036
3400	15.559	120.996	-8.681	44.330	-148.630	-149.846	10.736
3500	15.607	121.447	-11.006	45.886	-149.158	-149.736	10.396
3600	15.652	121.888	-13.331	47.441	-149.681	-149.596	10.016
3700	15.696	122.317	-15.656	48.996	-150.199	-149.426	9.596
3800	15.738	122.736	-17.981	50.551	-150.712	-149.226	9.136
3900	15.778	123.146	-20.306	52.106	-151.220	-148.996	8.636
4000	15.816	123.546	-22.631	53.661	-151.724	-148.736	8.096
4100	15.853	123.937	-24.956	55.216	-152.224	-148.446	7.516
4200	15.889	124.319	-27.281	56.771	-152.719	-148.126	6.896
4300	15.924	124.693	-29.606	58.326	-153.210	-147.776	6.236
4400	15.957	125.060	-31.931	59.881	-153.696	-147.406	5.536
4500	15.990	125.419	-34.256	61.436	-154.176	-146.916	4.796
4600	16.021	125.771	-36.581	62.991	-154.651	-146.406	4.036
4700	16.051	126.115	-38.906	64.546	-155.121	-145.876	3.276
4800	16.081	126.454	-41.231	66.101	-155.576	-145.326	2.516
4900	16.109	126.786	-43.556	67.656	-156.026	-144.756	1.756
5000	16.137	127.111	-45.881	69.211	-156.471	-144.166	1.006
5100	16.163	127.431	-48.206	70.766	-156.911	-143.556	0.246
5200	16.188	127.746	-50.531	72.321	-157.346	-142.926	-0.516
5300	16.212	128.054	-52.856	73.876	-157.776	-142.276	-1.276
5400	16.235	128.359	-55.181	75.431	-158.201	-141.606	-2.036
5500	16.257	128.655	-57.506	76.986	-158.621	-140.916	-2.796
5600	16.277	128.948	-59.831	78.541	-159.036	-140.206	-3.556
5700	16.297	129.237	-62.156	80.096	-159.446	-139.476	-4.316
5800	16.314	129.520	-64.481	81.651	-159.851	-138.726	-5.076
5900	16.331	129.799	-66.806	83.206	-160.251	-137.966	-5.836
6000	16.346	130.074	-69.131	84.761	-160.646	-137.196	-6.596

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	Log K _p
0					
100	21.750	23.500	0.000	-249.000	170.341
200	21.800	23.635	0.040	-248.960	169.215
300	21.800	23.635	0.040	-248.960	169.215
400	21.800	23.635	0.040	-248.960	169.215
500	21.800	23.635	0.040	-248.960	169.215
600	21.800	23.635	0.040	-248.960	169.215
700	21.800	23.635	0.040	-248.960	169.215
800	21.800	23.635	0.040	-248.960	169.215
900	21.800	23.635	0.040	-248.960	169.215
1000	21.800	23.635	0.040	-248.960	169.215
1100	21.800	23.635	0.040	-248.960	169.215
1200	21.800	23.635	0.040	-248.960	169.215
1300	21.800	23.635	0.040	-248.960	169.215
1400	21.800	23.635	0.040	-248.960	169.215
1500	21.800	23.635	0.040	-248.960	169.215
1600	21.800	23.635	0.040	-248.960	169.215
1700	21.800	23.635	0.040	-248.960	169.215
1800	21.800	23.635	0.040	-248.960	169.215
1900	21.800	23.635	0.040	-248.960	169.215
2000	21.800	23.635	0.040	-248.960	169.215

ΔH_f^o = UnknownΔH_f^o 298.15 = -249 ± 3 kcal. mole⁻¹ΔH_f^o 298.15 = [52.6] kcal. mole⁻¹S_{298.15}^o = [23.5 ± 2] cal. deg.⁻¹ mole⁻¹T_g = [1200]*K.

Heat of Formation.

The equilibrium pressures for the reaction $2\text{FeF}_3(\text{c}) + \text{H}_2(\text{g}) = 2\text{Fe}(\text{g}) + 2\text{HF}(\text{g})$ have been measured at temperatures 623, 723 and 823°K. by K. Jellinek and A. Rudat, Z. anorg. allgem. Chem. 175, 281 (1928). Using the reported data, the enthalpy change of the reaction was evaluated as 37.9 and 31.3 kcal. mole⁻¹ by the third and second law methods, respectively. The corresponding ΔH_f° 298.15 (FeF₃, c) values are calculated to be -252.4 and -249.2 kcal. mole⁻¹. The equilibrium constants for the reaction $2\text{FeF}_3(\text{c}) + 3\text{H}_2\text{O}(\text{g}) = \text{Fe}_2\text{O}_3(\text{c}) + 6\text{HF}(\text{g})$ were determined by L. Donange, Ann. Chim., 7, 225 (1937). Based on the third law value of ΔH_f° 298.15° 62.0 kcal. mole⁻¹, the ΔH_f° 298.15 (FeF₃, c) was calculated as -237.4 kcal. mole⁻¹. The value of ΔH_f° 298.15 for FeF₃(c) is selected to be -249 ± 3 kcal. mole⁻¹.

Heat Capacity and Entropy.

The heat capacities of FeF₃(c) at temperatures 100-450°K. were determined by H. Bizette, R. Mainard and J. Picard, Comp. rend. 5508 (1965). The results were presented graphically by plotting C_p vs. T. The C_p curve shows a peak at 367°K. An antiferromagnetic transition at about 394°K. was reported by E. O. Wollan, H. R. Child, W. C. Koshler and M. K. Wilkinson, Phys. Rev. 112, 1132 (1958). The heat capacities above 450°K. and 6298.15 were estimated by comparison with those for FeCl₃(c) AlCl₃(c) and AlF₃(c).

Sublimation Data.

The phenomenon that FeF₃(c) sublimes without fusion at temperatures near 1000°C has been observed and reported by Poulenc, Ann. Chim. phys. (7), 2, 1 (1894). Based on this data the value of T_m was estimated. The value of heat of sublimation (ΔH_s° 298.15) was calculated using an estimated entropy of sublimation, $\Delta S_s^\circ = 40$ e.u. in order to have $\Delta H_s^\circ = 0$ for the reaction $\text{FeF}_3(\text{c}) = \text{FeF}_3(\text{g})$ at 1200°K.

Iron Trifluoride (FeF₃)

(Ideal Gas) Mol. Wt. = 112.8422



MOL. WT. = 112.8422

IRON TRIFLUORIDE (FeF₃) (IDEAL GAS)

Point Group [D_{3h}]
 $S_{298.15}^\circ = [72.7] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = [1]
 $\Delta H_f^\circ 0 = [-195.5 \pm 5] \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = [-196.2 \pm 5] \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies
 $\omega, \text{ cm.}^{-1}$

[600] (1) [800] (2)
 [250] (1) [220] (2)

Bond Distance: Fe-F = [1.9] cm.⁻¹
 Bond Angle: F-Fe-F = [120]°
 Product of the Moments of Inertia: $I_A I_B I_C = [9.96723 \times 10^{-114}] \text{ g.}^3 \text{ cm.}^6$
 $\sigma^\circ = [6]$

Heat of Formation.

The value of $\Delta H_f^\circ 298.15$ (FeF₃, g) was calculated from $\Delta H_f^\circ 298.15$ and $\Delta H_f^\circ 298.15$ for FeF₃(c). The value $\Delta H_f^\circ 298.15 = 65.5 \text{ kcal. mole}^{-1}$ was derived from $\Delta H_f^\circ 1200$ (see FeF₃(c) table for details).

Heat Capacity and Entropy.

The molecular structure, bond distance and angle were estimated by comparison with those for AlF₃(g). The vibrational frequencies were estimated by comparison with those for AlF₃(g), TiF₃(g) and ZrF₃(g). The three principal moments of inertia are: $I_A = I_B = 1.7081 \times 10^{-38} \text{ g. cm.}^2$ and $I_C = 3.4162 \times 10^{-38} \text{ g. cm.}^2$.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f [°]	ΔF _f [°]	Log K _p
0	+0.00	INFINITE	-3.539	-195.499	-195.499	INFINITE
100	10.557	58.478	85.163	-195.474	-195.371	426.063
200	13.644	66.840	74.063	-196.022	-194.867	212.930
298	15.666	72.690	66.000	-196.200	-194.259	142.389
300	15.697	72.787	65.900	-196.203	-194.247	141.502
400	17.027	77.500	73.423	-196.343	-193.573	105.758
500	17.858	81.396	76.560	-196.481	-192.866	84.298
600	18.389	84.702	79.982	-196.644	-192.128	69.979
700	18.782	87.525	82.805	-196.832	-191.356	59.742
800	19.086	90.084	85.263	-197.047	-190.552	51.565
900	19.310	92.331	87.437	-197.288	-189.713	45.066
1000	19.488	94.357	89.337	-197.557	-188.820	40.264
1100	19.625	96.200	91.000	-197.845	-187.851	37.321
1200	19.728	97.890	92.560	-198.152	-186.807	35.045
1300	19.800	99.450	94.040	-198.477	-185.681	33.313
1400	19.856	100.898	95.473	-198.819	-184.484	32.005
1500	19.895	102.250	96.870	-199.177	-183.225	30.981
1600	19.927	103.516	98.233	-199.550	-181.913	29.995
1700	19.953	104.700	99.567	-199.937	-180.558	28.998
1800	19.974	105.832	100.877	-200.338	-179.162	27.948
1900	19.990	106.920	102.159	-200.753	-177.728	26.799
2000	19.999	107.980	103.410	-201.182	-176.257	25.595
2100	19.999	108.970	104.633	-201.625	-174.750	24.285
2200	19.990	109.900	105.827	-202.082	-173.208	22.918
2300	19.977	110.667	106.990	-202.553	-171.632	21.445
2400	19.957	111.308	108.123	-203.038	-170.023	20.018
2500	19.935	112.315	109.233	-203.537	-168.382	18.587
2600	19.909	113.091	110.316	-204.050	-166.710	17.155
2700	19.882	113.691	111.373	-204.577	-165.018	15.733
2800	19.854	114.157	112.406	-205.118	-163.307	14.330
2900	19.825	114.500	113.416	-205.673	-161.578	12.931
3000	19.804	115.252	114.403	-206.242	-159.832	11.801
3100	19.800	115.272	115.373	-206.825	-158.070	10.804
3200	19.800	115.272	116.316	-207.422	-156.294	9.907
3300	19.816	116.000	117.233	-208.033	-154.505	9.104
3400	19.819	116.403	118.123	-208.657	-152.696	8.381
3500	19.822	116.977	119.000	-209.294	-150.868	7.733
3600	19.825	117.596	119.867	-209.944	-149.023	7.155
3700	19.828	120.079	120.723	-210.607	-147.162	6.639
3800	19.830	120.608	121.573	-211.284	-145.287	6.176
3900	19.832	121.123	122.406	-211.973	-143.398	5.763
4000	19.834	121.625	123.223	-212.673	-141.494	5.398
4100	19.836	122.115	124.027	-213.384	-139.576	5.081
4200	19.838	122.593	124.816	-214.106	-137.644	4.804
4300	19.839	123.060	125.590	-214.839	-135.696	4.568
4400	19.841	123.516	126.350	-215.584	-133.733	4.369
4500	19.842	123.962	127.096	-216.341	-131.756	4.200
4600	19.844	124.398	127.827	-217.110	-129.765	4.059
4700	19.845	124.825	128.543	-217.891	-127.759	3.944
4800	19.846	125.242	129.246	-218.684	-125.738	3.854
4900	19.847	125.652	129.935	-219.489	-123.703	3.787
5000	19.848	126.053	130.610	-220.306	-121.656	3.740
5100	19.849	126.446	131.273	-221.134	-119.600	3.703
5200	19.850	126.831	131.923	-221.973	-117.535	3.676
5300	19.851	127.209	132.560	-222.824	-115.460	3.658
5400	19.851	127.580	133.183	-223.687	-113.376	3.649
5500	19.852	127.945	133.793	-224.562	-111.283	3.640
5600	19.853	128.302	134.390	-225.449	-109.181	3.634
5700	19.854	128.654	134.973	-226.347	-107.071	3.634
5800	19.854	128.999	135.543	-227.256	-104.954	3.634
5900	19.855	129.338	136.100	-228.176	-102.831	3.634
6000	19.855	129.672	136.643	-229.106	-100.703	3.634



Trifluorosilane (SiHF₃)
(Ideal Gas) Mol. Wt. = 86.098

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	INFINITE	3.249	-281.316	-281.316	INFINITE	INFINITE
100	7.337	66.317	66.317	1.000	-281.316	-281.316	201.668	30.173
200	12.146	66.317	66.317	1.000	-281.316	-281.316	201.668	201.668
300	15.146	66.317	66.317	1.028	-281.008	-281.008	200.369	
400	17.453	71.102	68.941	1.664	-283.383	-283.383	188.816	
500	19.163	75.190	68.191	3.499	-283.657	-283.657	117.036	
600	20.433	78.401	69.664	5.482	-283.865	-283.865	97.166	
700	21.392	82.027	71.204	7.576	-283.969	-283.969	82.393	
800	22.112	84.933	72.762	9.753	-284.046	-284.046	71.310	
900	22.712	87.575	74.285	11.997	-284.086	-284.086	62.687	
1000	23.173	89.993	75.701	14.292	-284.103	-284.103	55.769	
1100	23.545	92.219	77.103	16.628	-284.099	-284.099	50.145	
1200	23.847	94.281	78.449	18.998	-284.080	-284.080	45.441	
1300	24.096	96.200	79.742	21.396	-284.051	-284.051	41.442	
1400	24.303	97.994	80.982	23.816	-284.014	-284.014	38.051	
1500	24.476	99.677	82.125	26.255	-283.973	-283.973	35.056	
1600	24.623	101.261	83.317	28.711	-283.930	-283.930	32.510	
1700	24.747	102.758	84.417	31.179	-283.890	-283.890	30.215	
1800	24.854	104.175	85.476	33.660	-283.846	-283.846	28.102	
1900	24.947	105.522	86.496	36.150	-283.804	-283.804	26.211	
2000	25.027	106.803	87.479	38.648	-283.729	-283.729	24.510	
2100	25.097	108.026	88.429	41.155	-283.642	-283.642	22.972	
2200	25.158	109.195	89.346	43.666	-283.558	-283.558	21.573	
2300	25.212	110.315	90.234	46.186	-283.474	-283.474	20.297	
2400	25.260	111.389	91.093	48.710	-283.394	-283.394	19.127	
2500	25.303	112.421	91.926	51.238	-283.316	-283.316	18.052	
2600	25.341	113.414	92.733	53.770	-283.243	-283.243	17.059	
2700	25.376	114.371	93.517	56.306	-283.171	-283.171	16.140	
2800	25.407	115.294	94.278	58.845	-283.102	-283.102	15.287	
2900	25.435	116.187	95.018	61.387	-283.037	-283.037	14.492	
3000	25.460	117.049	95.739	63.932	-282.977	-282.977	13.752	
3100	25.483	117.884	96.440	66.479	-282.918	-282.918	13.059	
3200	25.504	118.694	97.122	69.029	-282.864	-282.864	12.409	
3300	25.523	119.479	97.786	71.580	-282.813	-282.813	11.798	
3400	25.541	120.241	98.437	74.133	-282.766	-282.766	11.224	
3500	25.557	120.982	99.071	76.688	-282.725	-282.725	10.683	
3600	25.572	121.702	99.690	79.245	-282.661	-282.661	10.183	
3700	25.585	122.403	100.294	81.802	-282.595	-282.595	9.704	
3800	25.598	123.085	100.885	84.362	-282.528	-282.528	9.248	
3900	25.610	123.750	101.463	86.922	-282.462	-282.462	8.824	
4000	25.620	124.399	102.028	89.483	-282.397	-282.397	8.424	
4100	25.631	125.032	102.581	92.046	-282.330	-282.330	8.046	
4200	25.640	125.649	103.123	94.609	-282.264	-282.264	7.690	
4300	25.649	126.253	103.654	97.178	-282.198	-282.198	7.356	
4400	25.657	126.842	104.174	99.739	-282.132	-282.132	7.042	
4500	25.665	127.419	104.685	102.305	-282.066	-282.066	6.747	
4600	25.672	127.983	105.185	104.872	-282.000	-282.000	6.470	
4700	25.679	128.535	105.676	107.440	-281.934	-281.934	6.210	
4800	25.685	129.076	106.158	110.008	-281.868	-281.868	5.964	
4900	25.691	129.606	106.631	112.577	-281.802	-281.802	5.731	
5000	25.696	130.125	107.096	115.146	-281.736	-281.736	5.506	
5100	25.702	130.634	107.552	117.716	-281.670	-281.670	5.295	
5200	25.707	131.133	108.001	120.286	-281.604	-281.604	5.096	
5300	25.711	131.623	108.442	122.857	-281.538	-281.538	4.908	
5400	25.716	132.103	108.876	125.429	-281.472	-281.472	4.731	
5500	25.720	132.575	109.302	128.000	-281.406	-281.406	4.564	
5600	25.724	133.039	109.722	130.573	-281.340	-281.340	4.406	
5700	25.728	133.494	110.135	133.146	-281.274	-281.274	4.256	
5800	25.732	133.942	110.542	135.718	-281.208	-281.208	4.114	
5900	25.735	134.381	110.942	138.291	-281.142	-281.142	3.977	
6000	25.738	134.814	111.336	140.865	-281.076	-281.076	3.844	

December 31, 1960.

Trifluorosilane (SiHF₃)
(Ideal Gas)

Mol. Wt. = 86.098

ΔH_f^o 298.15 = [-283 ± 15] kcal. mole⁻¹S_{298.15} = 66.304 cal. deg.⁻¹ mole⁻¹Point Group C_{3v}

Vibrational Frequencies and Degeneracies

ω cm. ⁻¹	
2315 (1)	999 (2)
859 (1)	844 (2)
425 (1)	305 (2)

Moments of Inertia: I_A = 11.7272 X 10⁻³⁹ g. cm.² I_C = 20.6927 X 10⁻³⁹ g. cm.² σ = 3

Heat of Formation. ΔH_f^o 298.15 was found estimated in C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

Heat Capacity and Entropy. Vibrational levels and multiplicities were assigned by C. Newman, S. Polo and M. Wilson, Spec. Chim. Acta 15, 793 (1959). Constants used in calculating moment of inertia came from G. Heath, L. Thomas, and J. Sheridan, Trans. Far. Soc. 50, 779 (1954).

Lithium Fluoride, Trimeric (Li_3F_3)

(Ideal Gas) $\text{GFW} = 77.8122$

LITHIUM FLUORIDE, TRIMERIC (Li₃F₃)

(IDEAL GAS)

GFW = 77.8122

Point Group $[D_{2h}]$
$$\Delta H_f^\circ = -361.02 \pm 6.0 \text{ kcal/mol}$$
 $\Delta G_{298}^{\circ} = [76 \pm 2] \text{ kJ/mol}$
$$\Delta H_{f, 298.15}^{\circ} = -362.62 \pm 6.0 \text{ kcal/mol}$$

Ground State Quantum Weight = [1]

weight = [1]
Vibrational Frequencies and Degeneracies

Bond Distance: Li-F = [1.68] Å

Bond Angles: $F-Li-F = 120^\circ$ $Li-F-Li = 120^\circ$

Product of the Moments of Inertia: $I_{YY} = [1.2122 \times 10^{-11}] \text{ cm}^6$

Heat of Formation

The heat of formation (ΔH_f°) is based on the adopted value $\Delta H_{298}^\circ = 79.73$ kcal/mol for the reaction $3\text{LiF}(c) = \text{Li}_3\text{F}_3(g)$, using $\Delta H_f^\circ(\text{LiF}, c) = -147.45$ kcal/mol. The ΔH_{298}° value is calculated to be 73.9 kcal/mol at 1000°K, which is in good agreement with the values $\Delta H_{1000}^\circ = 73.9 \pm 3$ and 74.9 ± 1 kcal/mol reported by Buchler and Stauffer (3) and Aikshin et al. (2), respectively. Using the adopted ΔH_{298}° values for monomer, dimer, and trimer, we also evaluate the value $\Delta H_{298}^\circ(\text{Li}_3\text{F}_3, g) = 53.8$ kcal/mol for the reaction $\text{Li}_3\text{F}_3(g) = \text{Li}_2\text{F}_2(g) + \text{LiF}(g)$ which is in agreement with the value 50 ± 4 kcal/mol reported by Porter and Schoonmaker (3). Rothberg et al. (4) have determined the partial pressures of LiF monomer, dimer, and trimer in the temperature range 980–1070°K, using the molecular-beam velocity-selector method (5). However, the total pressures derived from these data are too low in comparison with the other reported vapor pressures. Thus our data are not adopted for evaluation.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of the BeO trimer. The Li-F bond distance is taken from that of the Li_2F_2 molecule determined by Akishin and Rambidi (6). Four vibrational frequencies, ν_1 and three ν_2 , are reported by Shelnov (7) from analysis of the infrared spectra of LiF using the matrix isolation technique. The reported frequencies are corrected to the average isotopic species. The other four frequencies, ν_3 and three ν_4 , are estimated by comparison with those for the isoelectronic molecule Be_3O_3 . The three principal moments of inertia are $I_A = I_B = 0.923 \times 10^{-38}$ and $I_C = 3.646 \times 10^{-38}$ g cm².

References

1. A. Büchler and J. C. Stauffer, "Thermodynamics," Vol. I, International Atomic Agency, Vienna, 1966, p. 271.
2. P. A. Axilshin, L. N. Gorokhov, and L. N. Sidorov, *Russ. J. Phys. Chem. (English Transl.)* **33**, 848 (1959).
3. R. F. Porter and R. C. Schoonmaker, *J. Chem. Phys.* **29**, 1070 (1958).
4. G. M. Rotberg, M. Eisenstadt, and P. Kusch, *J. Chem. Phys.* **30**, 517 (1959).
5. P. C. Miller and P. Kusch, *J. Chem. Phys.* **23**, 860 (1956); **27**, 991 (1957).
6. P. A. Axilshin and N. G. Rambid, *Physik. Chem.* **213**, 111 (1960).
7. A. Snelson, ITRR-U6001-13, 14 May 1963 - 12 August 1966, Illinois Institute of Technology Research Institute, Chicago, Illinois.

T, °K	C _p ^a	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	H ^b -H ^c ₂₉₈	ΔH°	kcal/mol	ΔG°	Log K ^d
0	11.900	INFINITE	-	-0.883	-361.053	-361.053	361.053	INFINITE
10	11.943	55.008	94.436	-1.902	-360.371	-360.371	360.371	787.596
20	26.151	67.065	78.114	2.210	-362.119	-359.024	359.024	394.323
298	24.498	75.997	75.997	2.000	-362.650	-357.392	357.392	261.975
300	24.559	76.149	75.997	2.005	-362.659	-357.360	357.360	260.337
400	26.534	69.804	75.953	5.625	-365.731	-353.382	353.382	154.463
500	29.429	95.972	81.214	8.137	-366.217	-348.863	348.863	127.802
600	30.008	98.675	83.531	11.301	-366.619	-348.214	348.214	108.736
800	30.402	103.709	85.806	14.382	-366.937	-347.450	347.450	94.422
900	30.680	107.551	87.967	17.356	-367.183	-346.587	346.587	81.472
1000	30.864	110.551	90.994	20.356	-367.365	-345.677	345.677	70.456
1100	31.037	113.502	92.990	23.532	-367.589	-344.741	344.741	61.047
1200	31.155	116.407	93.989	26.662	-367.751	-343.680	343.680	53.953
1300	31.247	118.705	95.975	29.672	-367.858	-342.512	342.512	48.793
1400	31.321	121.023	97.515	32.671	-367.908	-341.250	341.250	44.220
1500	31.381	123.163	98.950	35.656	-367.908	-340.000	340.000	40.120
1600	31.430	125.211	100.721	39.167	-367.933	-338.760	338.760	36.463
1700	31.471	127.120	102.819	42.332	-367.876	-337.541	337.541	33.202
1800	31.506	128.920	105.253	45.481	-367.776	-336.351	336.351	30.282
1900	31.535	130.624	108.028	48.613	-367.656	-335.191	335.191	27.592
2000	31.558	132.242	109.346	51.746	-367.536	-334.061	334.061	25.120
2100	31.582	133.783	107.618	54.945	-367.351	-332.961	332.961	22.869
2200	31.605	135.252	106.841	58.104	-367.131	-331.891	331.891	20.800
2300	31.617	136.657	110.020	61.245	-366.886	-330.851	330.851	18.900
2400	31.631	138.003	111.156	64.467	-366.626	-329.841	329.841	17.169
2500	31.644	139.243	112.250	67.751	-366.356	-328.851	328.851	15.590
2600	31.655	140.436	113.322	70.756	-366.086	-327.881	327.881	14.150
2700	31.665	141.531	114.352	73.932	-365.816	-326.931	326.931	12.840
2800	31.674	142.631	115.351	77.089	-365.546	-325.991	325.991	11.640
2900	31.683	143.694	116.319	80.257	-365.276	-325.061	325.061	10.540
3000	31.690	144.769	117.260	83.426	-365.006	-324.141	324.141	9.540
3100	31.696	146.108	118.174	86.595	-364.736	-323.231	323.231	8.640
3200	31.702	147.114	119.063	89.765	-364.466	-322.331	322.331	7.840
3300	31.708	148.090	119.928	92.935	-364.196	-321.441	321.441	7.140
3400	31.713	149.036	120.770	96.106	-363.926	-320.551	320.551	6.540
3500	31.718	149.956	121.591	99.278	-363.656	-319.661	319.661	6.040
3600	31.722	150.849	122.391	102.450	-363.386	-318.771	318.771	5.540
3700	31.726	151.749	123.172	105.652	-363.116	-317.881	317.881	5.040
3800	31.729	152.565	123.934	108.785	-362.846	-316.991	316.991	4.540
3900	31.733	153.386	124.679	111.968	-362.576	-316.101	316.101	4.040
4000	31.736	154.192	125.407	115.181	-362.306	-315.211	315.211	3.540
4100	31.738	154.976	126.119	118.415	-362.036	-314.321	314.321	3.040
4200	31.741	155.741	126.815	121.663	-361.766	-313.431	313.431	2.540
4300	31.744	156.488	127.496	124.931	-361.496	-312.541	312.541	2.040
4400	31.746	157.218	128.163	128.219	-361.226	-311.651	311.651	1.540
4500	31.748	157.931	128.817	131.513	-360.956	-310.761	310.761	1.040
4600	31.750	158.629	129.458	134.817	-360.686	-309.871	309.871	0.540
4700	31.752	159.312	130.086	138.137	-360.416	-308.981	308.981	0.040
4800	31.754	159.980	130.701	141.463	-360.146	-308.091	308.091	-0.460
4900	31.756	160.635	131.306	144.795	-359.876	-307.201	307.201	-0.960
5000	31.757	161.276	131.899	148.069	-359.606	-306.311	306.311	-1.460
5100	31.758	161.905	132.481	151.345	-359.336	-305.421	305.421	-1.960
5200	31.760	162.522	133.053	154.617	-359.066	-304.531	304.531	-2.460
5300	31.761	163.127	133.614	157.889	-358.796	-303.641	303.641	-2.960
5400	31.762	163.721	134.166	161.161	-358.526	-302.751	302.751	-3.460
5500	31.763	164.304	134.709	164.435	-358.256	-301.861	301.861	-3.960
5600	31.764	164.876	135.243	167.709	-357.986	-300.971	300.971	-4.460
5700	31.766	165.438	135.766	170.983	-357.716	-300.081	300.081	-4.960
5800	31.767	165.991	136.284	174.257	-357.446	-299.191	299.191	-5.460
5900	31.767	166.534	136.792	177.531	-357.176	-298.301	298.301	-5.960
6000	31.768	167.068	137.292	180.805	-356.906	-297.411	297.411	-6.460

Dec. 31, 1962; Sept. 30, 1962; Dec. 31, 1962.

Dec. 31, 1960; Sept. 30, 1962; Dec. 31, 1963; Dec. 31, 1968

Nitrogen Trifluoride (NF₃)

(Ideal Gas) GFW = 71.0019

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	.0000	.0000	INFINITE	= 2.832	= 30.061	INFINITE
100	8.135	51.551	71.897	= 2.035	= 27.795	60.746
200	10.224	63.387	= 1.131	= 31.147	= 24.731	27.075
298	12.756	62.299	.000	= 31.430	= 21.515	15.771
300	12.799	62.378	.024	= 31.434	= 21.454	15.629
400	14.765	66.349	62.827	= 1.409	= 18.104	9.692
500	16.149	69.804	63.685	= 2.960	= 14.740	6.443
600	17.072	72.836	65.129	= 3.153	= 11.379	4.105
700	17.708	75.518	66.426	= 3.150	= 8.033	2.508
800	18.157	77.614	67.715	= 3.179	= 4.704	1.285
900	18.484	79.072	68.970	= 3.190	= 1.390	.537
1000	18.728	82.033	70.180	= 11.853	= 1.907	.417
1100	18.914	83.827	71.340	= 13.736	= 30.442	5.190
1200	19.059	85.429	72.450	= 15.636	= 30.449	1.591
1300	19.174	87.009	73.512	= 17.547	= 30.537	11.717
1400	19.266	88.434	74.528	= 19.469	= 30.364	14.661
1500	19.342	89.766	75.499	= 21.399	= 30.237	18.196
1600	19.404	91.016	76.431	= 23.337	= 30.090	2.924
1700	19.454	92.186	77.324	= 25.280	= 29.945	3.167
1800	19.500	93.307	78.181	= 27.227	= 29.805	3.340
1900	19.537	94.363	79.005	= 29.179	= 29.666	3.479
2000	19.569	95.366	79.798	= 31.135	= 29.530	3.741
2100	19.597	96.321	80.562	= 33.093	= 29.394	3.894
2200	19.621	97.233	81.296	= 35.057	= 29.269	4.034
2300	19.642	98.106	82.011	= 37.017	= 29.143	4.159
2400	19.660	98.942	82.700	= 38.982	= 29.020	4.274
2500	19.677	99.745	83.365	= 40.949	= 28.903	4.379
2600	19.691	100.517	84.010	= 42.917	= 28.787	4.474
2700	19.704	101.262	84.636	= 44.886	= 28.670	4.564
2800	19.716	101.977	85.242	= 46.856	= 28.554	4.648
2900	19.726	102.669	85.831	= 48.830	= 28.438	4.725
3000	19.736	103.338	86.404	= 50.803	= 28.325	4.796
3100	19.744	103.985	86.961	= 52.777	= 28.217	4.863
3200	19.752	104.612	87.502	= 54.752	= 28.112	4.925
3300	19.759	105.220	88.030	= 56.728	= 28.070	4.983
3400	19.766	105.810	88.544	= 58.704	= 27.980	5.038
3500	19.771	106.383	89.046	= 60.681	= 27.895	5.089
3600	19.777	106.940	89.535	= 62.658	= 27.812	5.138
3700	19.782	107.482	90.013	= 64.636	= 27.735	5.183
3800	19.787	108.010	90.480	= 66.615	= 27.658	5.227
3900	19.791	108.524	90.936	= 68.593	= 27.587	5.267
4000	19.795	109.025	91.382	= 70.573	= 27.517	5.306
4100	19.799	109.514	91.818	= 72.552	= 27.453	5.342
4200	19.802	109.991	92.246	= 74.531	= 27.390	5.377
4300	19.805	110.457	92.663	= 76.513	= 27.331	5.410
4400	19.808	110.912	93.073	= 78.493	= 27.277	5.442
4500	19.811	111.358	93.474	= 80.474	= 27.225	5.472
4600	19.814	111.793	93.868	= 82.456	= 27.176	5.501
4700	19.816	112.219	94.264	= 84.439	= 27.131	5.528
4800	19.818	112.636	94.652	= 86.419	= 27.080	5.554
4900	19.820	113.045	95.034	= 88.401	= 27.051	5.580
5000	19.822	113.446	95.399	= 90.383	= 27.017	5.604
5100	19.824	113.838	95.757	= 92.365	= 26.985	5.627
5200	19.826	114.223	96.109	= 94.349	= 26.932	5.650
5300	19.828	114.601	96.459	= 96.332	= 26.881	5.671
5400	19.829	114.971	96.765	= 98.313	= 26.812	5.691
5500	19.831	115.335	97.099	= 100.296	= 26.694	5.711
5600	19.832	115.683	97.428	= 102.279	= 26.680	5.730
5700	19.833	116.024	97.750	= 104.264	= 26.661	5.746
5800	19.835	116.399	98.070	= 106.246	= 26.654	5.763
5900	19.836	116.728	98.384	= 108.230	= 26.654	5.783
6000	19.837	117.061	98.692	= 110.213	= 26.654	5.800

Dec. 31, 1960; Mar. 31, 1961; Mar. 31, 1964; June 30, 1969

Vibrational Frequencies and Degeneracies

 $\frac{\omega_e}{\text{cm}^{-1}}$

1032 (1)

642 (1)

906 (2)

492 (2)

 $\sigma = 3$

Bond Distance: N-F = 1.371 Å

Bond Angle: F-N-F = 102.9°

Product of the Moments of Inertia: $I_A I_B I_C = 8.855 \times 10^{-115} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The adopted heat of formation was obtained from a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, g table 12-31-68). The data which was considered relating directly to NF₃ was as follows.

A. $8 \text{ NF}_3(\text{g}) + 3 \text{ C}_2\text{H}_4(\text{g}) \rightarrow 6 \text{ CF}_4(\text{g}) + 7 \text{ N}_2(\text{g})$ Walker (1) reported $\Delta H_r^\circ = -1308.8 \pm 1.3 \text{ kcal/mol}$.B. $\text{NF}_3(\text{g}) + 1.5 \text{ H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g}) + 0.5 \text{ N}_2(\text{g})$ Sinko (2) reported $\Delta H_r^\circ = -199.49 \pm 0.22 \text{ kcal/mol}$ for a final state of HF(123 H₂O); the corrected value is $-199.40 \pm 0.22 \text{ kcal/mol}$.C. $2 \text{ NF}_3(\text{g}) + \text{S}(\text{c, rh}) \rightarrow \text{SF}_6(\text{g}) + \text{N}_2(\text{g})$ Walker (3) reported $\Delta H_r^\circ = -228.26 \pm 0.25 \text{ kcal/mol}$.D. $\text{NF}_3(\text{g}) \rightarrow 0.5 \text{ N}_2(\text{g}) + 1.5 \text{ F}_2(\text{g})$ Sinko (4) reported $\Delta H_r^\circ = 31.44 \pm 0.3 \text{ kcal/mol}$ for the above dissociation from experimental explosion of hydrogen in 10 percent and 100 percent excess NF₃.E. $\text{NF}_3(\text{g}) + \text{H}(\text{c, p}) \rightarrow \text{BF}_3(\text{g}) + 0.5 \text{ N}_2(\text{g})$ Ludwig and Cooper (5) reported $\Delta H_r^\circ = -239.46 \pm 1.2 \text{ kcal/mol}$, 5 percent of the boron remained unreacted and was detected by analysis.

Further details of the simultaneous adjustment are given by Syverud (6).

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Schatz and Levin (7) and are in good agreement with those of Pace and Pierce (8), and Wilson and Polo (9). The adopted values are also in agreement with the Raman studies of Kotov and Tatevskii (10). The bond length and angle were from the microwave studies of Sheridan and Gordy (11), whose values are in substantial agreement with the electron diffraction results of Schomaker and Lu (12).

The individual moments of inertia are $I_A = I_B = 7.854 \times 10^{-39} \text{ g cm}^2$ and $I_C = 14.354 \times 10^{-39} \text{ g cm}^2$.

Pierce and Pace (13) have obtained the entropy of the gas at 144.15°K from solid heat capacity measurements and the heats of melting and vaporization. Their reported value of 54.50 eu is in good agreement with our calculated value of 54.56 eu.

References

1. L. C. Walker, paper presented at 22nd Annual Calorimetry Conference, Thousand Oaks, Calif., June 1967.
2. G. C. Sinko, J. Chem. Eng. Data **10**, 295 (1965).
3. L. C. Walker, J. Phys. Chem. **71**, 361 (1967).
4. G. C. Sinko, J. Phys. Chem. **71**, 359 (1967).
5. J. R. Ludwig and W. J. Cooper, J. Chem. Eng. Data **2**, 76 (1963).
6. A. N. Syverud, AFRL-TR-69-70, Jan. 1969.
7. F. N. Schatz and I. W. Levin, J. Chem. Phys. **29**, 475 (1958).
8. E. L. Pace and L. Pierce, J. Chem. Phys. **23**, 1248 (1955).
9. M. K. Wilson and S. R. Polo, J. Chem. Phys. **20**, 1716 (1952).
10. Yu. I. Kotov and V. M. Tatevskii, Opt. Spectry. (Eng. Transl.) **13**, 160 (1963), Supplement 2 Molecular Spectroscopy.
11. J. Sheridan and W. Gordy, Phys. Rev. **79**, 513 (1950).
12. V. Schomaker and C. Lu, J. Amer. Chem. Soc. **72**, 1182 (1950).
13. L. Pierce and E. L. Pace, J. Chem. Phys. **23**, 561 (1955).

(IDEAL GAS)

GFW = 87.0013

TRIFLUORAMINE OXIDE (NOF₃)Point Group C_{3v} $\Delta H_f^\circ = -37.0 \pm 5.0$ kcal/mol $S^\circ_{298.15} = 66.54 \pm 0.05$ gibbs/mol $\Delta H_f^\circ = -39.0 \pm 5.0$ kcal/mol

Ground State Quantum Weight = 1

GFW = 87.0013

Trifluoramine Oxide (NOF₃)

(Ideal Gas)

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	3.266	-	37.027	INFINITE
100	53.146	2.045	2.045	1.794	-	37.027	2.045
200	66.404	6.809	6.809	1.821	-	36.864	6.809
298	66.535	66.535	66.535	1.821	-	23.042	16.891
300	16.277	66.636	66.536	0.030	-	22.944	16.715
400	18.024	71.692	71.708	1.794	-	39.099	9.600
500	20.535	76.089	68.554	3.767	-	5.329	5.329
600	21.721	79.944	70.138	5.683	-	6.830	2.468
700	22.569	83.359	71.787	6.100	-	38.731	1.496
800	23.191	86.416	73.428	6.390	-	36.511	3.807
900	23.658	89.175	75.027	12.733	-	38.268	9.083
1000	24.016	91.687	76.569	15.116	-	38.012	14.330
1100	24.295	93.990	78.050	17.534	-	37.787	19.551
1200	24.517	96.114	79.468	19.975	-	37.476	24.749
1300	24.695	98.063	80.825	22.436	-	37.204	29.924
1400	24.840	99.919	82.124	24.913	-	36.930	35.077
1500	24.959	101.637	83.366	27.403	-	36.656	40.212
1600	25.059	103.251	84.561	29.904	-	36.384	45.326
1700	25.142	104.773	85.706	32.414	-	36.113	50.428
1800	25.213	106.212	86.805	34.932	-	35.848	55.506
1900	25.274	107.577	87.863	37.456	-	35.583	60.576
2000	25.326	108.875	88.881	39.986	-	35.323	65.632
2100	25.372	110.111	89.863	42.521	-	35.066	70.670
2200	25.412	111.293	90.810	45.061	-	34.815	75.699
2300	25.446	112.423	91.726	47.604	-	34.567	80.718
2400	25.477	113.507	92.611	50.150	-	34.325	85.726
2500	25.504	114.547	93.468	52.699	-	34.089	90.721
2600	25.528	115.548	94.298	55.251	-	33.858	95.710
2700	25.550	116.512	95.103	57.804	-	33.628	100.691
2800	25.570	117.441	95.884	60.360	-	33.400	105.659
2900	25.587	118.339	96.643	62.918	-	33.187	110.626
3000	25.603	119.207	97.381	65.478	-	32.976	115.577
3100	25.617	120.046	98.098	68.039	-	32.767	120.525
3200	25.630	120.860	98.797	70.601	-	32.565	125.467
3300	25.642	121.649	99.478	73.165	-	32.368	130.402
3400	25.653	122.414	100.141	75.730	-	32.175	135.333
3500	25.663	123.156	100.788	78.295	-	31.989	140.256
3600	25.672	123.881	101.420	80.862	-	31.805	145.179
3700	25.681	124.585	102.036	83.430	-	31.628	150.091
3800	25.689	125.270	102.639	85.998	-	31.455	155.003
3900	25.696	125.937	103.227	88.568	-	31.287	159.902
4000	25.703	126.586	103.803	91.136	-	31.123	164.804
4100	25.709	127.223	104.367	93.708	-	30.965	169.699
4200	25.715	127.842	104.918	96.279	-	30.811	174.592
4300	25.720	128.447	105.459	98.851	-	30.659	179.485
4400	25.725	129.039	105.988	101.423	-	30.515	184.367
4500	25.730	129.617	106.507	103.996	-	30.374	189.247
4600	25.734	130.182	107.015	106.569	-	30.236	194.130
4700	25.738	130.736	107.514	109.143	-	30.105	199.005
4800	25.742	131.278	108.004	111.717	-	29.976	203.882
4900	25.746	131.809	108.484	114.291	-	29.852	208.749
5000	25.749	132.329	108.956	116.866	-	29.732	213.617
5100	25.753	132.839	109.419	119.441	-	29.616	218.477
5200	25.756	133.339	109.874	122.017	-	29.504	223.347
5300	25.758	133.829	110.321	124.592	-	29.396	228.211
5400	25.761	134.311	110.761	127.166	-	29.293	233.061
5500	25.764	134.784	111.194	129.744	-	29.192	237.926
5600	25.766	135.248	111.619	132.321	-	29.097	242.781
5700	25.769	135.704	112.038	134.898	-	29.005	247.636
5800	25.771	136.152	112.450	137.475	-	28.916	252.491
5900	25.773	136.596	112.855	140.052	-	28.832	257.345
6000	25.775	137.026	113.254	142.626	-	28.751	262.197

June 30, 1970

Vibrational Frequencies and Degeneracies

ω, cm⁻¹ω, cm⁻¹

Bond Distance: N-O = [1.15] Å N-F = 1.48 ± 0.1 Å

Bond Angle: ONF = [109° 28'] ONF = [109° 28']

Product of the Moments of Inertia: I_AI_BI_C = [4.0703 × 10⁻¹¹⁴] g³ cm⁶

Heat of Formation

Bougon et al. (1) determined equilibrium constants for the reaction NOF(g) + F₂(g) ⇌ NOF₃(g) as a function of temperature and total pressure. Second and third law analyses of these equilibrium data are given below:

Set I	Set II	No. of Points	Temp. Range, °K	ΔH _f ° ₂₉₈ , kcal/mol	Drift
7	1	7	533-643	-17.1	-18.7
		1	533.2	-18.2	-2.442.1

Set I contains their equilibrium data as a function of temperature, while Set II is their adopted equilibrium constant, K_p(533.2°K) = 0.015 ± 0.005 atm.⁻¹, corresponding to the lowest pressure (103 atm.) that was studied. Estimated corrections for nonideality are small and neglected. Adopting ΔH_f°₂₉₈ = -18.7 ± 1.0 kcal/mol, we derive ΔH_f°(NOF₃, g) = -34.4 ± 1.4 kcal/mol with ΔH_f°(NOF, g) = -15.7 ± 0.4 kcal/mol (2).

Armstrong and King (3) determined ΔH_f°₃₀₀ = -253.7 ± 0.6 kcal/mol for the reaction NOF₃(g) + 5/2 H₂(g) + 122 H₂O(l) + 1/2 N₂(g) + [3HF·123 H₂O(l)] in a constant pressure flame calorimeter. Combining this result with their earlier enthalpy data for reduction reactions involving F₂(g) and O₂(g) with H₂(g), they obtained ΔH_f°₃₀₄(NOF₃, g) = -44.7 ± 1.5 kcal/mol. Very recently, Dibeir and Walker (4) investigated the photolysis of NOF₃ by mass spectrometry. From their ionization threshold data, they determined ΔH_f°₀(NOF₃, g) = -69.6 ± 1.2 kcal/mol.

The value for the heat of formation of gaseous NOF₃ is tentatively selected as -39.0 ± 5.0 kcal/mol.

Heat Capacity and Entropy

Several recent infrared (5, 6, and 7) and Raman (8) studies of NOF₃ have been reported in the literature. The fundamental vibrational frequencies observed in the infrared spectrum of the molecule by the various investigators are in good agreement, although the assignment of the ν₃ and ν₅ bending modes has varied. Fox et al. (6) assigned ν₃ = 558 cm⁻¹ and ν₅ = 528 cm⁻¹, while Curtis et al. (7) reversed the assignments. Very recently, Abramowitz and Levin (8) investigated the Raman spectrum of polycrystalline film of NOF₃ at 78°K and assigned ν₃ = 535 cm⁻¹ and ν₅ = 522 cm⁻¹, consistent with the infrared work of Fox et al. (6). The fundamental vibrational frequencies and assignments given by Fox et al. (6) are adopted here.

Fox et al. (6) also investigated the nuclear magnetic resonance spectrum of NOF₃ which indicated that the molecule contained three equivalent fluorine atoms. This result, along with the general appearance of the infrared spectrum, clearly establishes that the molecule has C_{3v} symmetry. The N-O bond distance and bond angles are estimated quantities from the work of Curtis et al. (7). These estimated data have been used in calculating the N-F bond distance from the rotational constants given by Curtis et al. (7). Individual moments of inertia calculated from the structural data given above are: I_A = I_B = 14.86 × 10⁻³⁹ g cm², and I_C = 18.44 × 10⁻³⁹ g cm².

References

1. R. Bougon, J. Chatelet, J. P. Desmoulin, and P. Plurien, *Compt. Rend.*, **275C**, 760 (1968).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., June 30, 1961.
3. G. T. Armstrong and R. C. King, *Natl. Bur. Std.*, AFOSR 69-2154 TR, July 1, 1969.
4. V. H. Dibeir and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969).
5. N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, **1966**, 213.
6. W. B. Fox, J. S. Mackenzie, N. Vanderkooi, B. S. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, *J. Am. Chem. Soc.*, **88**, 2804 (1966).
7. E. C. Curtis, D. Filipovich, and W. H. Hoberly, *J. Chem. Phys.*, **46**, 2904 (1967).
8. S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **51**, 463 (1969).
9. W. B. Fox, J. S. Mackenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, *Inorg. Chem.*, **7**, 2084 (1968).

PHOSPHORYL FLUORIDE (POF₃)

(IDEAL GAS)

GFW = 103.9684

Point Group C_{3v}S_{298.15} = 68.10 ± 0.07 gibbs/mol

ΔHf° = -293.9 ± 1.9 kcal/mol

ΔHf°_{298.15} = -295.6 ± 1.9 kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
1417.7 (1)	994 (2)
872.8 (1)	483.2 (2)
473.2 (1)	335.6 (2)

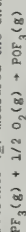
Bond Distances: P-O = 1.45 ± 0.03 Å P-F = 1.52 ± 0.02 Å

Bond Angle: F-P-F = 102.5° ± 2° F-P-O = 115.8° ± 2°

Product of Moments of Inertia: I_AI_BI_C = 5.9019 × 10⁻¹¹⁴ g³ cm⁶

Heat of Formation

Ebel and Bretcher (1) measured the enthalpy change for the following reaction:



They reported a heat of reaction of -70.6 ± 1 kcal/mol. Combining this result with the heat of formation of PF₃, ΔHf°₂₉₈ = -224.9 ± 0.9 kcal/mol (2), we derive, ΔHf°₂₉₈(POF₃, g) = -295.6 ± 1.9 kcal/mol.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Selig and Claassen (3) and are in good agreement with the Raman and infrared studies of Gutowsky and Liehr (4). Several microwave studies (5, 6, 7) of POF₃ have been reported. As pointed out by Williams et al. (7), the rotational constant calculated from their microwave studies leads to a moment of inertia, I_B, which is in disagreement with the moment of inertia calculated from the molecular constants obtained from electron-diffraction studies by Brockway and Beach (8). Since insufficient microwave data were available for an independent determination, Williams et al. (7) sought to find parameters which were consistent with both measurements. Their molecular constants are adopted for this tabulation. Individual moments of inertia are I_A = I_B = 18.244 × 10⁻³⁹ g cm² and I_C = 17.731 × 10⁻³⁹ g cm².

References

1. F. Ebel and E. Bretcher, *Helv. Chim. Acta*, **12**, 450 (1929).
2. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, Dec. 31, 1969.
3. H. Selig and H. H. Claassen, *J. Chem. Phys.*, **44**, 1404 (1966).
4. H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).
5. S. J. Sonatore, *Phys. Rev.*, **78**, 293 (1950).
6. N. J. Hawkins, V. W. Cohen, and W. S. Koski, *J. Chem. Phys.*, **20**, 528 (1952).
7. Q. Williams, J. Sheridan, and W. Gordy, *J. Chem. Phys.*, **20**, 164 (1952).
8. C. A. Burrus and W. Gordy, *J. Chem. Phys.*, **26**, 391 (1957).
9. L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.*, **50**, 1636 (1938).

Phosphoryl Fluoride (POF₃)

(Ideal Gas)

GFW = 103.9684

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	8.000	0.00	INFINITE	3.386	293.019	INFINITE
100	8.199	84.177	293.019	293.019	293.019	293.019
200	13.182	62.264	69.593	1.461	293.585	315.413
298	16.447	68.187	68.187	0.000	295.193	269.155
300	16.499	68.249	68.188	0.030	295.406	297.849
400	18.904	73.385	68.866	1.368	295.473	354.767
500	20.604	77.797	70.221	3.768	296.039	411.617
600	21.605	81.666	71.613	5.912	296.142	460.047
700	22.662	85.095	73.470	8.137	296.215	504.635
800	23.287	86.184	75.118	10.436	296.297	545.955
900	23.752	86.936	76.724	12.789	296.301	584.914
1000	24.104	87.456	78.273	15.183	296.287	621.251
1100	24.377	87.767	79.760	17.608	296.258	654.949
1200	24.591	87.966	81.184	20.056	296.217	685.718
1300	24.762	88.073	82.566	22.524	296.166	713.564
1400	24.901	88.103	83.851	25.008	296.108	738.507
1500	25.015	88.143	85.059	27.504	296.049	760.576
1600	25.110	88.183	86.226	30.010	295.974	779.813
1700	25.189	88.218	87.445	32.525	295.892	796.159
1800	25.256	88.248	88.619	35.047	295.804	809.659
1900	25.313	88.274	89.746	37.574	295.714	820.375
2000	25.362	88.296	90.831	40.110	295.626	829.311
2100	25.405	88.313	91.874	42.648	295.533	836.482
2200	25.442	88.326	92.884	45.191	295.437	841.894
2300	25.474	88.336	93.864	47.736	295.338	845.564
2400	25.503	88.343	94.813	50.285	295.236	847.501
2500	25.529	88.348	95.733	52.837	295.131	847.652
2600	25.551	88.351	96.633	55.391	295.024	846.921
2700	25.571	88.352	97.507	57.947	294.915	845.309
2800	25.589	88.353	98.357	60.505	294.804	842.819
2900	25.606	88.354	99.184	63.065	294.691	839.461
3000	25.620	88.355	99.993	65.626	294.576	835.254
3100	25.634	88.356	100.787	68.189	294.461	830.209
3200	25.646	88.357	101.567	70.753	294.346	824.336
3300	25.657	88.358	102.333	73.318	294.231	817.649
3400	25.667	88.359	103.087	75.884	294.116	810.254
3500	25.676	88.360	103.830	78.451	294.001	802.164
3600	25.685	88.361	104.563	81.019	293.886	793.484
3700	25.693	88.362	105.287	83.586	293.771	784.224
3800	25.700	88.363	106.003	86.154	293.656	774.484
3900	25.707	88.364	106.711	88.722	293.541	764.264
4000	25.713	88.365	107.411	91.290	293.426	753.574
4100	25.718	88.366	108.103	93.857	293.311	742.424
4200	25.724	88.367	108.787	96.424	293.196	730.824
4300	25.729	88.368	109.467	99.001	293.081	718.774
4400	25.733	88.369	110.143	101.569	292.966	706.274
4500	25.736	88.370	110.815	104.132	292.851	693.324
4600	25.742	88.371	111.483	106.696	292.736	679.924
4700	25.746	88.372	112.147	109.259	292.621	666.074
4800	25.749	88.373	112.807	111.818	292.506	651.774
4900	25.753	88.374	113.463	114.374	292.391	637.024
5000	25.756	88.375	114.115	116.927	292.276	621.824
5100	25.759	88.376	114.763	119.476	292.161	606.174
5200	25.762	88.377	115.407	122.021	292.046	590.074
5300	25.764	88.378	116.047	124.562	291.931	573.524
5400	25.767	88.379	116.683	127.099	291.816	556.524
5500	25.769	88.380	117.315	129.632	291.701	539.074
5600	25.771	88.381	117.943	132.161	291.586	521.174
5700	25.774	88.382	118.567	134.686	291.471	503.824
5800	25.776	88.383	119.187	137.207	291.356	486.024
5900	25.778	88.384	119.803	139.724	291.241	468.774
6000	25.779	88.385	120.415	142.237	291.126	451.074

Mar. 31, 1963; Dec. 31, 1963; Dec. 31, 1969

Phosphorus Trifluoride (PF₃)
(Ideal Gas)

GFW = 87.969

PHOSPHORUS TRIFLUORIDE (PF₃)

(IDEAL GAS)

GFW = 87.969

Point Group C_{3v} $\Delta H_f^\circ = -224.0 \pm 0.9 \text{ kcal/mol}$ $\Delta H_f^\circ = -224.9 \pm 0.9 \text{ kcal/mol}$ $S_{298.15}^\circ = 65.23 \pm 0.03 \text{ gibbs/mol}$

Ground State Quantum Weight = 1

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	cal/mol ΔH°	ΔG°	Log Kp
0	8.7000	INFINITE	-223.045	-223.045	INFINITE
100	53.0000	53.0000	-223.045	-223.045	INFINITE
200	11.4020	40.1233	-223.045	-223.045	INFINITE
298	14.027	65.233	-224.000	-224.000	292.000
300	14.066	65.320	-224.000	-224.000	292.000
400	15.791	65.619	-225.093	-219.712	170.045
500	16.920	66.841	-225.235	-218.352	95.441
600	17.678	68.431	-225.351	-216.964	79.029
700	18.187	69.637	-225.466	-215.557	67.300
800	18.543	70.906	-225.572	-214.144	59.949
900	18.799	72.297	-225.672	-212.730	52.483
1000	18.990	73.553	-225.769	-211.316	46.512
1100	19.135	74.754	-225.862	-209.903	41.632
1200	19.247	75.900	-225.951	-208.490	37.566
1300	19.336	76.993	-226.036	-207.077	34.127
1400	19.407	78.036	-226.118	-205.664	31.182
1500	19.465	79.033	-226.197	-204.251	28.630
1600	19.513	79.986	-226.272	-202.838	26.399
1700	19.553	80.899	-226.344	-201.425	24.430
1800	19.587	81.774	-226.412	-200.012	22.642
1900	19.615	82.615	-226.477	-198.600	21.119
2000	19.638	83.423	-226.539	-197.187	19.712
2100	19.661	84.201	-226.600	-195.774	18.440
2200	19.680	84.950	-226.658	-194.361	17.245
2300	19.696	85.674	-226.714	-192.948	16.230
2400	19.710	86.373	-226.768	-191.535	15.375
2500	19.723	87.049	-226.820	-190.122	14.668
2600	19.734	87.703	-226.870	-188.709	14.065
2700	19.744	88.337	-226.918	-187.296	13.555
2800	19.753	88.950	-226.964	-185.883	13.137
2900	19.761	89.548	-227.008	-184.470	12.799
3000	19.769	90.126	-227.050	-183.057	12.531
3100	19.774	90.691	-227.090	-181.644	12.321
3200	19.780	91.239	-227.128	-180.231	12.167
3300	19.786	91.773	-227.164	-178.818	12.066
3400	19.791	92.293	-227.198	-177.405	12.006
3500	19.795	92.800	-227.230	-175.992	11.986
3600	19.799	93.294	-227.260	-174.579	11.966
3700	19.803	93.777	-227.288	-173.166	11.946
3800	19.807	94.248	-227.314	-171.753	11.926
3900	19.810	94.708	-227.339	-170.340	11.906
4000	19.813	95.159	-227.363	-168.927	11.886
4100	19.816	95.599	-227.386	-167.514	11.866
4200	19.818	96.029	-227.408	-166.101	11.846
4300	19.821	96.451	-227.429	-164.688	11.826
4400	19.823	96.864	-227.449	-163.275	11.806
4500	19.825	97.269	-227.468	-161.862	11.786
4600	19.827	97.665	-227.486	-160.449	11.766
4700	19.829	98.054	-227.503	-159.036	11.746
4800	19.831	98.436	-227.519	-157.623	11.726
4900	19.833	98.811	-227.534	-156.210	11.706
5000	19.834	99.179	-227.548	-154.797	11.686
5100	19.836	99.539	-227.561	-153.384	11.666
5200	19.837	99.893	-227.573	-151.971	11.646
5300	19.838	100.242	-227.584	-150.558	11.626
5400	19.839	100.586	-227.595	-149.145	11.606
5500	19.841	100.927	-227.605	-147.732	11.586
5600	19.842	101.251	-227.614	-146.319	11.566
5700	19.843	101.569	-227.622	-144.906	11.546
5800	19.844	101.881	-227.629	-143.493	11.526
5900	19.845	102.188	-227.636	-142.080	11.506
6000	19.846	102.493	-227.642	-140.667	11.486

Dec. 31, 1960; June 30, 1962; Dec. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
892 (1)	860 (2)
487 (1)	344 (2)

Bond Distance: P-F = $1.5700 \pm 0.0012 \text{ \AA}$ P...F = $2.3643 \pm 0.0028 \text{ \AA}$ Bond Angle: F-P-F = $97.8 \pm 0.2^\circ$ Product of Moments of Inertia: $2.0621 \times 10^{-114} \text{ g}^3 \text{ cm}^6$ $\sigma = 3$

Heat of Formation

Berthelot (1) measured the heats of hydrolysis of PF₃(g) and PCl₃(l). These results can be combined to give, $\Delta H_f^\circ =$ 24.5 kcal/mol , for the reaction $\text{PF}_3(\text{g}) + 3\text{HCl} \cdot 157 \text{ H}_2\text{O} + \text{PCl}_3(\text{l}) + 3\text{H}_2\text{O} \cdot 112 \text{ H}_2\text{O}$

Combining this result with the following heat of formation data,

 $\Delta H_f^\circ(\text{PCl}_3, \text{l}) = -72.2 \text{ kcal/mol}$ (2) $\Delta H_f^\circ(\text{PCl}_3, \text{g}) = -100.0 \text{ kcal/mol}$ (3) $\Delta H_f^\circ(\text{HCl} \cdot 157 \text{ H}_2\text{O}) = -138.5 \text{ kcal/mol}$ (3) $\Delta H_f^\circ(\text{H}_2\text{O} \cdot 112 \text{ H}_2\text{O}) = -138.5 \text{ kcal/mol}$ (3)we derive, $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -212.2 \text{ kcal/mol}$.Dunn and Mykytyk (4) reported a heat of reaction of -2.361 kcal/mol (corrected to 25°C) for the following reaction $\text{PCl}_3(\text{g}) + 3/2 \text{ CaF}_2(\text{s}) + \text{PF}_3(\text{g}) + 3/2 \text{ CaCl}_2(\text{s})$

Combining this result with the following heat of formation data,

 $\Delta H_f^\circ(\text{PCl}_3, \text{g}) = -84.4 \text{ kcal/mol}$ (2) $\Delta H_f^\circ(\text{CaF}_2, \text{s}) = -212.9 \text{ kcal/mol}$ (3) $\Delta H_f^\circ(\text{CaCl}_2, \text{s}) = -190.0 \text{ kcal/mol}$ (3)we derive, $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -224.9 \pm 0.9 \text{ kcal/mol}$.Recently, Rudzitis et al. (5) measured the heat of combustion of PF₃ in fluorine in a two-chambered bomb calorimeterat 25°C . They reported a heat of combustion of $-152.0 \pm 0.2 \text{ kcal/mol}$ for the reaction $\text{PF}_3(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{PF}_5(\text{g})$ Combining this result with the heat of formation of PF₅, $\Delta H_f^\circ(\text{PF}_5, \text{g}) = -376.9 \pm 0.7 \text{ kcal/mol}$ (7), we derive, $\Delta H_f^\circ(\text{PF}_3, \text{g}) = -224.9 \pm 0.9 \text{ kcal/mol}$. This result is adopted for this tabulation.

Heat Capacity and Entropy

The vibrational frequencies are those reported by Wilson and Palo (8). Several different values for the P-F bond

length and F-P-F bond angle have been reported in the literature. This problem was recently discussed by Morino et al.

(9), who also reported new data obtained from electron-diffraction studies. Their results are adopted for this tabulation.

Individual moments of inertia calculated according to their structure are: $I_A = I_B = 10.814 \times 10^{-39} \text{ g cm}^2$ and $I_C =$ $17.634 \times 10^{-39} \text{ g cm}^2$.

References

1. M. Berthelot, *Compt. Rend.* 100, 81 (1885). M. Berthelot and W. Loungine, *Ann. Chim. Phys.* [5], 305 (1875).

2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.

3. U. S. Natl. Bur. Std. Circ. 500, 1962.

4. H. C. Dunn and D. P. Mykytyk, *J. Chem. Eng. Data*, 9, 585 (1964).

5. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, December 31, 1968.

6. E. Rudzitis, private communication, Argonne Natl. Lab., 1969.

7. Ref. 5, December 31, 1969.

8. M. Kent Wilson and S. R. Palo, *J. Chem. Phys.*, 20, 1716 (1952).9. Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, 8, 867 (1969).

THIOPHOSPHORYL FLUORIDE (PSF₃)

(IDEAL GAS)

GFW = 120.033

Point Group C_{3v}

$$\Delta H_f^\circ = [-236 \pm 15] \text{ kcal/mol}$$

$$\Delta H_f^\circ = [-237 \pm 15] \text{ kcal/mol}$$

$$S_{298.15}^\circ = 71.23 \pm 0.05 \text{ gibbs/mol}$$

Ground State Quantum Weight = [1]

Thiophosphoryl Fluoride (PSF₃)

(Ideal Gas)

GFW = 120.033

T, °K	C _p ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{H^\circ - H_{298}^\circ}{T}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	235.567	235.567	INFINITE
100	9.747	56.533	84.656	235.133	513.683	42.863
200	14.852	44.793	72.740	236.572	234.019	295.724
298	17.616	41.230	63.000	237.000	170.552	170.552
300	17.616	41.230	63.000	237.000	170.552	170.552
400	20.202	38.130	53.000	237.000	169.491	169.491
500	21.744	36.145	44.047	238.499	231.114	100.249
600	22.771	35.170	37.276	238.976	227.473	92.857
700	23.372	34.606	32.000	239.000	227.473	92.857
800	23.824	34.263	28.000	239.000	230.072	84.563
900	24.324	34.000	25.000	239.000	228.693	84.563
1000	24.590	33.726	22.000	239.000	219.342	47.937
1100	24.793	33.488	18.295	239.000	218.016	42.521
1200	25.000	33.284	15.000	239.000	203.424	38.199
1300	25.216	33.104	12.000	239.000	203.424	38.199
1400	25.176	33.000	10.000	239.000	198.161	30.934
1500	25.258	32.899	8.699	239.000	192.916	28.108
1600	25.326	32.800	7.600	239.000	187.689	25.637
1700	25.382	32.716	6.716	239.000	182.489	23.169
1800	25.428	32.644	6.000	239.000	177.284	21.525
1900	25.470	32.584	5.470	239.000	172.100	19.794
2000	25.505	32.534	5.000	239.000	166.933	18.242
2100	25.535	32.488	4.570	239.000	161.780	16.837
2200	25.561	32.444	4.125	239.000	156.636	15.460
2300	25.584	32.400	3.750	239.000	151.500	14.113
2400	25.604	32.364	3.425	239.000	146.366	12.800
2500	25.622	32.336	3.136	239.000	141.273	12.340
2600	25.638	32.314	2.884	239.000	136.174	11.446
2700	25.652	32.296	2.664	239.000	131.062	10.610
2800	25.664	32.280	2.476	239.000	125.936	9.833
2900	25.674	32.266	2.316	239.000	120.800	9.113
3000	25.682	32.253	2.180	239.000	115.662	8.441
3100	25.695	32.240	2.066	239.000	110.503	7.812
3200	25.704	32.229	1.971	239.000	105.323	7.223
3300	25.711	32.219	1.895	239.000	100.136	6.673
3400	25.718	32.210	1.836	239.000	95.000	6.160
3500	25.725	32.202	1.785	239.000	90.000	5.660
3600	25.731	32.194	1.740	239.000	85.000	5.197
3700	25.736	32.187	1.700	239.000	80.594	4.761
3800	25.741	32.181	1.664	239.000	76.797	4.354
3900	25.745	32.176	1.632	239.000	72.574	3.985
4000	25.750	32.172	1.604	239.000	68.920	3.642
4100	25.754	32.168	1.579	239.000	65.711	3.329
4200	25.758	32.164	1.557	239.000	62.944	3.042
4300	25.762	32.160	1.536	239.000	60.611	2.780
4400	25.766	32.156	1.516	239.000	58.711	2.542
4500	25.769	32.153	1.497	239.000	57.244	2.326
4600	25.770	32.150	1.479	239.000	56.211	2.131
4700	25.773	32.147	1.462	239.000	55.574	1.954
4800	25.776	32.144	1.446	239.000	55.311	1.794
4900	25.779	32.141	1.431	239.000	55.000	1.649
5000	25.780	32.138	1.417	239.000	54.644	1.517
5100	25.782	32.135	1.404	239.000	54.244	1.394
5200	25.784	32.132	1.391	239.000	53.800	1.280
5300	25.786	32.129	1.379	239.000	53.311	1.174
5400	25.788	32.126	1.367	239.000	52.777	1.076
5500	25.791	32.123	1.356	239.000	52.199	1.000
5600	25.792	32.120	1.345	239.000	51.574	0.934
5700	25.794	32.117	1.334	239.000	50.900	0.876
5800	25.796	32.114	1.323	239.000	50.177	0.824
5900	25.798	32.111	1.312	239.000	49.400	0.776
6000	25.799	32.108	1.301	239.000	48.574	0.732

Mar. 31, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$
 $\frac{\omega_e}{\text{cm}^{-1}}$

Silicon Trifluoride (SiF₃)

GFW = 85.0812

Point Group C_{3v}Point Group C_{3v}S_{298.15} = 67.45 ± 0.5 gibbs/molΔH_{f,0}^o = [-282.3 ± 5] kcal/mol

Ground State Quantum Weight = 2

ΔH_{f,0}^o = [-282.3 ± 5] kcal/mol

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹
832 (1)
406 (1)
954 (2)
290 (2)

Bond Distance: Si-F = (1.56) Å

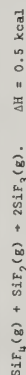
Bond Angle: F-Si-F = (109.47)°

Product of the Moments of Inertia: I_AI_BI_C = 2.5135 × 10⁻¹¹⁴ g³ cm⁶

σ = 3

Heat of Formation

The heat of formation is estimated from the assumption of a 0.5 kcal heat for the reaction:



ΔH_{f,298}^o(SiF₃, g) = -263 kcal/mol is derived from ΔH_{f,298}^o(SiF₄, g) = -385.98 kcal/mol and ΔH_{f,298}^o(SiF₂, g) = -140.5 kcal/mol. The above value is confirmed by the observations of Layne (1), whose total pressure data above the silicon-fluoride system agree with those calculated from these tables.

Heat Capacity and Entropy

The bond length is estimated between those of SiF₄ and SiF₂. The vibrational frequencies are from Milligan et al. (2), and the angle is taken to be tetrahedral, since they also reported an angle of approximately 71° between the Si-F bonds and the threefold axis. The spectra of the radical were obtained in inert gas matrices and all the fundamentals were observed. The individual moments of inertia are I_A = I_C = 11.081 × 10⁻³⁹ g cm², I_B = 20.472 × 10⁻³⁹ g cm².

References

1. G. S. Layne, Dow Chemical Co., Midland, Mich., private communication, Aug. 1969.
2. D. E. Milligan, M. E. Jacox and W. A. Guillory, J. Chem. Phys. **53**, 5330 (1969).

T, K	Cp ^o	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log Kp
0	9.000	56.000	INFINITE	-3.202	-262.268	-262.268	INFINITE
100	12.185	62.195	66.698	-1.300	-262.803	-261.021	190.231
200	14.250	67.454	67.454	0.000	-263.000	-260.104	190.661
300	14.285	67.483	67.455	0.024	-263.004	-260.046	189.573
400	15.266	71.561	66.035	1.526	-263.154	-259.069	141.559
500	16.532	74.342	65.140	3.191	-263.268	-258.059	112.798
600	17.660	76.698	70.510	4.913	-263.350	-257.010	93.016
700	18.142	81.660	71.881	6.705	-263.419	-255.947	79.910
800	18.517	83.910	73.234	8.540	-263.483	-254.877	69.059
900	18.776	86.517	74.565	10.406	-263.543	-253.796	61.030
1000	18.866	88.095	75.802	12.293	-263.607	-252.711	55.230
1100	19.115	89.910	77.003	14.198	-263.676	-251.618	49.492
1200	19.230	91.579	78.169	16.115	-263.749	-250.518	45.026
1300	19.300	93.122	79.282	18.043	-263.830	-249.412	41.930
1400	19.383	94.556	80.285	19.979	-263.920	-248.300	39.161
1500	19.453	95.886	81.282	21.921	-264.019	-247.174	36.714
1600	19.502	97.153	82.235	23.869	-264.129	-246.054	34.609
1700	19.543	98.337	83.168	25.821	-264.242	-244.914	31.673
1800	19.578	99.455	84.023	27.778	-264.314	-243.765	29.900
1900	19.607	100.514	84.863	29.737	-264.395	-242.611	27.734
2000	19.633	101.521	85.671	31.699	-264.474	-241.454	26.184
2100	19.654	102.479	86.449	33.663	-264.554	-240.297	24.705
2200	19.673	103.394	87.199	35.630	-264.637	-239.142	23.397
2300	19.690	104.269	87.922	37.598	-264.722	-237.985	22.209
2400	19.705	105.101	88.615	39.561	-264.809	-236.827	21.106
2500	19.718	105.812	89.280	41.539	-264.899	-235.667	20.098
2600	19.729	106.485	89.950	43.511	-264.991	-234.501	19.166
2700	19.739	107.130	90.584	45.484	-265.086	-233.338	18.303
2800	19.748	107.748	91.198	47.457	-265.182	-232.178	17.503
2900	19.756	108.341	91.795	49.430	-265.281	-231.021	16.766
3000	19.764	108.911	92.374	51.410	-265.385	-229.864	16.080
3100	19.771	109.459	92.938	53.387	-265.489	-228.715	15.408
3200	19.777	110.087	93.486	55.364	-265.597	-227.569	14.796
3300	19.783	111.396	94.019	57.342	-265.704	-226.428	14.222
3400	19.788	112.566	94.539	59.321	-265.821	-225.293	13.691
3500	19.793	113.580	95.048	61.306	-265.939	-224.164	13.170
3600	19.797	113.118	95.540	63.279	-266.017	-223.043	12.651
3700	19.801	113.660	96.023	65.259	-266.040	-221.928	12.151
3800	19.804	114.186	96.494	67.240	-266.065	-220.818	11.674
3900	19.807	114.694	96.953	69.220	-266.096	-219.713	11.223
4000	19.811	115.204	97.404	71.200	-266.126	-218.613	10.784
4100	19.814	115.694	97.844	73.182	-266.156	-217.518	10.354
4200	19.817	116.171	98.275	75.164	-266.185	-216.428	9.942
4300	19.819	116.637	98.696	77.146	-266.215	-215.343	9.542
4400	19.821	117.094	99.107	79.128	-266.245	-214.263	9.154
4500	19.824	117.538	99.514	81.110	-266.275	-213.188	8.786
4600	19.826	117.974	99.911	83.092	-266.305	-212.118	8.437
4700	19.828	118.401	100.299	85.075	-266.335	-211.053	8.106
4800	19.829	118.819	100.681	87.058	-266.365	-210.000	7.791
4900	19.831	119.228	101.053	89.041	-266.395	-208.950	7.491
5000	19.833	119.628	101.423	91.024	-266.425	-207.906	7.201
5100	19.834	120.020	101.784	93.008	-266.455	-206.868	6.933
5200	19.836	120.406	102.138	94.991	-266.485	-205.836	6.688
5300	19.837	120.783	102.486	96.975	-266.515	-204.810	6.454
5400	19.839	121.151	102.831	98.961	-266.545	-203.788	6.231
5500	19.839	121.518	103.165	100.942	-266.575	-202.770	6.019
5600	19.841	121.876	103.494	102.926	-266.605	-201.756	5.817
5700	19.842	122.227	103.821	104.910	-266.635	-200.746	5.624
5800	19.843	122.572	104.142	106.895	-266.665	-199.740	5.440
5900	19.844	122.912	104.459	108.878	-266.695	-198.738	5.266
6000	19.845	123.245	104.767	110.863	-266.725	-197.740	5.100

Titanium Trifluoride (TiF₃)

(Crystal) GFW = 104.8952

TITANIUM TRIFLUORIDE (TiF₃)

(CRYSTAL)

GFW = 104.8952

T, °K	Cp°	qBbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	21.594	21.000	21.000	.000	-343.100	-325.510	238.406
300	22.000	21.136	21.000	.041	-343.091	-325.402	237.055
400	22.300	21.497	21.666	2.253	-342.838	-324.852	174.506
500	22.570	21.790	23.513	4.716	-342.655	-324.560	137.104
600	23.536	36.783	25.381	6.861	-341.834	-308.210	112.265
700	24.128	40.455	27.278	9.224	-341.414	-302.638	94.888
800	24.746	43.717	29.132	11.668	-340.979	-297.159	81.172
900	25.390	46.669	30.919	14.174	-340.523	-291.674	70.528
1000	26.060	49.378	32.632	16.747	-340.042	-286.274	62.265
1100	26.756	51.894	34.270	19.387	-339.528	-280.920	55.814
1200	27.478	54.253	35.838	22.069	-339.914	-275.578	50.190
1300	28.226	56.462	37.341	24.684	-339.195	-270.245	45.432
1400	28.999	58.502	38.784	27.245	-338.426	-264.970	41.464
1500	29.790	60.434	40.174	30.690	-337.593	-259.751	37.846
1600	30.600	62.563	41.513	33.680	-336.738	-254.590	34.775
1700	30.200	64.368	42.806	36.690	-335.668	-249.481	32.073
1800	30.400	66.120	44.053	39.720	-335.046	-244.426	29.677
1900	30.600	67.769	45.258	42.770	-334.209	-239.413	27.539
2000	30.800	69.343	46.424	45.840	-333.168	-234.290	25.602

ΔHf° = unknown

S°_{298.15} = [21.0 ± 3.0]ΔHf°_{298.15} = -343.1 ± 10.0 kcal/mol

ΔHs° = 52.97 kcal/mol

T₈ = 1309.7 °K

Heat of Formation

Blocher and Hall (1) have reported vapor pressure data for the process $1/2\text{Hg}_2\text{F}_2 + \text{TiF}_3(\text{c}) = \text{TiF}_4(\text{g}) + \text{Hg}(\text{l})$. Second and third law analyses of their data give a second law ΔH_{298} of 23.7 kcal/mol, a third law ΔH_{298} of 29.86 kcal/mol, and a third law drift of 11.9 ± 1.0 eu. The third law value is combined with the JANAF values for the heat of formation of $\text{Hg}_2\text{F}_2(\text{c})$ and $\text{TiF}_4(\text{g})$ to give a ΔH_{298} of -343.1 ± 10.0 kcal/mol. The large uncertainty on ΔH_{298} is assigned because Blocher and Hall were not able to identify $\text{TiF}_3(\text{c})$ as the reaction product in the above process. They reported that the X-ray pattern of the products contained lines corresponding to $\text{Hg}_2\text{F}_2(\text{c})$ plus others that did not correspond to $\text{TiF}_3(\text{c})$.

Heat Capacity and Entropy

The heat capacity of $\text{TiF}_3(\text{c})$ is estimated from the heat capacities of ZrF_4 and TiF_4 . The entropy, S_{298} , is estimated from CrF_3 and from ionic entropy contributions. Both methods give values which are within ±0.8 eu of the chosen value of 21 ± 3 eu.

Heat of Sublimation

The heat of sublimation is calculated from the vapor pressure data of Zmbov and Margrave (2). See $\text{TiF}_3(\text{g})$ table for details. The sublimation temperature is taken as the point at which $\Delta G = 0$ for the reaction $\text{TiF}_3(\text{c}) = \text{TiF}_3(\text{g})$.

References

1. J. N. Blocher, Jr. and E. N. Hall, J. Phys. Chem. **53**, 127 (1959).
2. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).

Dec. 31, 1960; June 30, 1964; Dec. 31, 1967; June 30, 1968

Titanium Trifluoride (TiF₃)

(Ideal Gas)

GFW = 104.8952

T, °K	Cp°	gibbs/mol S° - (C°-H°900)/T	H°-H°900 ΔH°	kcal/mol ΔH°	Log Kp
0	6.000	INFINITE	3.323	-283.106	INFINITE
100	9.131	56.491	61.514	-282.810	618.040
200	12.794	63.437	70.671	-281.492	308.138
298	15.675	65.622	75.861	-281.007	205.984
300	15.718	65.710	75.922	-281.033	206.700
400	17.513	78.509	91.563	-279.930	151.447
500	18.567	78.541	91.526	-278.657	121.488
600	19.150	81.686	92.990	-277.775	101.179
700	19.569	84.975	94.693	-276.689	86.366
800	19.868	87.505	96.591	-275.380	75.290
900	20.081	89.241	98.641	-273.880	65.752
1000	20.274	92.057	100.758	-273.400	58.752
1100	20.451	93.574	102.056	-272.285	54.098
1200	20.609	95.730	103.290	-271.120	49.378
1300	20.751	97.487	104.372	-269.902	45.172
1400	20.881	98.987	105.314	-268.635	41.400
1500	20.999	100.252	106.146	-267.460	38.569
1600	20.328	101.563	106.663	-266.229	36.365
1700	20.342	102.796	107.435	-265.091	34.667
1800	20.343	103.959	108.253	-264.004	32.973
1900	20.328	105.059	109.099	-262.959	31.623
2000	20.367	106.104	109.914	-261.958	29.528
2100	20.372	107.098	110.637	-261.296	27.613
2200	20.376	108.046	111.330	-260.651	25.835
2300	20.368	108.879	111.994	-260.023	24.375
2400	20.352	109.619	112.635	-259.406	23.156
2500	20.382	110.251	113.248	-258.799	22.156
2600	20.383	111.450	113.832	-258.201	21.173
2700	20.384	112.219	114.395	-257.620	20.243
2800	20.385	112.674	114.931	-257.056	19.376
2900	20.385	113.367	115.440	-256.509	18.562
3000	20.385	114.367	116.340	-255.984	17.692
3100	20.384	115.036	116.971	-255.473	17.202
3200	20.384	115.683	117.546	-254.960	16.555
3300	20.382	116.318	118.073	-254.453	15.976
3400	20.382	116.949	118.550	-253.953	15.476
3500	20.381	117.509	119.000	-253.459	14.932
3600	20.379	118.083	119.427	-252.971	14.405
3700	20.377	118.682	119.842	-252.490	13.855
3800	20.375	119.296	120.237	-252.017	13.285
3900	20.373	119.914	120.617	-251.552	12.696
4000	20.371	120.530	120.985	-251.096	12.096
4100	20.369	120.733	121.105	-250.647	11.466
4200	20.366	121.224	121.554	-250.190	10.841
4300	20.364	121.714	121.999	-249.732	10.241
4400	20.360	122.171	122.428	-249.274	9.616
4500	20.357	122.629	122.846	-248.816	9.016
4600	20.353	123.076	123.259	-248.357	8.456
4700	20.350	123.514	123.664	-247.897	7.936
4800	20.346	123.941	124.064	-247.437	7.456
4900	20.342	124.362	124.459	-246.976	6.936
5000	20.338	124.773	124.846	-246.514	6.456
5100	20.334	125.175	125.209	-246.052	5.936
5200	20.330	125.566	125.577	-245.589	5.456
5300	20.326	125.949	125.941	-245.126	4.936
5400	20.322	126.337	126.295	-244.662	4.456
5500	20.318	126.710	126.645	-244.197	3.936
5600	20.313	127.076	126.988	-243.732	3.456
5700	20.308	127.436	127.326	-243.266	2.936
5800	20.303	127.789	127.659	-242.800	2.456
5900	20.300	128.136	127.986	-242.333	1.936
6000	20.296	128.477	128.308	-241.866	1.456

Dec. 31, 1950; June 30, 1964; Dec. 31, 1967; June 30, 1968

TITANIUM TRIFLUORIDE (TiF₃)

(IDEAL GAS)

Point Group = C_{3v}

ΔHf° = -283.1 ± 10.0

GFW = 104.8952

S°_{298.15} = [69.6 ± 1.0] gibbs/molΔHf°_{298.15} = -284.1 ± 10.0 kcal/mol

Ground State Quantum Weight = [2]

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	G _i
0	(2)
[600]	(2)
[1500]	(2)
[4000]	(2)
[10000]	(2)

Vibrational Frequencies and Degeneracies

ν _i , cm ⁻¹	D _i
[800] (1)	
[450] (1)	
[750] (2)	
[300] (2)	

Bond Distance: Ti-F = [1.9] Å

Bond Angle: F-Ti-F = [100°]

Product of the Moments of Inertia: I_AI_BI_C = [7.45 × 10⁻¹¹⁴ g³ cm⁶]

σ = 3

Heat of Formation

The heat of formation of TiF₃(g) is calculated from that of TiF₃(c) and the heat of sublimation determined from the mass spectrometric vapor pressure data of Zmbov and Margrave (1). Their data give nine points over the temperature range 759 - 865°K.

Second and third law analyses of their data give a second law ΔHf°₂₉₈ of 61.2 ± 0.4 kcal/mol and a third law ΔHf°₂₉₈ of 59.0 kcal/mol with an entropy drift of -2.7 ± 0.5 units. The third law value is used to calculate ΔHf°₂₉₈.

Heat Capacity and Entropy

The internuclear distance is estimated from those of TiF₄(g), and TiCl₃(g), and TiCl₄(g). The pyramidal bond angle is estimated assuming TiF₃(g) similar to the group V trihalides. The principal moments of inertia are I_A = 1.68 × 10⁻³⁸ g cm² and I_C = 2.66 × 10⁻³⁸ g cm². The vibrational frequencies are estimated from those of PF₃ and AsF₃. The electronic levels are estimated from the levels of Ti³⁺ (2).

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

F₃Ti

Zirconium Trifluoride (ZrF₃)

GFW = 148.2152

$$S_{298.15}^{\circ} = \{21 \pm 2\} \text{ gibbs/mol}$$

$$\Delta H_f^{\circ} = \text{Unknown}$$

$$\Delta H_f^{\circ} = [-335 \pm 20] \text{ kcal/mol}$$

$$\Delta H_{298.15}^{\circ} = [70.1] \text{ kcal/mol}$$

Heat of Formation

The heat of formation at 298°K for ZrF₃(c) was reported as -350 kcal/mol (1) which was estimated by Brewer (2). Based on this ΔH_{298}° value, the crystal lattice energy (U) of ZrF₃(c) is calculated to be 1371 kcal/mol by the Born-Haber cycle method (3). For the evaluation of U from the relation: $\Delta H_f^{\circ}(\text{ZrF}_3, c) = \Sigma I_i + L - 3(E - D/2) - U$, the following values (kcal/mol) are used: ΣI_i (the sum of the successive three ionization potentials of Zr metal) = 1055 (4), L (the enthalpy of sublimation of Zr metal) = 148.3 (5), E (the electron affinity of fluorine) = 79.5 (6), and D (the enthalpy of dissociation of fluorine) = 37.7 (2). The derived value of U(ZrF₃, c) is of the same order of magnitude of the value, U(TiF₃, c) = 1376 kcal/mol, calculated by Cavell and Clark (3) using the same method.

From $\Delta H_{298}^{\circ}(\text{ZrF}_3, c) = -350$ kcal/mol, the derived $\Delta G_f^{\circ}(\text{ZrF}_3, c)$ values indicate that ZrF₃(c) is thermodynamically more stable than the system ZrF₄(c) + Zr(c). For example, in the temperature range 798-1200°K, the Gibbs energy changes for the reaction $3 \text{ ZrF}_3(c) + \text{Zr}(c) = 4 \text{ ZrF}_4(c)$ are about -29 ± 1 kcal/mol. However, this product ZrF₃(c) has never been prepared successfully from this reaction in many laboratories (8). In order to make the $\Delta G_f^{\circ}(\text{ZrF}_3, c)$ values consistent with the experimental observations, the heat of formation of ZrF₃(c) is arbitrarily adjusted to be 15 kcal/mol less negative, or $\Delta H_{298}^{\circ}(\text{ZrF}_3, c) = -335$ kcal/mol with uncertainty as high as ±20 kcal/mol. This value is tentatively adopted.

The Gibbs energy changes for the reaction $3 \text{ ZrF}_3(g) + \text{Zr}(c) = 4 \text{ ZrF}_4(c)$ are evaluated to be very favorable at temperatures below 900°K, e.g., $\Delta G_r^{\circ} = -93.9$ and -6.7 kcal/mol at 298 and 900°K, respectively. But according to Larsen and Leddy (9), this reaction does not occur in the temperature range 473-973°K, and pressure range 5-15 atm. One possible explanation is that these heterogeneous reactants may require very high activation energy to initiate the reaction. In other words, this reaction is unfavorable at these temperatures probably due to kinetic rather than thermodynamic reasons.

Heat Capacity and Entropy

The heat capacities of ZrF₃(c) are not available in the literature. They are estimated from the Cp values of ZrF₄(c) by deduction of one F atom Cp contributions which are calculated as $1/4(Cp_{\text{ZrF}_4(c)} - Cp_{\text{Zr}(c)})$. The $S_{298.15}^{\circ}$ is taken to be $1/2(S_{298}^{\circ}(\text{ZrF}_4, c) + S_{298}^{\circ}(\text{ZrF}_2, c))$ of which the value $S_{298}^{\circ}(\text{ZrF}_2, c)$ is estimated (see ZrF₂(c) table for details).

Heat of Sublimation

The difference between ΔH_{298}° for ZrF₃(g) and ZrF₃(c) is ΔH_{298}° . Actually, ZrF₃(c) is thermodynamically unstable, e.g., the Gibbs energy changes for the reaction $4 \text{ ZrF}_3(c) = 3 \text{ ZrF}_4(c) + \text{Zr}(c)$ are about -30 kcal/mol in the temperature range 298-1400°K. In other words, ZrF₃(c) decomposes into ZrF₄(c) + Zr(c) before sublimation occurs.

References

1. U. S. Natl. Bur. Std. Circ. 500, 1952.
2. L. Brewer, private communication, University of California, Berkeley, California; cited in reference 1.
3. R. G. Cavell and H. C. Clark, J. Chem. Soc. 1965, 444 (1965).
4. C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.
5. JANAF Zr(c) table, Dec. 31, 1967.
6. U. S. Natl. Bur. Std. Rept. 8628, January 1965.
7. JANAF F(g) table, Sept. 30, 1965.
8. T. B. Douglas, private communication, Natl. Bur. Std., July 10, 1961.
9. E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. 78, 5983 (1956).

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
-------	-----	-----------------	----------------------------	----------------------	-----------------	-----	--------

0							
100							
200							
298	20,000	21,000		.000	= 335,000	= 316,617	232.233
300	20,150	21,000		.037	= 334,995	= 316,705	230.719
400	21,950	21,814	2,187	2,187	= 334,563	= 316,710	228.716
500	23,150	23,405	4,405	4,405	= 334,768	= 306,698	133.184
600							
700	24,000	25,241	6,765	6,765	= 333,833	= 286,625	106.667
800	24,600	27,124	9,195	9,195	= 333,385	= 283,026	91.487
900	25,100	28,978	11,682	11,682	= 332,930	= 287,292	76.484
1000	25,450	30,769	14,210	14,210	= 332,604	= 287,292	63.317
1100	25,750	32,484	16,771	16,771	= 332,638	= 275,987	
1200	25,930	34,123	19,355	19,355	= 331,604	= 270,403	53.724
1300	26,020	35,684	21,953	21,953	= 332,048	= 264,605	46.228
1400	26,100	37,173	24,559	24,559	= 331,490	= 259,224	43.573
1500	26,230	38,592	27,173	27,173	= 330,945	= 254,685	41.160
		39,947	29,793	29,793	= 330,405	= 248,184	36.160

June 30, 1961; June 30, 1964; June 30, 1969

ZIRCONIUM TRIFLUORIDE (ZrF₃)Point Group [C_{3v}]

(IDEAL GAS)

ΔH_f⁰ = -263.3 ± 5 kcal/molΔH_f⁰_{298.15} = -264.2 ± 5 kcal/molS⁰_{298.15} = [73.0 ± 2] gibbs/mol

Ground State Quantum Weight = [2]

Zirconium Trifluoride (ZrF₃)
(Ideal Gas) GFW = 148.2152

T, °K	C _p ⁰	S ⁰	gibbs/mol -(G ⁰ -H ⁰ ₂₉₈)/T	H ⁰ -H ⁰ ₂₉₈	kcal/mol ΔH ⁰	ΔG ⁰	Log Kp
0	0	0	INFINITE	3.610	-263.324	-263.324	INFINITE
100	10.621	46.513	95.684	2.737	-263.704	-263.117	575.042
200	14.099	67.004	74.667	1.492	-264.037	-262.386	286.771
298	16.212	73.047	68.000	1.000	-264.200	-262.155	191.710
300	16.244	73.147	73.047	1.030	-264.202	-261.519	190.516
400	17.616	78.023	73.703	1.728	-264.282	-260.610	142.391
500	18.524	82.058	74.942	3.538	-264.134	-259.687	113.509
600	19.165	85.495	76.455	5.424	-264.373	-258.753	94.251
700	19.528	88.486	77.944	7.365	-264.615	-257.813	80.491
800	19.695	91.130	79.448	9.346	-264.864	-256.866	70.173
900	20.210	93.496	80.860	11.355	-264.533	-255.914	62.144
1000	20.390	95.636	82.250	13.386	-264.619	-254.952	55.770
1100	20.523	97.586	83.587	15.432	-264.728	-253.981	50.441
1200	20.620	99.376	84.852	17.489	-264.712	-252.994	46.004
1300	20.692	101.029	85.987	19.555	-265.465	-251.882	42.395
1400	20.743	102.565	87.117	21.627	-265.468	-250.820	39.155
1500	20.779	103.997	88.195	23.703	-265.495	-249.756	36.349
1600	20.803	105.339	89.235	25.782	-265.714	-248.695	33.970
1700	20.817	106.601	90.210	27.863	-265.750	-247.628	31.835
1800	20.824	107.791	91.154	29.945	-265.801	-246.564	29.917
1900	20.825	108.917	92.060	32.028	-265.865	-245.493	28.238
2000	20.822	109.985	92.930	34.110	-265.945	-244.417	26.709
2100	20.816	111.000	93.766	36.192	-266.041	-243.341	25.325
2200	20.808	111.969	94.572	38.273	-266.157	-242.260	24.088
2300	20.798	112.893	95.348	40.354	-266.279	-241.175	22.877
2400	20.787	113.778	96.068	42.433	-266.407	-240.082	21.693
2500	20.776	114.627	96.822	44.511	-266.540	-238.979	20.614
2600	20.765	115.441	97.523	46.588	-266.677	-237.867	19.601
2700	20.753	116.225	98.201	48.664	-266.819	-236.742	18.644
2800	20.742	116.979	98.858	50.739	-266.965	-235.602	17.749
2900	20.731	117.707	99.496	52.812	-267.116	-234.446	16.936
3000	20.720	118.410	100.115	54.885	-267.273	-233.273	16.193
3100	20.710	119.089	100.719	56.956	-267.433	-232.087	15.518
3200	20.700	119.746	101.300	59.027	-267.598	-230.894	14.912
3300	20.691	120.383	101.869	61.096	-267.767	-229.697	14.368
3400	20.682	121.001	102.423	63.165	-267.940	-228.494	13.884
3500	20.673	121.600	102.942	65.233	-268.114	-227.282	13.451
3600	20.665	122.182	103.488	67.300	-268.298	-226.062	13.068
3700	20.657	122.748	104.001	69.366	-268.484	-224.834	12.734
3800	20.650	123.299	104.501	71.431	-268.674	-223.600	12.447
3900	20.643	123.835	105.000	73.496	-268.869	-222.362	12.204
4000	20.636	124.358	105.468	75.560	-269.066	-221.120	12.000
4100	20.629	124.867	105.935	77.623	-269.268	-219.874	11.844
4200	20.623	125.364	106.392	79.685	-269.474	-218.624	11.731
4300	20.617	125.850	106.839	81.747	-269.682	-217.371	11.658
4400	20.611	126.324	107.276	83.809	-269.892	-216.116	11.624
4500	20.605	126.787	107.704	85.870	-270.103	-214.862	11.600
4600	20.599	127.239	108.124	87.930	-270.314	-213.608	11.584
4700	20.594	127.682	108.536	89.989	-270.525	-212.354	11.571
4800	20.589	128.116	108.939	92.049	-270.736	-211.100	11.558
4900	20.584	128.548	109.335	94.107	-270.947	-209.846	11.544
5000	20.579	128.976	109.723	96.165	-271.158	-208.592	11.531
5100	20.574	129.394	110.104	98.223	-271.369	-207.338	11.518
5200	20.569	129.763	110.478	100.280	-271.580	-206.084	11.504
5300	20.564	130.155	110.846	102.337	-271.791	-204.830	11.491
5400	20.560	130.539	111.207	104.393	-272.002	-203.576	11.478
5500	20.556	130.916	111.562	106.449	-272.213	-202.322	11.464
5600	20.551	131.287	111.911	108.504	-272.424	-201.068	11.451
5700	20.547	131.650	112.254	110.559	-272.635	-199.814	11.438
5800	20.543	132.008	112.592	112.614	-272.846	-198.560	11.424
5900	20.540	132.359	112.924	114.668	-273.057	-197.306	11.411
6000	20.536	132.704	113.251	116.721	-273.268	-196.052	11.398

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies

ω_i , cm ⁻¹	ω_i , cm ⁻¹
[611] (1)	[655] (2)
[203] (1)	[240] (2)

Bond Distance: Zr-F = [1.93] Å

Bond Angle: F-Zr-F = [105°]

Product of the Moments of Inertia: $I_A I_B I_C = [9.8857 \times 10^{-114}]$ g³ cm⁶

Heat of Formation

Murad and Hildenbrand (1) studied the gaseous equilibria involving ZrF₄, ZrF₃, ZrF₂, Ca and CaF₂. These species were generated at high temperatures in a graphite Knudsen cell containing powdered calcium fluoride and elemental zirconium. Ion intensities were measured 3 eV above threshold over the temperature range 1665-1747°K and the equilibrium constants were calculated for the following isomolecular reaction: Ca(g) + ZrF₄(g) = CaF(g) + ZrF₃(g). Based on the reported equilibrium constants, the enthalpy change of this reaction is evaluated by the second and third law methods as -8.0 ± 25 and 28.0 ± 2 kcal/mol, respectively. The third law entropy drift is 20 ± 15 eu. Using the third law value and ΔH_f⁰₂₉₈ = 42.85 ± 0.3, -400.0 ± 0.5, and -65.0 ± 2 kcal/mol for Ca(g), ZrF₄(g), and CaF(g) we obtain ΔH_f⁰₂₉₈(ZrF₃, g) = -264.2 ± 5 kcal/mol, which is adopted. Employing slightly different Gibbs energy functions and ΔH_f⁰₂₉₈ values for the products and reactants, Murad and Hildenbrand (1) evaluated the third law enthalpy change of the above reaction as 28.4 ± 5 and ΔH_f⁰₂₉₈(ZrF₃, g) = -262 ± 5 kcal/mol, which are in reasonable agreement with the values adopted here.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of TiF₃(g). The Zr-F bond distance is estimated by comparison with those for ZrF₄(g) and ZrF₂(g). The F-Zr-F bond angle is taken to be slightly larger than the F-Ti-F bond angle in the TiF₃(g) molecule. The vibrational frequencies are calculated by the valence force method (2) using force constants transferred from those for the ZrF₂(g) molecule. The three principal moments of inertia are: $I_A = I_B = 1.8280 \times 10^{-38}$ g cm², and $I_C = 2.9593 \times 10^{-38}$ g cm². The electronic levels are estimated to be three times higher than those of TiF₃(g), based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by C. E. Moore (3). The quantum weights are assumed to be the same as those of TiF₃(g).

References

1. E. Murad and D. L. Hildenbrand, J. Chem. Phys. **45**, 4751 (1966).
2. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945.
3. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std. Circ. 467.

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	ΔH _f ^o	Log K _p
0	∞	∞	∞	∞	∞
100	10.361	57.433	90.824	-409.478	INFINITE
200	17.222	66.520	111.957	-407.475	890.535
298	22.287	74.659	141.467	-404.983	441.869
300	22.361	74.767	142.029	-405.002	293.649
400	25.499	81.607	175.548	-400.532	201.798
500	27.376	87.574	214.737	-395.682	171.672
600	28.559	92.678	259.512	-388.782	141.614
700	29.337	97.162	310.797	-384.775	120.132
800	30.021	101.194	366.610	-380.680	101.470
900	30.251	104.638	426.010	-376.500	85.000
1000	30.530	107.641	489.035	-372.222	81.349
1100	30.741	110.761	555.709	-367.855	73.042
1200	30.903	113.453	626.252	-363.014	66.114
1300	31.034	115.826	699.986	-357.719	60.066
1400	31.134	118.226	776.256	-352.119	54.666
1500	31.217	120.376	855.475	-345.611	50.064
1600	31.286	122.383	938.393	-338.435	45.695
1700	31.343	124.252	1025.661	-329.471	41.642
1800	31.392	125.993	1117.928	-318.729	36.950
1900	31.432	127.793	1215.700	-307.200	31.660
2000	31.467	129.596	1319.619	-294.861	32.606
2100	31.497	130.932	1429.169	-281.767	30.118
2200	31.523	132.308	1544.073	-267.876	27.656
2300	31.546	133.724	1664.876	-253.186	25.273
2400	31.566	135.183	1792.058	-237.667	22.933
2500	31.584	136.632	1926.144	-221.346	20.561
2600	31.600	137.671	2066.794	-204.268	18.177
2700	31.614	138.664	2214.581	-186.471	15.780
2800	31.626	139.612	2369.976	-167.931	13.373
2900	31.638	140.514	2533.356	-148.684	10.956
3000	31.648	142.196	2705.144	-128.766	8.522
3100	31.657	143.234	2885.991	-108.191	6.076
3200	31.666	144.239	3076.470	-86.961	3.626
3300	31.673	145.216	3277.156	-65.086	1.176
3400	31.680	146.160	3488.611	-42.566	-1.274
3500	31.687	147.078	3701.404	-19.300	-3.705
3600	31.693	147.971	3926.191	4.595	-6.098
3700	31.698	148.839	4162.541	28.744	-8.456
3800	31.703	149.683	4410.926	52.561	-10.776
3900	31.708	150.508	4670.819	75.941	-13.061
4000	31.712	151.311	4942.706	97.876	-15.316
4100	31.716	152.094	5226.163	118.366	-17.542
4200	31.720	152.858	5521.686	137.402	-19.736
4300	31.724	153.603	5829.789	154.986	-21.900
4400	31.729	154.327	6150.000	171.216	-24.036
4500	31.732	155.047	6482.941	186.100	-26.156
4600	31.732	155.745	6829.178	199.636	-28.266
4700	31.735	156.427	7189.261	211.831	-30.366
4800	31.739	157.093	7563.751	222.681	-32.456
4900	31.742	157.750	7952.316	232.191	-34.536
5000	31.742	158.391	8355.616	240.361	-36.606
5100	31.744	159.019	8774.416	247.191	-38.666
5200	31.747	159.636	9209.481	252.681	-40.716
5300	31.749	160.243	9661.481	256.831	-42.756
5400	31.751	160.834	10130.116	259.641	-44.786
5500	31.751	161.417	10616.116	261.111	-46.806
5600	31.752	161.989	11119.116	261.241	-48.816
5700	31.754	162.551	11639.881	260.031	-50.816
5800	31.756	163.103	12178.116	257.481	-52.806
5900	31.757	163.646	12734.616	253.591	-54.786
6000	31.758	164.180	13309.116	248.261	-56.756

$\Delta H_f^o = -409.5 \pm 3.4 \text{ kcal. mole}^{-1}$

$\Delta H_f^o 298.15 = -411.9 \pm 3.4 \text{ kcal. mole}^{-1}$

Point group [D_{2h}]

$S_{298.15} = [74.63] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[430] (1)	[390] (1)
[260] (1)	[680] (1)
[330] (1)	[930] (1)
[250] (1)	[700] (1)
[720] (1)	[500] (1)
[700] (1)	[500] (1)

Bond Distance: Mg-F = [1.77] Å

Bond Angle: F-Mg-F = [135]°

Product of the Moments of Inertia: $I_{AB} I_C = [5.571 \times 10^{-11}] \text{ g.}^2 \text{ cm.}^2$

The enthalpy change, $\Delta H_f^o = 30 \text{ kcal. mole}^{-1}$, for the reaction $\text{MgF}_2(c) + \text{MgF}_2(g) = (\text{MgF}_2)_2(g)$ was determined by J. Berkowitz and J. R. Marquart, J. Chem. Phys. 9, 1853 (1962). Hence the heat of formation for $(\text{MgF}_2)_2(g)$ was calculated.

Heat Capacity and Entropy.

The molecular structure was assumed to be planar. The two Mg atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two F atoms. The two remaining F atoms are situated outside the square on a straight line joining the two Mg atoms. The bond distance between Mg and F atom was estimated to be the same as that in the $\text{MgF}_2(g)$ molecule. Vibrational frequencies were estimated by comparison with those for $\text{MgF}(g)$ and $(\text{NaF})_2$. The vibrational frequencies for $(\text{NaF})_2$ were calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960). The three principal moments are 9.895×10^{-39} , 7.0235×10^{-39} , and $8.01631 \times 10^{-39} \text{ g. cm.}^2$.

GFW = 187.933

(IDEAL GAS)

MOLYBDENUM OXYTETRAFLUORIDE (MoOF₄)Molybdenum Oxytetrafluoride (MoOF₄)
(Ideal Gas) GFW = 187.933 $\Delta H_f^\circ = [-298 \pm 30] \text{ kcal/mol}$ Point Group $[C_{4v}]$ $\Delta H_f^\circ = [-298 \pm 30] \text{ kcal/mol}$ $S_{298.15}^\circ = [78.99 \pm 2.00] \text{ gibbs/mol}$

Ground State Quantum Weight = {1}

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
1045 (1)	[600] (1)	720 (2)
1245 (1)	[300] (1)	530 (2)
680 (1)	[200] (1)	[150] (2)

Bond Distance: Mo-O = $(1.64) \text{ \AA}$ Mo-F = $(1.82) \text{ \AA}$ Bond Angle: O-Mo-F = $[90^\circ]$ F-Mo-F = $[90^\circ]$ Product of Moments of Inertia: $I_A I_B I_C = [3.1468 \times 10^{-113}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

Zimov et al. (1) investigated the stabilities of some molybdenum and tungsten oxyfluorides by means of mass spectrometry. These studies led to heats of formation for $\text{MoO}_2\text{F}_2(\text{g})$, $\text{WO}_2\text{F}_2(\text{g})$, and $\text{MoF}_4(\text{g})$ which were used by the authors to develop a correlation among the heats of formation of the oxides, oxyfluorides, and fluorides of Mo and W. ΔH_f° varies almost linearly with the number of oxygen atoms (1) for the series WF_6 , MoF_6 , and WO_2F_2 . Assuming a similar variation for MoF_4 , MoOF_4 , and Mo_2F_4 , we estimate $\Delta H_f^\circ(\text{MoOF}_4, \text{g}) = -320 \text{ kcal/mol}$.

Heat of formation data (2) for $\text{MoF}_6(\text{g})$, $\text{MoO}(\text{g})$, and $\text{MoO}_3(\text{g})$ have been used to derive the following average bond dissociation energies:

 $\bar{D}(\text{Mo-F}) = 107 \text{ kcal/mol}$ $\bar{D}(\text{Mo-O}) = 135 \text{ kcal/mol}$ From these data we derive $\Delta H_f^\circ(\text{MoOF}_4, \text{g}) = -271 \text{ kcal/mol}$.The heat of formation for MoOF_4 is tentatively selected as $300 \pm 30 \text{ kcal/mol}$.

Heat Capacity and Entropy

Blanchard (3) suggested that $\text{MoOF}_4(\text{g})$ possessed C_{4v} symmetry by reason of the similarity of its infrared spectra with that of XeOF_4 . X-ray diffraction studies of crystalline MoOF_4 by Edwards et al. (4, 5) support this view. The structure of the molecule is assumed to be square-pyramidal. The bond lengths are from the crystallographic studies of MoOF_4 by Edwards et al. (4, 5). Individual moments of inertia are $I_A = 27.437 \times 10^{-39} \text{ g cm}^2$, $I_B = 41.801 \times 10^{-39} \text{ g cm}^2$.

Blanchard (3) reported the following vibrational frequencies and assignments:

 $\nu_1 = 1045$, $\nu_2 = 720$, $\nu_3 = 680$, and $\nu_6 = 530 \text{ cm}^{-1}$.Similar frequencies have been reported by Edwards et al. (4) from their study of the infrared spectra of gaseous MoOF_4 .The rest of the frequencies and assignments are estimated by comparison with data for XeOF_4 (5).

References

1. K. F. Zimov, O. H. Uy, and J. L. Margrave, *J. Phys. Chem.*, **73**, 3008 (1969).
2. JANAF Data.
3. S. Blanchard, Commissariat a l'Energie Atomique report CEA-R 3194, 1967.
4. A. J. Edwards, G. R. Jones, and B. R. Stevenson, *Chem. Commun.*, 462 (1967).
5. A. J. Edwards and B. R. Stevenson, *J. Chem. Soc.*, 2503 (1968).
6. G. M. Bagun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	0.000	INFINITE	INFINITE	0.000	-298.285	INFINITE
100	12.901	56.771	56.771	4.638	-298.173	644.226
200	23.121	78.992	78.992	2.672	-298.000	209.144
298	23.121	78.992	78.992	0.000	-298.119	
300	23.185	79.135	79.135	.043	-298.229	207.769
400	25.959	86.213	79.939	2.510	-300.021	153.146
500	27.631	92.186	81.608	5.194	-299.932	120.366
600	29.720	97.337	83.978	8.015	-299.784	96.520
700	29.445	101.622	10.926	-299.607	-265.602	62.925
800	29.948	105.769	88.417	13.897	-299.419	71.236
900	30.308	109.336	90.548	18.911	-299.222	62.150
1000	30.575	112.546	109.956	19.956	-299.027	54.687
1100	30.776	115.470	94.539	23.024	-298.836	48.947
1200	30.932	118.155	66.397	26.109	-298.655	44.001
1300	31.055	120.636	98.187	29.209	-298.490	39.618
1400	31.154	122.941	99.655	32.320	-298.344	36.234
1500	31.234	125.093	101.487	35.439	-298.219	33.130
1600	31.301	127.111	103.007	38.566	-298.116	30.415
1700	31.356	129.011	104.482	41.699	-298.041	28.020
1800	31.402	130.604	105.895	44.837	-297.995	25.692
1900	31.442	132.053	107.251	47.979	-297.973	23.987
2000	31.476	134.117	109.554	51.125	-297.962	22.273
2100	31.505	135.653	109.608	54.274	-298.022	20.723
2200	31.530	137.119	111.017	57.426	-298.096	19.133
2300	31.553	138.521	112.182	60.580	-298.205	18.025
2400	31.572	139.665	113.306	63.736	-298.356	16.884
2500	31.589	141.154	114.396	66.895	-298.562	15.757
2600	31.605	142.393	115.449	70.054	-298.832	14.723
2700	31.618	143.566	116.469	73.215	-299.174	13.622
2800	31.631	144.736	117.458	76.376	-299.598	12.547
2900	31.642	145.866	118.418	79.542	-300.738	12.148
3000	31.652	146.919	119.351	82.706	-300.956	11.578
3100	31.661	147.937	120.257	85.872	-307.177	10.656
3200	31.669	148.963	121.138	89.036	-307.405	9.979
3300	31.676	149.937	121.996	92.206	-307.639	9.342
3400	31.683	150.863	122.832	95.374	-307.878	8.743
3500	31.689	151.802	123.647	98.542	-308.125	8.177
3600	31.695	152.694	124.441	101.712	-308.374	7.642
3700	31.700	153.563	125.216	104.881	-308.632	7.136
3800	31.705	154.408	125.974	108.052	-308.894	6.656
3900	31.710	155.232	126.713	111.222	-309.163	6.201
4000	31.714	156.035	127.436	114.394	-309.436	5.767
4100	31.718	156.818	128.143	117.565	-309.716	5.355
4200	31.721	157.582	128.835	120.737	-310.000	4.941
4300	31.725	158.329	129.513	123.909	-310.286	4.568
4400	31.728	159.056	130.176	127.082	-310.585	4.228
4500	31.731	159.771	130.826	130.255	-310.884	3.885
4600	31.734	160.469	131.462	133.428	-311.189	3.556
4700	31.736	161.151	132.087	136.601	-311.500	3.242
4800	31.739	161.819	132.699	139.775	-311.814	2.939
4900	31.741	162.474	133.300	142.949	-312.135	2.650
5000	31.743	163.115	133.899	146.124	-312.475	2.269
5100	31.745	163.744	134.469	149.298	-312.827	1.880
5200	31.747	164.360	135.036	152.473	-313.186	1.506
5300	31.749	164.965	135.597	155.647	-313.549	1.145
5400	31.750	165.558	136.147	158.822	-313.919	.797
5500	31.752	166.141	136.687	161.997	-314.296	.461
5600	31.753	166.713	137.218	165.173	-314.677	.137
5700	31.755	167.275	137.740	168.348	-315.051	.177
5800	31.756	167.827	138.254	171.524	-315.428	.480
5900	31.758	168.370	138.760	174.699	-315.804	.773
6000	31.759	168.904	139.256	177.875	-316.179	1.056

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	.000	INFINITE	-3.710	.582	INFINITE	
100	9.981	57.235	-2.835	.618	5.609	-12.258
200	14.303	65.365	-2.437	.618	12.219	-13.352
298	18.922	71.962	.000	2.000	18.080	-13.985
300	19.000	72.079	.036	2.005	19.210	-13.984
400	22.584	78.066	2.125	2.081	26.113	-14.376
500	25.047	83.388	6.514	2.081	33.423	-14.600
600	26.717	88.112	7.408	1.863	40.507	-14.754
700	27.682	92.242	7.471	1.500	47.246	-14.844
800	28.686	95.810	8.022	1.150	53.756	-14.888
900	29.277	99.514	8.224	.817	61.481	-14.929
1000	29.719	102.623	8.410	.410	68.380	-14.944
1100	30.057	105.472	85.917	.007	75.239	-14.948
1200	30.327	108.023	88.921	.857	82.061	-14.945
1300	30.528	110.334	92.329	1.584	88.861	-14.934
1400	30.696	112.463	96.022	2.184	95.598	-14.923
1500	30.833	114.425	99.927	2.653	102.321	-14.907
1600	30.946	116.249	104.019	2.993	109.014	-14.890
1700	31.037	117.957	108.309	3.253	115.683	-14.871
1800	31.110	119.559	112.797	3.453	122.331	-14.850
1900	31.168	121.059	117.484	3.593	128.964	-14.831
2000	31.246	123.460	122.359	3.702	135.544	-14.811
2100	31.296	125.386	127.447	4.108	142.117	-14.790
2200	31.327	127.277	132.742	4.507	148.516	-14.769
2300	31.378	129.220	138.259	4.897	154.746	-14.748
2400	31.441	131.213	143.987	5.279	160.814	-14.728
2500	31.481	133.256	149.922	5.653	166.725	-14.707
2600	31.468	135.350	156.057	6.155	172.477	-14.687
2700	31.493	137.493	162.415	6.534	178.071	-14.668
2800	31.513	139.683	168.997	6.834	183.516	-14.649
2900	31.532	141.920	175.811	7.079	188.813	-14.629
3000	31.549	144.203	182.864	7.264	193.961	-14.610
3100	31.564	146.534	190.167	8.004	200.561	-14.592
3200	31.579	148.913	197.720	8.459	206.085	-14.574
3300	31.593	151.340	205.533	8.710	211.400	-14.556
3400	31.603	153.813	213.606	8.898	216.502	-14.538
3500	31.614	156.331	221.946	9.398	222.378	-14.522
3600	31.624	158.893	230.557	9.736	228.052	-14.506
3700	31.633	161.500	239.444	10.069	233.521	-14.490
3800	31.642	164.153	248.617	10.397	238.886	-14.474
3900	31.649	166.853	258.074	10.720	244.156	-14.458
4000	31.657	169.600	267.821	11.039	249.336	-14.443
4100	31.663	172.393	277.858	11.352	254.426	-14.428
4200	31.668	175.232	288.185	11.654	259.426	-14.413
4300	31.672	178.117	298.802	11.948	264.336	-14.398
4400	31.676	181.047	309.710	12.235	269.156	-14.383
4500	31.681	184.020	320.909	12.516	273.886	-14.368
4600	31.685	187.037	332.392	12.791	278.526	-14.353
4700	31.689	190.099	344.159	13.060	283.076	-14.338
4800	31.693	193.207	356.212	13.324	287.536	-14.323
4900	31.697	196.361	368.559	13.583	291.906	-14.308
5000	31.701	199.561	381.202	13.837	296.186	-14.293
5100	31.705	202.807	394.149	14.086	300.376	-14.278
5200	31.709	206.099	407.402	14.330	304.476	-14.263
5300	31.713	209.437	420.961	14.569	308.486	-14.248
5400	31.717	212.821	434.826	14.803	312.406	-14.233
5500	31.722	216.251	448.997	15.032	316.236	-14.218
5600	31.725	219.726	463.474	15.256	320.076	-14.203
5700	31.729	223.246	478.259	15.475	323.826	-14.188
5800	31.732	226.811	493.352	15.689	327.486	-14.173
5900	31.736	230.421	508.763	15.898	331.056	-14.158
6000	31.739	234.076	524.497	16.102	334.536	-14.143

Mar. 31, 1964

TETRAFLUOROHYDRAZINE (N₂F₄)Point Group = C₂S_{298.15} = 71.96 cal. deg.⁻¹ mole⁻¹.

Ground State Quantum Weight = 1

(IDEAL GAS)

MOL. WT. = 104.016

ΔH_f⁰ = 0.6 ± 2.5 kcal. mole⁻¹ΔH_f⁰ 298.15 = -2.0 ± 2.5 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹	ω, cm. ⁻¹
1010 (1)	549 (1)	946 (1)	
933 (1)	390 (1)	737 (1)	
591 (1)	122 (1)	519 (1)	
	959 (1)	467 (1)	

Bond Distances: N-N = [1.47 Å] N-F = [1.37 Å]

Bond Angles: F-N-F = [108°] N-N-F = [104°] Dihedral Angle = [65°]

Product of the Moments of Inertia: I_AI_BI_C = [1.1817 X 10⁻¹¹³] gm.³ cm.⁶

Heat of Formation.

G. T. Armstrong, S. Marantz, and C. F. Coyle, National Bureau of Standards Report No. 6584, October, 1959, studied the reaction



From this reaction, they calculate the heat of formation of N₂F₄ to be -2.0 ± 2.5 kcal. mole⁻¹. The recalculated heat of formation of NH₄F(s) (see NF₂ table) differs from the value quoted in Circular 500 by 0.06 kcal. mole⁻¹. This correction would make the heat of formation of tetrafluorohydrazine more negative by 0.24 kcal. mole⁻¹. In view of the large uncertainty in the heat of formation, however, this correction was not applied.

Heat Capacity and Entropy.

The fundamental frequencies were taken from the vapor phase infrared work of J. R. Durig and R. C. Lord, Spectrochim. Acta 19, 1877 (1963). The principal moments of inertia were calculated from the rotational constants reported by D. R. Lide, Jr. and D. E. Mann, J. Chem. Phys. 31, 1129 (1959). Lide and Mann calculated the bond angles for assumed values of the NN and NF distances.

The principal moments of inertia are: I_A = 1.5051 X 10⁻³⁸ gm. cm.², I_B = 2.6315 X 10⁻³⁸ gm. cm.², I_C = 2.9836 X 10⁻³⁸ gm. cm.².

continued from the table nitrogen difluoride (NF₂) (ideal gas).

Heat Capacity and Entropy.

M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. 35, 1129 (1961), investigated the infrared spectrum of NF₂. They were able to assign the band center at 1074 cm.⁻¹ to the symmetric stretching mode ω₁. The absorption in the 930-940 cm.⁻¹ region was assigned to ω₃.

M. D. Harmony and R. J. Myers, J. Chem. Phys. 37, 636 (1962), performed matrix isolation experiments on NF₂. They arrived at the assignments ω₁ = 1070 cm.⁻¹, ω₂ = 573 cm.⁻¹, and ω₃ = 931 cm.⁻¹. The stretching frequencies for similar molecules in an N₂ matrix are about 5 cm.⁻¹ below the gas phase values. A comparison of the gas phase and matrix values of ω₁ show excellent agreement.

F. A. Johnson and C. B. Colburn, Inorg. Chem. 1, 431 (1962), report infrared studies on NF₂ but they draw no definite conclusions.

The gas phase value for ω₁ and the matrix values for ω₂ and ω₃ were taken to represent the fundamental vibrational frequencies of NF₂.

Harmony, Myers, Schoen, Lide, and Mann estimated the N-F distance as 1.37 Å and used this with their data to calculate an F-N-F angle of 104.2°. Using these data the moments of inertia are: I_A = 7.3728 X 10⁻³⁹ gm. cm.², I_B = 1.2035 X 10⁻³⁹ gm. cm.², I_C = 8.5763 X 10⁻³⁹ gm. cm.².

Tungsten Oxytetrafluoride (WOF₄)
(Crystal) GFW = 275.843

OPW = 275.843 F₄OW

(CRYSTAL)

T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	31.926	42.000	42.000	.000	-355.370	-329.371	241.435
300	32.000	42.198	42.001	.059	-355.354	-329.210	240.829
400	36.000	46.151	45.306	1.845	-353.527	-312.682	235.500
500	39.800	49.410	45.696	7.257	-353.224	-312.304	136.509
600	42.700	51.937	46.954	11.390	-351.743	-304.256	110.625
700	44.600	54.070	52.156	15.760	-350.085	-296.470	92.562
800	46.100	55.715	53.384	20.529	-348.321	-288.933	78.933
900	47.300	57.117	54.541	24.646	-346.461	-281.586	68.006
1000	47.300	57.137	55.502	29.635	-344.613	-274.511	59.094

ΔH°₀ = Unknown

ΔH°_{298.15} = [-355.37 ± 6] kcal/mol

ΔH°_m = 1.219 ± 2 kcal/mol

S°_{298.15} = [42.0 ± 4] gibbs/mol

T_m = 379°K

Heat of Formation.

The heat of formation, ΔH°_f(WOF₄, c) = -355.37 kcal/mol, is calculated from that of the gas less the heat of sublimation, ΔH°_{sub} = 16.97 kcal/mol. The latter is calculated by the third law method from the vapor pressure equation determined by G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961). The second law ΔH°_{f298} is 17.01 kcal/mol.

Heat Capacity and Entropy.

The heat capacities are estimated from those of WOCl₄(c), WO₃(c), WO₂(c), WOCl₆(c) and WF₆(c,l).

The entropy, S°₂₉₈ = 42.0 eu, is calculated from ΔS°₃₄₈ = 37.0 eu for WOF₄(c) → WOF₄(g), obtained from the second law analysis of the vapor pressure equation given by Cady and Hargreaves, loc. cit.

It is surprising that this entropy is larger than the corresponding value for WOCl₄(c) (JANAF WOCl₄(c) table dated Mar. 31, 1967). In both cases the entropies of the condensed phases are derived from the gas phase values using second law analysis of sublimation and vaporization data. The resulting entropy of melting for WOF₄, 3.2 eu, is much smaller than the value 22.4 eu for WOCl₄. This extreme difference may be a reflection of the uncertainty inherent in derivation of ΔS°_m as the difference between the values for sublimation and vaporization. If the values of ΔS°_m are correct, they suggest the possibility of an undiscovered solid state transition for WOF₄ similar to that observed for WF₆.

Melting Data.

T_m is calculated as the temperature at which the Gibbs energy of reaction WOF₄(c) → WOF₄(l) approaches zero. The difference between the heats of formation for crystal and liquid at the melting point is ΔH°_m.

O. Ruff, F. Elander, and W. Heller, Z. Anorg. Chem. 52, 256 (1907), reported the melting point as 393°K. Cady and Hargreaves, loc. cit., derived the melting point as 378°K, and the heat of fusion as 2.26 kcal/mol from vapor pressure equations for crystal and liquid. This second law value of ΔH°_m, when corrected for ΔC_p of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

T, °K	C _p ^a	$\mu\text{bbh/mol}$ S ^b	$-(G^\circ - H^\circ_{298})/T$	H ^c - H ²⁹⁸	ΔH°	ΔG°	Log K _p
0							
100							
200							
298	43.500	42.800	42.800	.000	-354.955	-329.194	241.306
300	43.500	43.049	42.801	.080	-354.920	-329.035	239.702
400	43.500	45.583	44.507	4.330	-351.055	-325.490	175.217
500	43.500	48.280	47.729	6.785	-351.285	-312.807	136.728
600	43.500	51.221	51.337	13.130	-349.568	-305.271	111.195
700	43.500	54.252	54.252	21.430	-347.530	-298.093	79.006
800	43.500	57.255	57.255	29.730	-345.530	-290.993	79.006
900	43.500	60.259	61.769	26.180	-344.815	-285.163	69.004
1000	43.500	63.262	64.911	30.530	-343.302	-277.505	60.649

June 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF₄)

(LIQUID)

OFW = 275.843

$$\Delta H^\circ_{298,15} = [-354.955] \text{ kcal/mol}$$

$$\Delta H_m^\circ = 1.219 \pm 2 \text{ kcal/mol}$$

$$\Delta H_v^\circ = 13.4 \text{ kcal/mol}$$

$$S^\circ_{298,15} = [42.8 \pm 4] \text{ gibbs/mol}$$

$$T_m = 379^\circ\text{K}$$

$$T_b = 460^\circ\text{K}$$

Heat of Formation.

The heat of formation, $\Delta H^\circ_{298}(\text{WOF}_4, l) = -354.955 \text{ kcal/mol}$, is calculated from that of the gas less the heat of vaporization, $\Delta H^\circ_{298} = 16.555 \text{ kcal/mol}$. The latter is calculated by the third law method from the vapor pressure equation determined by G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961). The second law ΔH°_{298} is 16.60 kcal/mol.

Heat Capacity and Entropy.

The heat capacity is assumed to be constant at 7.25 gibbs/g-atom as suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, 1959.

The entropy, $S^\circ_{298} = 42.8 \text{ eu}$, is calculated from $\Delta S^\circ_{298} = 31.2 \text{ eu}$ for $\text{WOF}_4(l) \rightarrow \text{WOF}_4(g)$, obtained from the second law analysis of the vapor pressure equation given by Cady and Hargreaves, loc. cit.

Melting Data.

See WOF₄(c) table (Mar. 31, 1967).

Vaporization Data.

T_b is calculated as the temperature at which the Gibbs energy of reaction $\text{WOF}_4(l) \rightarrow \text{WOF}_4(g)$ approaches zero. The difference between the heats of formation for liquid and gas at the boiling point is ΔH_v° .

O. Ruff, P. Eisner and W. Heller, Z. Anorg. Chem. 52, 256 (1907), reported the boiling point as 459°K. Cady and Hargreaves, loc. cit., derived the boiling point as 459°K, and the heat of vaporization as 14.23 kcal/mol from the vapor pressure equation for the liquid. This second law value of ΔH_v° , when corrected for ΔC_p of vaporization, is in good agreement with the value adopted in the tabulation.

Tungsten Oxytetrafluoride (WOF₄)
(Ideal Gas) $\Delta H_f^\circ = 275.843$

T, °K	Cp°	gibbs/mol S°	(G°-H° ₂₉₈)/T	— kcal/mol — H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	-0.000	0.000	INFINITE	- 9.467	- 336.420	- 336.420	INFINITE
100	17.552	61.438	97.238	- 3.540	- 337.387	- 333.132	726.059
200	18.170	72.462	82.338	- 1.975	- 338.050	- 329.067	359.067
298	21.914	80.448	60.448	0.000	- 338.400	- 323.464	237.399
300	21.975	80.583	60.468	0.041	- 338.405	- 323.774	235.849
400	24.749	83.309	43.346	2.385	- 338.505	- 318.451	177.223
500	26.441	85.049	31.127	4.691	- 338.550	- 313.051	137.228
600	27.919	86.026	22.505	7.693	- 338.470	- 309.037	112.566
700	28.900	86.400	17.355	10.531	- 338.344	- 304.139	94.956
800	29.472	86.789	13.484	13.484	- 338.195	- 299.266	81.756
900	29.872	87.181	10.532	16.415	- 338.024	- 294.431	71.282
1000	30.212	87.566	8.153	19.415	- 337.862	- 289.731	63.282
1100	30.670	87.940	6.141	22.450	- 337.695	- 285.156	56.575
1200	30.870	88.300	4.524	25.507	- 337.531	- 280.709	50.865
1300	31.050	88.640	3.251	28.583	- 337.369	- 276.387	45.257
1400	31.219	88.960	2.280	31.673	- 337.209	- 272.191	40.739
1500	31.061	89.260	1.592	34.773	- 337.054	- 268.124	36.597
1600	31.147	89.540	1.120	37.884	- 336.971	- 264.184	32.829
1700	31.219	89.790	0.820	41.002	- 336.860	- 260.374	29.421
1800	31.280	90.020	0.590	44.127	- 336.766	- 256.679	26.316
1900	31.329	90.230	0.420	47.259	- 336.684	- 253.192	23.428
2000	31.376	90.420	0.300	50.391	- 336.617	- 249.825	20.848
2100	31.414	90.590	0.220	53.523	- 336.567	- 246.576	18.541
2200	31.447	90.740	0.160	56.656	- 336.535	- 243.344	16.485
2300	31.475	90.870	0.110	59.782	- 336.517	- 240.131	14.631
2400	31.502	90.990	0.070	62.912	- 336.510	- 236.943	12.973
2500	31.525	91.100	0.040	66.042	- 336.516	- 233.774	11.503
2600	31.545	91.200	0.020	69.176	- 336.570	- 230.631	10.191
2700	31.563	91.290	0.010	72.311	- 336.627	- 227.511	9.003
2800	31.579	91.370	0.005	75.446	- 336.684	- 224.414	7.923
2900	31.593	91.440	0.002	78.581	- 336.744	- 221.338	6.943
3000	31.606	91.500	0.001	81.716	- 336.803	- 218.281	6.063
3100	31.618	91.550	0.000	84.851	- 336.864	- 215.241	5.283
3200	31.629	91.590	0.000	87.986	- 336.926	- 212.214	4.603
3300	31.638	91.620	0.000	91.121	- 336.989	- 209.201	4.013
3400	31.646	91.640	0.000	94.256	- 337.054	- 206.201	3.513
3500	31.656	91.656	0.000	97.391	- 337.120	- 203.214	3.093
3600	31.664	91.668	0.000	100.526	- 337.187	- 200.241	2.743
3700	31.671	91.676	0.000	103.661	- 337.254	- 197.281	2.453
3800	31.677	91.682	0.000	106.796	- 337.321	- 194.331	2.213
3900	31.683	91.687	0.000	109.931	- 337.388	- 191.391	2.003
4000	31.688	91.691	0.000	113.066	- 337.454	- 188.461	1.813
4100	31.693	91.693	0.000	116.201	- 337.521	- 185.541	1.643
4200	31.698	91.695	0.000	119.336	- 337.588	- 182.631	1.493
4300	31.703	91.696	0.000	122.471	- 337.654	- 179.731	1.363
4400	31.707	91.697	0.000	125.606	- 337.721	- 176.841	1.253
4500	31.711	91.698	0.000	128.741	- 337.788	- 173.961	1.163
4600	31.714	91.698	0.000	131.876	- 337.854	- 171.091	1.093
4700	31.716	91.698	0.000	135.011	- 337.921	- 168.231	1.043
4800	31.718	91.698	0.000	138.146	- 337.988	- 165.381	0.993
4900	31.724	91.699	0.000	141.281	- 338.054	- 162.541	0.953
5000	31.727	91.700	0.000	144.416	- 338.121	- 159.711	0.923
5100	31.729	91.700	0.000	147.551	- 338.188	- 156.891	0.893
5200	31.732	91.700	0.000	150.686	- 338.254	- 154.081	0.873
5300	31.734	91.700	0.000	153.821	- 338.321	- 151.281	0.853
5400	31.736	91.700	0.000	156.956	- 338.388	- 148.491	0.833
5500	31.738	91.700	0.000	160.091	- 338.454	- 145.711	0.813
5600	31.740	91.700	0.000	163.226	- 338.521	- 142.941	0.793
5700	31.742	91.700	0.000	166.361	- 338.588	- 140.181	0.773
5800	31.744	91.700	0.000	169.496	- 338.654	- 137.431	0.753
5900	31.746	91.700	0.000	172.631	- 338.721	- 134.691	0.733
6000	31.747	91.700	0.000	175.766	- 338.788	- 131.961	0.713

June 30, 1962; Mar. 31, 1967

TUNGSTEN OXYTETRAFLUORIDE (WOF₄)
(IDEAL GAS)

Point Group [C_{2v}]
S_{298.15} = [80.4] gibbs/mol
Ground State Quantum Weight = 1

$\Delta H_f^\circ = -336.4 \pm 6$ kcal/mol
 $\Delta H_f^\circ = -338.15$ kcal/mol

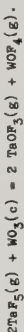
Vibrational Frequencies and Degeneracies	w, cm ⁻¹	w, cm ⁻¹	w, cm ⁻¹
	[1000] (1)	[700] (1)	[250] (1)
	[1000] (1)	[700] (1)	[250] (1)
	[900] (1)	[300] (1)	[200] (1)
	[900] (1)	[300] (1)	[200] (1)

Bond Distance: W-F = [1.83] Å W-O = [1.81] Å
Bond Angle: F-W-O = F-W-F = [120°]
F-W-F = F-W-O = [90°]
F-W-F = F-W-O = [180°]

*Equatorial **Axial
Product of the Moments of Inertia: I_{ABC} = [3.868] × 10⁻¹¹³ g³ cm⁶
σ = [2]

Heat of Formation.

The heat of formation, ΔH_f° (WOF₄, g) = -338.4 kcal/mol, is the value determined mass spectrometrically by K. P. Zmbov and J. L. Margrave, Rice Univ., private communication, Mar. 1967, from equilibrium studies of



Heat Capacity and Entropy.

The molecular configuration is assumed to be a trigonal bipyramid similar to that of SOF₄(g), reported by P. L. Oggien, H. L. Roberts and L. A. Woodward.¹ The bond distances W-O and W-F are estimated to be the same as those in WO₃(g) and WF₆(g), respectively. The three principal moments of inertia are I_A = 3.509 × 10⁻³⁸, I_B = 3.698 × 10⁻³⁸ and I_C = 2.981 × 10⁻³⁸ g cm².

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for SOF₄(g),² MoOCl₄(g),³ WO₂Cl₂(g),⁴ CrO₂Cl₂(g),⁵ WO₃(g),⁶ and WF₆(g).⁷ These frequencies are not in point group order.

References.

1. P. L. Oggien, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. **57**, 1877 (1961).
2. T. V. Iorns and F. E. Stafford, J. Am. Chem. Soc. **88**, 4619 (1966).
3. C. G. Barracough and J. Stala, Aust. J. Chem. **19**, 741 (1966).
4. P. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta, **1959**, 709 (1953).
5. H. Stammreich, K. Kawai and Y. Tavares, Spectrochim. Acta, **1959**, 438 (1959).
6. JANAF WO₃(g) table (Sept. 30, 1966), WF₆(g) table (Mar. 31, 1967).

Lead Tetrafluoride (PbF₄) (Ideal Gas) Mol. Wt. = 283.21

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	g° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	-0.000	INF INITE	-4.723	-184.859	-184.859	INF INITE
100	14.123	60.071	3.697	-185.568	-185.568	309.118
200	10.019	71.555	2.4013	-185.965	-179.564	196.100
298	21.735	79.709	0.000	-186.000	-176.260	129.186
300	21.772	79.844	0.040	-186.000	-176.200	128.355
400	22.470	82.187	2.669	-185.850	-174.496	104.456
500	24.076	91.616	4.669	-185.650	-169.704	74.114
600	24.571	96.053	7.103	-185.770	-166.481	60.638
700	24.886	99.866	9.577	-186.868	-163.081	50.914
800	25.099	103.204	12.077	-186.821	-159.087	43.622
900	25.258	106.149	14.605	-186.769	-155.298	37.953
1000	25.355	108.655	17.125	-186.715	-151.510	33.416
1100	25.436	111.256	19.665	-186.658	-147.859	29.709
1200	25.499	113.472	22.212	-186.596	-144.369	26.619
1300	25.547	115.515	24.764	-186.536	-141.024	24.005
1400	25.586	117.409	27.321	-186.476	-137.837	21.766
1500	25.618	119.116	29.881	-186.424	-134.771	19.825
1600	25.644	120.630	32.444	-186.378	-131.723	18.128
1700	25.665	122.385	35.010	-186.337	-128.694	16.631
1800	25.683	124.393	37.577	-186.308	-125.624	15.301
1900	25.697	126.242	40.146	-186.285	-122.674	14.110
2000	25.712	128.500	42.717	-186.271	-119.824	13.038
2100	25.723	130.815	45.289	-186.261	-117.047	12.080
2200	25.733	133.012	47.862	-186.256	-114.427	11.208
2300	25.742	135.156	50.435	-186.256	-111.858	10.426
2400	25.750	137.252	53.010	-186.251	-109.349	9.739
2500	25.756	139.303	55.585	-186.245	-106.895	9.102
2600	25.762	141.313	58.161	-186.239	-104.493	8.514
2700	25.767	143.286	60.737	-186.234	-102.141	7.974
2800	25.772	145.223	63.314	-186.234	-99.839	7.474
2900	25.776	147.127	65.892	-186.232	-97.587	7.009
3000	25.780	149.001	68.470	-186.232	-95.385	6.574
3100	25.783	150.847	71.048	-186.232	-93.233	6.169
3200	25.786	152.665	73.626	-186.232	-91.139	5.794
3300	25.789	154.459	76.205	-186.232	-89.095	5.449
3400	25.792	156.232	78.784	-186.232	-87.101	5.134
3500	25.794	157.976	81.363	-186.232	-85.157	4.849
3600	25.796	161.703	83.943	-186.232	-83.263	4.584
3700	25.798	162.410	86.523	-186.232	-81.419	4.339
3800	25.800	163.098	89.103	-186.232	-79.625	4.114
3900	25.802	163.768	91.683	-186.232	-77.881	3.909
4000	25.804	164.421	94.263	-186.232	-76.187	3.724
4100	25.805	165.059	96.843	-186.232	-74.543	3.559
4200	25.807	165.680	99.424	-186.232	-72.949	3.414
4300	25.808	166.288	102.005	-186.232	-71.405	3.289
4400	25.809	166.881	104.586	-186.232	-69.911	3.174
4500	25.810	167.461	107.167	-186.232	-68.467	3.069
4600	25.811	168.028	109.748	-186.232	-67.073	2.974
4700	25.812	168.584	112.329	-186.232	-65.729	2.889
4800	25.813	169.127	114.910	-186.232	-64.435	2.814
4900	25.814	169.659	117.491	-186.232	-63.191	2.749
5000	25.815	170.181	120.073	-186.232	-62.000	2.694
5100	25.816	170.692	122.654	-186.232	-60.860	2.649
5200	25.816	171.193	125.236	-186.232	-59.771	2.614
5300	25.817	171.685	127.817	-186.232	-58.732	2.589
5400	25.818	172.168	130.399	-186.232	-57.743	2.564
5500	25.818	172.651	132.981	-186.232	-56.804	2.549
5600	25.819	173.106	135.563	-186.232	-55.915	2.534
5700	25.819	173.563	138.145	-186.232	-55.076	2.519
5800	25.820	174.012	140.727	-186.232	-54.287	2.504
5900	25.821	174.464	143.309	-186.232	-53.548	2.489
6000	25.821	174.888	145.891	-186.232	-52.859	2.474

June 30, 1962

Lead Tetrafluoride (PbF₄) (Ideal Gas)

Mol. Wt. = 283.21

 ΔH_f^0 298.15 = [-186] kcal. mole⁻¹ ΔF_f^0 298.15 = 79.7 cal. deg.⁻¹ mole⁻¹Point group T_d

Vibrational Levels and Multiplicities

 ω_e , cm.⁻¹

564 (1)

158 (2)

570 (3)

180 (3)

Pb-F distance = 2.08 Å P-Pb-F angle = 109° 28'

 $I_{A_1, E_C} = 4.8233 \times 10^{-113}$ g.³ cm.⁶ $\sigma = 12$ Heat of Formation. ΔH_f^0 298.15 was estimated by comparison with the value of ΔH_f^0 298.15 for PbF₂(g).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from G. Nagelschen, Bull. Soc. Chim. Belg., 71, 119 (1962).

GFW = 108.058

(IDEAL GAS)

SULFUR TETRAFLUORIDE (SF₄)Point Group C_{2v}S_{298.15} = 71.83 ± 0.10 gibbs/mol

Ground State Quantum Weight = 1

Sulfur Tetrafluoride (SF₄)

(Ideal Gas)

GFW = 108.058

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	HF-H° ₂₉₈	kcal/mol ΔH°	Log Kp
0	10.000	56.000	185.095	185.095	185.095	185.095
100	14.757	62.248	185.095	185.095	185.095	185.095
200	18.270	67.336	185.095	185.095	185.095	185.095
298	20.916	71.829	185.095	185.095	185.095	185.095
300	18.325	71.830	185.095	185.095	185.095	185.095
400	20.691	72.580	185.095	185.095	185.095	185.095
500	22.161	72.334	185.095	185.095	185.095	185.095
600	23.136	75.802	185.095	185.095	185.095	185.095
700	23.776	80.107	185.095	185.095	185.095	185.095
800	24.217	83.312	185.095	185.095	185.095	185.095
900	24.533	86.184	185.095	185.095	185.095	185.095
1000	24.767	88.761	185.095	185.095	185.095	185.095
1100	24.943	91.150	185.095	185.095	185.095	185.095
1200	25.060	93.327	185.095	185.095	185.095	185.095
1300	25.188	95.339	185.095	185.095	185.095	185.095
1400	25.274	97.208	185.095	185.095	185.095	185.095
1500	25.344	98.955	185.095	185.095	185.095	185.095
1600	25.402	100.592	185.095	185.095	185.095	185.095
1700	25.450	102.134	185.095	185.095	185.095	185.095
1800	25.491	103.590	185.095	185.095	185.095	185.095
1900	25.525	104.969	185.095	185.095	185.095	185.095
2000	25.555	106.279	185.095	185.095	185.095	185.095
2100	25.581	107.526	185.095	185.095	185.095	185.095
2200	25.603	108.717	185.095	185.095	185.095	185.095
2300	25.622	109.855	185.095	185.095	185.095	185.095
2400	25.639	110.946	185.095	185.095	185.095	185.095
2500	25.654	121.993	185.095	185.095	185.095	185.095
2600	25.668	123.000	185.095	185.095	185.095	185.095
2700	25.680	124.903	185.095	185.095	185.095	185.095
2800	25.690	126.335	185.095	185.095	185.095	185.095
2900	25.700	127.519	185.095	185.095	185.095	185.095
3000	25.709	128.337	185.095	185.095	185.095	185.095
3100	25.716	129.072	185.095	185.095	185.095	185.095
3200	25.724	129.729	185.095	185.095	185.095	185.095
3300	25.730	130.308	185.095	185.095	185.095	185.095
3400	25.736	130.811	185.095	185.095	185.095	185.095
3500	25.741	131.241	185.095	185.095	185.095	185.095
3600	25.746	131.607	185.095	185.095	185.095	185.095
3700	25.751	131.910	185.095	185.095	185.095	185.095
3800	25.755	132.159	185.095	185.095	185.095	185.095
3900	25.759	132.454	185.095	185.095	185.095	185.095
4000	25.763	132.696	185.095	185.095	185.095	185.095
4100	25.766	132.884	185.095	185.095	185.095	185.095
4200	25.769	133.027	185.095	185.095	185.095	185.095
4300	25.772	133.126	185.095	185.095	185.095	185.095
4400	25.775	133.181	185.095	185.095	185.095	185.095
4500	25.778	133.195	185.095	185.095	185.095	185.095
4600	25.780	133.160	185.095	185.095	185.095	185.095
4700	25.782	133.082	185.095	185.095	185.095	185.095
4800	25.784	132.966	185.095	185.095	185.095	185.095
4900	25.786	132.811	185.095	185.095	185.095	185.095
5000	25.788	132.629	185.095	185.095	185.095	185.095
5100	25.790	132.433	185.095	185.095	185.095	185.095
5200	25.791	132.236	185.095	185.095	185.095	185.095
5300	25.793	132.043	185.095	185.095	185.095	185.095
5400	25.795	131.853	185.095	185.095	185.095	185.095
5500	25.796	131.669	185.095	185.095	185.095	185.095
5600	25.797	131.492	185.095	185.095	185.095	185.095
5700	25.798	131.321	185.095	185.095	185.095	185.095
5800	25.799	131.156	185.095	185.095	185.095	185.095
5900	25.800	130.997	185.095	185.095	185.095	185.095
6000	25.802	130.843	185.095	185.095	185.095	185.095

Sept. 30, 1965; Dec. 31, 1969

Point Group C_{2v}S_{298.15} = 71.83 ± 0.10 gibbs/mol

Ground State Quantum Weight = 1

Sulfur Tetrafluoride (SF₄)

(Ideal Gas)

GFW = 108.058

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	HF-H° ₂₉₈	kcal/mol ΔH°	Log Kp
0	10.000	56.000	185.095	185.095	185.095	185.095
100	14.757	62.248	185.095	185.095	185.095	185.095
200	18.270	67.336	185.095	185.095	185.095	185.095
298	20.916	71.829	185.095	185.095	185.095	185.095
300	18.325	71.830	185.095	185.095	185.095	185.095
400	20.691	72.580	185.095	185.095	185.095	185.095
500	22.161	72.334	185.095	185.095	185.095	185.095
600	23.136	75.802	185.095	185.095	185.095	185.095
700	23.776	80.107	185.095	185.095	185.095	185.095
800	24.217	83.312	185.095	185.095	185.095	185.095
900	24.533	86.184	185.095	185.095	185.095	185.095
1000	24.767	88.761	185.095	185.095	185.095	185.095
1100	24.943	91.150	185.095	185.095	185.095	185.095
1200	25.060	93.327	185.095	185.095	185.095	185.095
1300	25.188	95.339	185.095	185.095	185.095	185.095
1400	25.274	97.208	185.095	185.095	185.095	185.095
1500	25.344	98.955	185.095	185.095	185.095	185.095
1600	25.402	100.592	185.095	185.095	185.095	185.095
1700	25.450	102.134	185.095	185.095	185.095	185.095
1800	25.491	103.590	185.095	185.095	185.095	185.095
1900	25.525	104.969	185.095	185.095	185.095	185.095
2000	25.555	106.279	185.095	185.095	185.095	185.095
2100	25.581	107.526	185.095	185.095	185.095	185.095
2200	25.603	108.717	185.095	185.095	185.095	185.095
2300	25.622	109.855	185.095	185.095	185.095	185.095
2400	25.639	110.946	185.095	185.095	185.095	185.095
2500	25.654	121.993	185.095	185.095	185.095	185.095
2600	25.668	123.000	185.095	185.095	185.095	185.095
2700	25.680	124.903	185.095	185.095	185.095	185.095
2800	25.690	126.335	185.095	185.095	185.095	185.095
2900	25.700	127.519	185.095	185.095	185.095	185.095
3000	25.709	128.337	185.095	185.095	185.095	185.095
3100	25.716	129.072	185.095	185.095	185.095	185.095
3200	25.724	129.729	185.095	185.095	185.095	185.095
3300	25.730	130.308	185.095	185.095	185.095	185.095
3400	25.736	130.811	185.095	185.095	185.095	185.095
3500	25.741	131.241	185.095	185.095	185.095	185.095
3600	25.746	131.607	185.095	185.095	185.095	185.095
3700	25.751	131.910	185.095	185.095	185.095	185.095
3800	25.755	132.159	185.095	185.095	185.095	185.095
3900	25.759	132.454	185.095	185.095	185.095	185.095
4000	25.763	132.696	185.095	185.095	185.095	185.095
4100	25.766	132.884	185.095	185.095	185.095	185.095
4200	25.769	133.027	185.095	185.095	185.095	185.095
4300	25.772	133.126	185.095	185.095	185.095	185.095
4400	25.775	133.181	185.095	185.095	185.095	185.095
4500	25.778	133.195	185.095	185.095	185.095	185.095
4600	25.780	133.160	185.095	185.095	185.095	185.095
4700	25.782	133.082	185.095	185.095	185.095	185.095
4800	25.784	132.966	185.095	185.095	185.095	185.095
4900	25.786	132.811	185.095	185.095	185.095	185.095
5000	25.788	132.629	185.095	185.095	185.095	185.095
5100	25.790	132.433	185.095	185.095	185.095	185.095
5200	25.791	132.236	185.095	185.095	185.095	185.095
5300	25.793	132.043	185.095	185.095	185.095	185.095
5400	25.795	131.853	185.095	185.095	185.095	185.095
5500	25.796	131.669	185.095	185.095	185.095	185.095
5600	25.797	131.492	185.095	185.095	185.095	185.095
5700	25.798	131.321	185.095	185.095	185.095	185.095
5800	25.799	131.156	185.095	185.095	185.095	185.095
5900	25.800	130.997	185.095	185.095	185.095	185.095
6000	25.802	130.843	185.095	185.095	185.095	185.095

Sept. 30, 1965; Dec. 31, 1969

Point Group C_{2v}S_{298.15} = 71.83 ± 0.10 gibbs/mol

Ground State Quantum Weight = 1

Sulfur Tetrafluoride (SF₄)

(Ideal Gas)

GFW = 108.058

T, °K	C _p ^o	S ^o - gibbs/mol	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol - ΔH ^o	Log K _p
0	10.000	56.000	INFINITE	3.748	185.095	INFINITE
100	14.757	62.248	65.595	2.468	185.775	369.957
200	18.270	67.336	73.396	1.630	186.304	180.011
298	20.916	71.829	71.829	.000	176.852	196.770
300	18.325	71.830	71.830	.038	185.408	188.793
400	20.917	77.563	72.580	1.998	175.472	170.782
500	22.181	82.358	74.068	4.143	187.685	74.286
600	23.138	86.489	75.802	6.412	187.938	166.405
700	23.776	90.107	77.592	8.160	188.092	162.778
800	24.231	93.112	79.361	11.161	188.092	160.428
900	24.537	95.781	81.116	13.426	187.938	158.196
1000	24.767	98.181	82.718	16.065	187.685	156.063
1100	24.943	101.150	84.286	18.551	200.486	28.857
1200	25.080	103.327	85.783	21.052	200.423	145.241
1300	25.196	105.339	87.211	23.566	199.960	135.420
1400	25.294	107.193	88.583	26.000	199.337	125.423
1500	25.384	108.955	89.915	28.420	198.587	115.416
1600	25.462	110.592	91.119	31.157	199.178	120.391
1700	25.530	112.134	92.310	33.740	198.920	115.473
1800	25.591	113.590	93.452	36.207	198.667	110.576
1900	25.646	114.963	94.556	38.569	198.427	105.683
2000	25.695	116.279	95.603	41.352	198.165	100.810
2100	25.741	117.526	96.617	43.909	197.897	95.953
2200	25.783	118.717	97.595	46.468	197.629	91.101
2300	25.822	119.855	98.538	49.029	197.441	86.262
2400	25.858	120.943	99.445	51.572	197.237	81.435
2500	25.891	121.993	100.330	54.157	197.017	76.614
2600	25.918	123.000	101.183	56.723	196.775	71.804
2700	25.940	123.968	102.019	59.291	196.527	67.001
2800	25.958	124.903	102.800	61.859	196.308	62.212
2900	25.973	125.806	103.561	64.429	196.093	57.422
3000	25.979	126.674	104.381	66.999	195.885	52.649
3100	25.976	127.519	105.077	69.570	195.677	47.877
3200	25.964	128.335	105.791	72.142	195.476	43.112
3300	25.950	129.127	106.486	74.715	195.277	38.355
3400	25.935	129.896	107.158	77.289	195.085	33.590
3500	25.918	130.641	107.823	79.862	194.893	28.832
3600	25.900	131.367	108.467	82.437	194.707	24.079
3700	25.881	132.072	109.096	85.011	194.528	19.373
3800	25.861	132.759	109.710	87.587	194.350	14.640
3900	25.840	133.428	110.311	90.166	194.180	9.899
4000	25.818	134.080	110.899	92.736	194.010	5.151
4100	25.796	134.716	111.469	95.315	193.847	.475
4200	25.772	135.337	112.030	97.892	193.682	-.421
4300	25.747	135.944	112.579	100.469	193.531	-1.353
4400	25.721	136.536	113.116	103.046	193.383	-2.285
4500	25.695	137.113	113.643	105.624	193.236	-3.217
4600	25.670	137.682	114.160	108.202	193.093	-4.149
4700	25.642	138.236	114.666	110.780	192.956	-5.081
4800	25.614	138.779	115.163	113.358	192.822	-6.013
4900	25.586	139.311	115.650	115.937	192.693	-6.945
5000	25.558	139.832	116.129	118.515	192.570	-7.877
5100	25.530	140.343	116.594	121.094	192.450	-8.809
5200	25.501	140.843	117.060	123.673	192.334	-9.741
5300	25.473	141.335	117.513	126.253	192.221	-10.673
5400	25.444	141.816	117.959	128.832	192.111	-11.605
5500	25.416	142.290	118.401	131.412	192.002	-12.537
5600	25.387	142.755	118.828	133.991	191.891	-13.469
5700	25.358	143.212	119.252	136.571	191.782	-14.401
5800	25.329	143.660	119.669	139.151	191.673	-15.333
5900	25.300	144.101	120.073	141.731	191.567	-16.265
6000	25.269	144.535	120.463	144.311	191.461	-17.197

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	0.000	0.000	0.000	0.000	0.000	INFINITE
100	7.912	52.224	2.459	385.450	-385.450	-385.450	-385.450	85.477
200	18.503	61.039	6.436	382.294	-382.294	-382.294	-382.294	85.477
298	17.563	67.433	6.433	385.768	-385.768	-385.768	-385.768	85.477
300	17.563	67.433	6.433	385.768	-385.768	-385.768	-385.768	85.477
400	17.618	67.551	6.433	385.988	-385.988	-385.988	-385.988	85.477
500	17.650	67.634	6.433	386.153	-386.153	-386.153	-386.153	85.477
600	21.406	77.541	6.433	386.249	-386.249	-386.249	-386.249	85.477
700	22.427	81.544	6.433	386.289	-386.289	-386.289	-386.289	85.477
800	22.924	85.069	6.433	386.294	-386.294	-386.294	-386.294	85.477
900	23.756	87.206	6.433	386.287	-386.287	-386.287	-386.287	85.477
1000	24.402	88.159	6.433	386.211	-386.211	-386.211	-386.211	85.477
1100	24.667	95.929	6.433	386.171	-386.171	-386.171	-386.171	85.477
1200	24.662	98.083	6.433	386.128	-386.128	-386.128	-386.128	85.477
1300	24.561	100.078	6.433	386.084	-386.084	-386.084	-386.084	85.477
1400	24.385	101.668	6.433	386.040	-386.040	-386.040	-386.040	85.477
1500	24.145	102.887	6.433	385.997	-385.997	-385.997	-385.997	85.477
1600	23.841	103.629	6.433	385.956	-385.956	-385.956	-385.956	85.477
1700	23.495	103.929	6.433	385.918	-385.918	-385.918	-385.918	85.477
1800	23.118	103.787	6.433	385.884	-385.884	-385.884	-385.884	85.477
1900	22.714	103.202	6.433	385.854	-385.854	-385.854	-385.854	85.477
2000	22.287	102.287	6.433	385.828	-385.828	-385.828	-385.828	85.477
2100	21.841	101.041	6.433	385.806	-385.806	-385.806	-385.806	85.477
2200	21.378	99.462	6.433	385.788	-385.788	-385.788	-385.788	85.477
2300	20.901	97.545	6.433	385.774	-385.774	-385.774	-385.774	85.477
2400	20.411	95.295	6.433	385.764	-385.764	-385.764	-385.764	85.477
2500	19.908	92.717	6.433	385.758	-385.758	-385.758	-385.758	85.477
2600	19.393	89.808	6.433	385.756	-385.756	-385.756	-385.756	85.477
2700	18.867	86.565	6.433	385.758	-385.758	-385.758	-385.758	85.477
2800	18.331	83.000	6.433	385.764	-385.764	-385.764	-385.764	85.477
2900	17.786	79.115	6.433	385.774	-385.774	-385.774	-385.774	85.477
3000	17.233	74.925	6.433	385.788	-385.788	-385.788	-385.788	85.477
3100	16.672	70.440	6.433	385.806	-385.806	-385.806	-385.806	85.477
3200	16.104	65.672	6.433	385.828	-385.828	-385.828	-385.828	85.477
3300	15.530	60.630	6.433	385.854	-385.854	-385.854	-385.854	85.477
3400	14.951	55.322	6.433	385.884	-385.884	-385.884	-385.884	85.477
3500	14.368	49.737	6.433	385.918	-385.918	-385.918	-385.918	85.477
3600	13.781	43.887	6.433	385.956	-385.956	-385.956	-385.956	85.477
3700	13.190	37.787	6.433	385.997	-385.997	-385.997	-385.997	85.477
3800	12.595	31.452	6.433	386.040	-386.040	-386.040	-386.040	85.477
3900	11.997	24.895	6.433	386.084	-386.084	-386.084	-386.084	85.477
4000	11.397	18.135	6.433	386.128	-386.128	-386.128	-386.128	85.477
4100	10.795	11.185	6.433	386.171	-386.171	-386.171	-386.171	85.477
4200	10.191	4.962	6.433	386.211	-386.211	-386.211	-386.211	85.477
4300	9.585	-1.433	6.433	386.249	-386.249	-386.249	-386.249	85.477
4400	8.977	-7.787	6.433	386.289	-386.289	-386.289	-386.289	85.477
4500	8.368	-14.100	6.433	386.330	-386.330	-386.330	-386.330	85.477
4600	7.758	-20.372	6.433	386.372	-386.372	-386.372	-386.372	85.477
4700	7.147	-26.603	6.433	386.416	-386.416	-386.416	-386.416	85.477
4800	6.535	-32.784	6.433	386.461	-386.461	-386.461	-386.461	85.477
4900	5.922	-38.915	6.433	386.508	-386.508	-386.508	-386.508	85.477
5000	5.309	-44.997	6.433	386.556	-386.556	-386.556	-386.556	85.477
5100	4.695	-51.030	6.433	386.606	-386.606	-386.606	-386.606	85.477
5200	4.081	-57.015	6.433	386.658	-386.658	-386.658	-386.658	85.477
5300	3.467	-62.952	6.433	386.712	-386.712	-386.712	-386.712	85.477
5400	2.853	-68.841	6.433	386.768	-386.768	-386.768	-386.768	85.477
5500	2.239	-74.682	6.433	386.826	-386.826	-386.826	-386.826	85.477
5600	1.625	-80.475	6.433	386.886	-386.886	-386.886	-386.886	85.477
5700	1.011	-86.220	6.433	386.948	-386.948	-386.948	-386.948	85.477
5800	0.397	-91.917	6.433	387.012	-387.012	-387.012	-387.012	85.477
5900	-0.217	-97.565	6.433	387.078	-387.078	-387.078	-387.078	85.477
6000	-0.831	-103.164	6.433	387.146	-387.146	-387.146	-387.146	85.477

Dec. 31, 1960; Sept. 30, 1963

Point Group T_d
S_{298.15} = 67.433 cal. deg.⁻¹ mole⁻¹
Ground State Quantum Weight = [1]

ΔH_f^o 0 = -384.65 ± 0.19 kcal. mole⁻¹
ΔH_f^o 298.15 = -385.98 ± 0.19 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹ ω_g, cm.⁻¹

800 (1) 1031 (3)
268 (2) 391 (3)

Bond Distances Si-F = 1.54 ± 0.02 Å
Bond Angle: F-Si-F = 109° 29'
Product of the Moments of Inertia: I_AI_BI_C = 7.93269 X 10⁻¹¹⁴ g.³ cm.⁶
σ = 12

Heat of Formation.

The heat of formation of SiF₄(g) was measured by direct combination of the elements in a bomb calorimeter by S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, J. Phys. Chem. 67, 815 (1963). ΔH_f^o 298.15 was found to be -385.98 ± 0.19 kcal. mole⁻¹. Heats of the reaction between SiF₄(g) and Ne(g), 1.9% HF solution, 0.4% HP solution, a solution of NaF saturated with Ne₂SiF₆, and water have been measured by A. P. Vorob'ev, V. P. Kolesov, and S. M. Skuratov, Zh. Neorg. Khim. 5, 1402 (1960). The value of ΔH_f^o 298.15 for SiF₄(g) was reported to be -372.4 ± 0.4 kcal. mole⁻¹ which was not used.

Heat Capacity and Entropy.

The vibrational frequencies used were reported by E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz, and A. H. Nielsen, J. Chem. Phys. 19, 242 (1951). The values of vibrational frequencies were given as 800(1), 285(2), 1000(3), and 431(3) for SiF₄(g) by D. M. Yost, E. M. Lassette, and S. T. Gross, J. Chem. Phys. 4, 325 (1936). The molecular data were obtained from L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 57, 2684 (1935). The three principal moments of inertia are: I_A = I_B = I_C = 1.99437 X 10⁻³⁸ g. cm.²

Titanium Tetrafluoride (TiF₄)
(Crystal) GFW = 123.8936

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	13.000	10.000	INFINITE	- 4.841	- 393.659	- 393.659	INFINITE
100	15.000	12.000	32.017	- 2.942	- 393.659	- 393.659	INFINITE
200	22.080	22.173	32.016	- 2.639	- 393.659	- 379.652	415.063
298	27.310	32.016	32.016	0.000	- 394.200	- 372.673	273.176
300	27.390	32.185	32.017	- 0.051	- 394.188	- 372.540	271.395
400	30.270	40.483	33.128	2.942	- 393.659	- 365.457	199.660
500	32.160	47.451	35.315	6.068	- 392.589	- 357.222	127.222
600	33.480	53.437	37.848	9.353	- 391.634	- 351.795	128.161
700	34.450	58.673	40.457	12.751	- 390.624	- 345.234	107.787
800	35.190	63.324	43.030	16.235	- 389.582	- 338.622	92.562
900	35.770	67.503	45.521	19.784	- 388.521	- 332.539	80.752
1000	36.250	71.297	47.912	23.385	- 387.454	- 326.376	71.330
1100	36.640	74.771	50.198	27.030	- 386.382	- 320.321	63.642
1200	36.960	77.973	52.381	30.711	- 385.247	- 314.324	57.246
1300	37.240	80.943	54.465	34.421	- 384.057	- 308.379	51.843
1400	37.480	83.712	56.456	38.157	- 382.864	- 302.526	47.226
1500	37.690	86.305	58.361	41.916	- 382.672	- 296.756	43.737

TITANIUM TETRAFLUORIDE (TiF₄)
(CRYSTAL)

GFW = 123.8936

ΔHf°_O = -393.67 ± 0.9 kcal/mol
ΔHf°_{298.15} = -394.2 ± 0.9 kcal/mol
ΔHs°_{298.15} = 23.37 ± 0.1 kcal/mol

S°_{298.15} = 32.02 gibbs/mol
Ts = 558.6°K

Heat of Formation
The heat of formation (ΔHf°_{298.15}) of TiF₄(c) was measured using a fluorine bomb calorimeter by Greenberg et al. (1). Gross et al. (2) reported a value of -393.4 kcal/mol for ΔHf°₂₉₈. The latter measurements were not corrected for impurities in the titanium sample, thus the value reported by Greenberg et al. is adopted.

Heat Capacity and Entropy
The heat capacity of TiF₄(c) has been measured over the temperature range 6° to 304°K by Euler and Westrum (3). They obtained the value of S°₂₉₈ based on S°₁₀ = 0.11 eu. Heat capacities above 300°K are estimated from those of ZnF₄(c) (4).

Heat of Sublimation
The sublimation point is calculated as the temperature at which ΔGr° = 0 for TiF₄(c) = TiF₄(g). The heat of sublimation is obtained from the data of Hall et al. (5).

References

1. E. Greenberg, J. L. Sattle, and W. N. Hubbard, J. Phys. Chem. **66**, 1345 (1962).
2. P. Gross, C. Hayman, and D. L. Levi, XVIIIth Interim. Congr. Pure Appl. Chem. Abstr. **1**, 90 (1959).
3. R. D. Euler and E. F. Westrum, Jr., J. Phys. Chem. **65**, 132 (1961).
4. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data **7**, 83 (1962).
5. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. **105**, 275 (1958).

Titanium Tetrafluoride (TiF₄)
(Ideal Gas)

GFW = 123.8936

F₄Ti

TITANIUM TETRAFLUORIDE (TiF₄) (IDEAL GAS)

GFW = 123.8936

Point Group [*T_d*]
S_{298.15} = 75.24 ± 0.5 gibbs/mol
Ground State Quantum Weight = [1]

ΔHf° = -389.9 ± 1 kcal/mol
ΔHf°_{298.15} = -370.8 ± 1 kcal/mol

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹
[701] (1)	[750] (3)
[168] (2)	[178] (3)

Bond Distance: Ti-F = [1.80] Å
Bond Angle: F-Ti-F = [109°28']

Product of the Moments of Inertia: I_AI_BI_C = [2.02 × 10⁻¹¹³] g³ cm⁶ σ = [12]

Heat of Formation

The heat of formation of TiF₄(g) is calculated from that of the crystal and the heat of sublimation, ΔH_{sub}²⁹⁸, obtained from vapor pressure measurements. E. H. Hall, J. M. Blocher, Jr., and I. E. Campbell, J. Electrochem. Soc. 105, 275 (1958), have reported extensive vapor pressure data for the reaction TiF₄(c) = TiF₄(g). Second and third law analyses of their data yielded the following results.

Method	No. Pts.	Range, T°K	ΔH _f ²⁹⁸ , kcal/mol	Drift, eu	ΔH _f ²⁹⁸ *
1. Spoon Gauge	28**	441-552	23.5 ± 0.1	-0.3 ± 0.1	-370.8
2. Ruff-Fischer	6	435-498	23.0 ± 0.4	+0.9 ± 0.9	-370.8
3. Transpiration	3	426-512	25.8 ± 2.0	-4.5 ± 4.3	-370.5
4. Rodenbush	6	473-537	23.7 ± 0.6	-0.5 ± 1.2	-370.8
5. 1, 2, and 4	36***	435-552	23.4 ± 0.1	-0.1 ± 0.1	-370.8

*Calculation based on third law ΔH_f²⁹⁸.

**Four points rejected due to failure of a statistical test.

***Eight points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The interatomic distance is obtained from a correlation of the measured values for TiCl₄(g), TiBr₄(g), TiCl₃⁻², and TiF₆⁻². The principal moments of inertia are I_A = I_B = I_C = 2.724 × 10⁻³⁸ g cm².

The vibrational frequencies are estimated by a valence force field treatment of estimated force constants. The force constants are estimated from a correlation with the constants of CF₄, SiF₄, CCl₄, SiCl₄, CBr₄, SiBr₄, TiCl₄ and TiBr₄. The resulting frequencies are adjusted so that calculations of ΔH_f²⁹⁸ by both second and third law methods are in agreement.

Sept. 30, 1961; June 30, 1964; Sept. 30, 1967

F₄Ti

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔG ^o	Log K _p
0	14.013	0.000	INFINITE	-4.508	-369.936	-369.936	INFINITE
100	16.606	91.520	91.520	-3.491	-370.443	-367.768	803.756
200	17.607	67.630	77.026	-1.860	-370.690	-364.984	184.636
298	20.357	57.243	75.243	1.000	-370.900	-367.161	265.471
300	20.397	75.369	75.243	0.18	-370.801	-362.107	263.795
400	22.126	81.492	76.066	2.170	-370.827	-359.202	194.259
500	23.211	86.556	77.672	4.442	-370.815	-356.999	155.738
600	23.505	90.553	79.520	6.000	-370.787	-355.398	128.795
700	23.364	94.575	81.411	9.215	-370.760	-350.302	109.431
800	23.682	97.850	83.245	11.668	-370.749	-347.610	94.963
900	24.908	100.771	85.051	14.148	-370.757	-344.717	83.709
1000	25.075	103.405	86.757	16.648	-370.791	-341.823	74.705
1100	25.201	105.801	88.381	19.142	-370.850	-338.922	67.338
1200	25.294	107.984	89.925	21.687	-370.971	-335.978	61.140
1300	25.375	110.026	91.395	24.221	-371.057	-332.987	55.940
1400	25.436	111.909	92.793	26.741	-371.080	-329.998	51.515
1500	25.486	113.665	94.127	29.250	-371.080	-327.005	47.645
1600	25.527	115.312	95.400	31.658	-371.058	-324.013	44.288
1700	25.562	116.840	96.613	33.963	-371.007	-321.016	41.259
1800	25.591	118.262	97.763	36.170	-370.932	-318.019	38.613
1900	25.615	119.574	98.901	38.283	-370.835	-315.012	36.235
2000	25.636	121.021	99.974	40.293	-370.718	-312.005	34.077
2100	25.658	122.722	101.004	42.208	-370.588	-309.000	32.114
2200	25.670	124.666	102.000	44.024	-370.438	-306.000	30.332
2300	25.684	126.807	102.959	45.762	-370.270	-303.000	28.720
2400	25.696	129.101	103.884	47.431	-370.085	-300.000	27.269
2500	25.706	131.544	104.777	49.031	-369.885	-297.000	25.935
2600	25.714	134.127	105.622	50.562	-369.670	-294.000	24.685
2700	25.720	136.749	106.469	52.024	-369.440	-291.000	23.500
2800	25.723	139.405	107.261	53.417	-369.195	-288.000	22.366
2900	25.729	142.098	108.018	54.742	-368.935	-285.000	21.278
3000	25.745	144.840	108.682	56.000	-368.660	-282.000	20.238
3100	25.750	147.622	109.295	57.195	-368.375	-279.000	19.248
3200	25.756	150.445	109.858	58.328	-368.080	-276.000	18.308
3300	25.760	153.309	110.375	59.400	-367.775	-273.000	17.418
3400	25.764	156.211	110.844	60.417	-367.460	-270.000	16.578
3500	25.768	159.151	111.261	61.375	-367.135	-267.000	15.788
3600	25.772	162.127	111.622	62.280	-366.800	-264.000	15.048
3700	25.775	165.140	111.935	63.135	-366.455	-261.000	14.358
3800	25.778	168.190	112.200	63.940	-366.100	-258.000	13.718
3900	25.781	171.277	112.411	64.695	-365.735	-255.000	13.128
4000	25.783	174.401	112.572	65.400	-365.360	-252.000	12.588
4100	25.786	177.561	112.682	66.055	-364.975	-249.000	12.098
4200	25.788	180.755	112.744	66.660	-364.580	-246.000	11.658
4300	25.790	183.983	112.766	67.215	-364.175	-243.000	11.268
4400	25.792	187.245	112.740	67.720	-363.760	-240.000	10.928
4500	25.794	190.540	112.666	68.175	-363.335	-237.000	10.638
4600	25.796	193.867	112.544	68.580	-362.900	-234.000	10.398
4700	25.797	197.227	112.375	68.935	-362.455	-231.000	10.208
4800	25.799	200.621	112.150	69.240	-362.000	-228.000	10.068
4900	25.800	204.049	111.875	69.495	-361.535	-225.000	9.978
5000	25.801	207.511	111.550	69.700	-361.060	-222.000	9.928
5100	25.802	211.009	111.175	69.855	-360.575	-219.000	9.918
5200	25.803	214.543	110.750	69.960	-360.080	-216.000	9.938
5300	25.805	218.112	110.275	70.015	-359.575	-213.000	9.978
5400	25.806	221.715	109.750	70.020	-359.060	-210.000	10.038
5500	25.807	225.349	109.175	70.000	-358.535	-207.000	10.118
5600	25.808	229.013	108.550	69.955	-358.000	-204.000	10.218
5700	25.809	232.707	107.875	69.875	-357.455	-201.000	10.338
5800	25.810	236.431	107.150	69.750	-356.900	-198.000	10.478
5900	25.811	240.185	106.375	69.575	-356.325	-195.000	10.638
6000	25.811	243.969	105.550	69.350	-355.730	-192.000	10.818



GFW = 167.2136

(CRYSTAL)

ZIRCONIUM TETRAFLUORIDE (ZrF_4)

Zirconium Tetrafluoride (ZrF_4)

(Crystal) GFW = 167.2136

$S_{298.15}^\circ = 25.024 \pm 0.05$ gibbs/mol
 $T_f(\alpha + \beta) = 723^\circ\text{K}$
 $T_m = 1205 \pm 2^\circ\text{K}$
 $T_b = 1179^\circ\text{K}$

$\Delta H_f^\circ = -455.44 \pm 0.25$ kcal/mol
 $\Delta H_{298.15}^\circ = -456.80 \pm 0.25$ kcal/mol
 $\Delta H_c^\circ = \text{Unavailable}$
 $\Delta H_m^\circ = 15.35 \pm 0.10$ kcal/mol
 $\Delta H_s^\circ = 51.64$ kcal/mol
 $\Delta H_{298.15}^\circ = 56.80$ kcal/mol

Heat of Formation

The heat of formation of zirconium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter by Greenberg, Settle, Feder, and Hubbard (1). The reported value $\Delta H_{298}^\circ(\text{ZrF}_4, c) = -456.80 \pm 0.25$ kcal/mol is adopted.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range 5 to 307°K were determined by adiabatic calorimetry by Westrum (2). Using these low temperature Cp data the value of S_{298}° is derived as 25.024 ± 0.05 eu, based on $S_{10}^\circ = 0.0074$ eu. McDonald, Sinke, and Stull (3) measured the high temperature enthalpies of $\text{ZrF}_4(c)$ at temperatures 283.9 - 1275.8°K in a copper block drop calorimeter. Smith, Miller, and Taylor (4) used a Bunsen ice calorimeter for the heat-content measurements in the temperature range 273 - 1150°K. These two sets of enthalpy data are not in good agreement. It is possible that the discrepancies are due to the difference in crystal structure of the samples used (see "Transition Data" for more information). In order to join smoothly with the low temperature heat capacities at 298°K, the high temperature heat capacities derived from the enthalpy data of McDonald, Sinke, and Stull (3) are adopted. The Cp values above 1200°K are obtained by smooth extrapolation.

Transition Data

Zirconium tetrafluoride has three crystal structures (α , β and γ) and one amorphous form (δ). From a differential thermal analysis of $(\text{NH}_4)_3\text{ZrF}_7$ sample, Chretien and Gaudreau (5) found that $\text{ZrF}_4(c)$ has an α and β form with a transition temperature above 678°K. They also determined the densities of α (tetragonal) and β (monoclinic) as 4.25 ± 0.05 and 4.61 ± 0.03 gm/cc, and a transition temperature as $T(\alpha + \beta) = 723^\circ\text{K}$ (7). It was observed that the α phase is unstable at all temperatures above 298°K. In reference (5), Gaudreau mentioned the methods of preparation of the four varieties of ZrF_4 and indicated that α -, γ -, and amorphous ZrF_4 transform irreversibly to β - ZrF_4 at 723 - 773°K.

The ZrF_4 sample employed by McDonald, Sinke, and Stull (3) for enthalpy measurement was prepared by dissolving hafnium-free zirconium metal in 48% aqueous HF, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 773°K in a platinum boat in a glow current of anhydrous HF. X-ray diffraction showed only crystalline ZrF_4 . Wet analysis indicated 54.6% Zr (theory 54.55) and 44.9% F (theory 45.45). Due to the above facts we are uncertain whether the sample prepared is a mixture of α and β forms or a pure $\text{ZrF}_4(\beta)$. Smith, Miller, and Taylor (4) obtained their ZrF_4 sample from the Oak Ridge National Laboratories, Oak Ridge, Tenn. Since the method of preparation of the compound is unavailable from the report, we do not know what kind of sample they used for measurement.

Because of the above complicated situation, we emphasize that this $\text{ZrF}_4(c)$ table is not strictly a α , β -combined phase table. However, the differences in the calculated functions are probably not significant.

Melting Data

T_m and ΔH_m° are taken from McDonald, Sinke, and Stull (3). The values were obtained under conditions greater than one atmosphere.

Sublimation Data

The sublimation temperature (T_b) is calculated as the temperature at which the Gibbs energy change of the process $\text{ZrF}_4(c) = \text{ZrF}_4(g)$ approaches zero. The difference between ΔH_{298}° for $\text{ZrF}_4(g)$ and $\text{ZrF}_4(c)$ at 1179 and 298°K is ΔH_s° and ΔH_{298}° , respectively.

Since this sublimation temperature is lower than the melting point, the ZrF_4 sublimates before it melts.

References

1. E. Greenberg, J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem. **65**, 1168 (1961).
2. E. F. Westrum, Jr., J. Chem. Eng. Data **10**, 140 (1965).
3. R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data **7**, 83 (1962).
4. D. F. Smith, W. C. Miller, and A. R. Taylor, Jr., U. S. Bur. Mines RI 5964, 1962.
5. B. Gaudreau, Rev. Chim. Minerale **2** (1), 1 (1965); Chem. Abstr. **63**:17245d.
6. A. Chretien and B. Gaudreau, Compt. Rend. **246**, 2266 (1958).
7. A. Chretien and B. Gaudreau, Compt. Rend. **248**, 2878 (1959).

T, °K	Cp ^a	$-\frac{G^\circ - H_{298}^\circ}{T}$	— kcal/mol — ΔH_f°	$H^\circ - H_{298}^\circ$	ΔG_f°	Log Kp
0	0.000	INFINITE	— 455.441	— 4.182	— 455.441	INFINITE
100	10.060	5.481	— 456.672	— 3.811	— 464.744	980.733
200	20.210	15.991	— 457.022	— 2.235	— 460.614	681.080
298	24.760	25.024	— 456.800	0.000	— 432.595	317.101
300	24.810	25.177	— 456.793	0.046	— 432.445	315.036
400	27.120	32.663	— 456.349	2.653	— 474.391	231.676
500	29.610	36.083	— 455.851	5.444	— 416.463	182.036
600	29.430	44.195	— 455.250	8.359	— 404.444	168.988
700	30.350	48.620	— 454.657	11.360	— 400.922	159.721
800	30.930	52.911	— 454.058	14.424	— 193.244	107.441
900	31.510	56.587	— 453.450	17.546	— 365.724	93.668
1000	32.050	59.936	— 452.830	20.725	— 374.237	82.644
1100	32.560	63.014	— 452.201	23.955	— 370.600	73.673
1200	33.050	65.868	— 451.561	27.335	— 365.201	66.811
1300	33.550	68.533	— 451.000	30.565	— 358.999	59.849
1400	34.060	71.039	— 450.719	33.946	— 348.679	54.431

Zirconium Tetrafluoride (ZrF₄)

(Ideal Gas) GFW = 167.2136

Point Group T_d $\Delta H_f^\circ = -399.0 \pm 1.0$ kcal/mol $\Delta H_f^\circ = -400.0 \pm 1.0$ kcal/mol

Ground State Quantum Weight = 1

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0	0.000	INFINITE		4.527	-399.986	-399.986	INFINITE
100	13.653	92.910	3.535	399.596	-396.878	-396.878	167.375
200	18.119	68.546	1.925	390.912	-390.014	-390.014	330.559
298	20.867	76.339	1.000	400.000	-390.000	-390.000	286.660
300	20.927	76.468	0.939	400.000	-391.039	-391.039	286.872
400	22.603	62.740	2.223	399.979	-386.053	-386.053	212.022
500	23.593	47.699	4.537	399.930	-385.078	-385.078	168.316
600	24.205	32.950	6.929	399.880	-382.112	-382.112	139.188
700	24.673	20.326	9.622	399.837	-379.153	-379.153	119.377
800	24.873	10.326	11.865	399.813	-376.199	-376.199	102.773
900	25.065	102.267	86.331	399.853	-373.244	-373.244	90.616
1000	25.205	104.916	86.059	399.869	-370.284	-370.284	80.926
1100	25.310	107.923	89.703	399.874	-367.321	-367.321	72.989
1200	25.395	111.564	92.749	399.874	-364.358	-364.358	66.731
1300	25.455	115.214	95.506	399.867	-361.395	-361.395	61.017
1400	25.500	118.864	97.991	399.853	-358.432	-358.432	55.917
1500	25.528	122.563	101.398	399.834	-355.469	-355.469	51.345
1600	25.542	126.311	104.829	399.811	-352.506	-352.506	47.305
1700	25.548	129.999	108.291	399.784	-349.543	-349.543	43.787
1800	25.548	133.636	111.784	399.753	-346.580	-346.580	40.681
1900	25.542	137.223	115.200	399.718	-343.617	-343.617	37.907
2000	25.530	140.759	118.546	399.679	-340.654	-340.654	35.375
2100	25.506	144.246	121.823	399.636	-337.691	-337.691	33.077
2200	25.471	147.684	125.031	399.589	-334.728	-334.728	30.989
2300	25.427	151.071	128.171	399.542	-331.765	-331.765	29.091
2400	25.375	154.408	131.246	399.495	-328.802	-328.802	27.363
2500	25.317	157.695	134.256	399.448	-325.839	-325.839	25.775
2600	25.255	160.932	137.201	399.401	-322.876	-322.876	24.317
2700	25.189	164.119	140.081	399.354	-319.913	-319.913	22.979
2800	25.119	167.256	142.836	399.307	-316.950	-316.950	21.741
2900	25.045	170.343	145.491	399.260	-313.987	-313.987	20.593
3000	24.967	173.380	148.046	399.213	-311.024	-311.024	19.525
3100	24.885	176.367	150.501	399.166	-308.061	-308.061	18.527
3200	24.799	179.304	152.856	399.119	-305.098	-305.098	17.589
3300	24.711	182.191	155.111	399.072	-302.135	-302.135	16.701
3400	24.620	185.028	157.266	399.025	-299.172	-299.172	15.863
3500	24.527	187.815	159.321	398.978	-296.209	-296.209	15.075
3600	24.432	190.552	161.276	398.931	-293.246	-293.246	14.337
3700	24.335	193.239	163.131	398.884	-290.283	-290.283	13.649
3800	24.236	195.876	164.886	398.837	-287.320	-287.320	13.001
3900	24.135	198.463	166.541	398.790	-284.357	-284.357	12.393
4000	24.032	201.000	168.096	398.743	-281.394	-281.394	11.825
4100	23.927	203.487	169.551	398.696	-278.431	-278.431	11.297
4200	23.820	205.924	170.906	398.649	-275.468	-275.468	10.809
4300	23.711	208.311	172.161	398.602	-272.505	-272.505	10.361
4400	23.599	210.648	173.316	398.555	-269.542	-269.542	9.953
4500	23.485	212.935	174.371	398.508	-266.579	-266.579	9.585
4600	23.369	215.172	175.326	398.461	-263.616	-263.616	9.257
4700	23.251	217.359	176.181	398.414	-260.653	-260.653	8.969
4800	23.131	219.496	176.936	398.367	-257.690	-257.690	8.711
4900	23.009	221.583	177.591	398.320	-254.727	-254.727	8.483
5000	22.885	223.620	178.146	398.273	-251.764	-251.764	8.285
5100	22.759	225.607	178.601	398.226	-248.801	-248.801	8.117
5200	22.631	227.544	178.956	398.179	-245.838	-245.838	7.979
5300	22.499	229.431	179.211	398.132	-242.875	-242.875	7.861
5400	22.365	231.268	179.366	398.085	-239.912	-239.912	7.763
5500	22.229	233.055	179.421	398.038	-236.949	-236.949	7.685
5600	22.091	234.792	179.376	397.991	-233.986	-233.986	7.627
5700	21.951	236.479	179.231	397.944	-231.023	-231.023	7.589
5800	21.809	238.116	178.986	397.897	-228.060	-228.060	7.561
5900	21.665	239.703	178.641	397.850	-225.097	-225.097	7.543
6000	21.519	241.240	178.196	397.803	-222.134	-222.134	7.535

Dec. 31, 1960; June 30, 1961; Dec. 31, 1963; June 30, 1969

Vibrational Frequencies and Degeneracies

Bond Distance: Zr-F = 1.94 ± 0.02 Å
 Bond Angle: F-Zr-F = 109.47°
 Product of the Moments of Inertia: $I_A I_B I_C = 3.17347 \times 10^{-213}$ g cm⁶
 $\sigma = 12$

Heat of Formation
 The vapor pressures of ZrF₄(c) in the temperature range 617-1150°K were determined by many investigators using various methods. Based on the reported vapor pressure data, the corresponding heats of sublimation are evaluated by the second and third law methods. Using the third law ΔH_{298}° and ΔH_{298}° (ZrF₄, c) = -456.8 kcal/mol, the heats of formation at 298°K for ZrF₄(g) are evaluated. The results are presented in the table below. The values of ΔH_{298}° (ZrF₄, g) listed in the last column of this table are in excellent agreement which indicate that the estimated missing vibrational frequencies ν_1 and ν_2 are reasonable. The heat of formation at 298°K for ZrF₄(g) is adopted as -400.0 kcal/mol.

Investigator	Method	Temperature, °K	No. of Points	ΔH_{298}° , kcal/mol	Drift, eu	ΔH_{298}° , kcal/mol
1. Lauter (1948)	unavailable	950-1150	Equ.	56.49±0.12	56.83	0.3
2. Sense et al. (1954)	transpiration	617-881	14	60.67±0.09	57.13	-344.01
3. Sense et al. (1957)	transpiration	900-1150	6	60.64±0.13	57.24	-339.56
4. Cantor (1958)	quasistatic	710-808	29	56.11±0.62	56.65	0.540.6
5. Hildenbrand-Theard (1961)	torsion-effusion	748-849	15	55.81±1.44	57.05	1.551.8
6. Hildenbrand-Theard (1961)	torsion-effusion	735-825	10	52.59±0.39	57.09	5.7±0.5
7. Galkin et al. (1963)	Knudsen-effusion	720-850	5	51.53±0.06	54.79	4.1±0.1
8. Akishin et al. (1963)	mass spectrometry	700-900	5	59.25±2.34	57.30	-2.4±2.9
9. Fischer et al. (1964)	"bell method"	1000-1150	Equ.	57.38±0.12	56.89	-0.5
10. Sidorov et al. (1965)	mass spectrometry	769	1	—	57.58	-339.22

Heat Capacity and Entropy

The molecular structure of ZrF₄(g) has been studied by electron diffraction by Spidonov (11). The configuration was found to be a regular tetrahedron with interatomic distance Zr-F = 1.94 ± 0.02 Å and F-Zr-F bond angle = 109.47° which are adopted. Employing the estimated interaction coefficients and interatomic distance Zr-F = 1.85 Å, Godnev, Aleksandrova, and Rigina (12) calculated three vibrational frequencies for ZrF₄(g) as $\nu_1 = 600 - 725$, $\nu_2 = 150 - 200$, and $\nu_4 = 180 \pm 230$ cm⁻¹. Buchler, Berkowitz, and Dugre (13) observed the infrared spectra of some group IV halides and assigned $\nu_3 = 668$ and $\nu_4 = 190 \pm 20$ cm⁻¹ for ZrF₄(g). The frequency ν_3 has also been reported as 670 cm⁻¹ (14). The values of ν_3 and ν_4 adopted here are those reported by Buchler, Berkowitz, and Dugre (13). The adopted ν_1 is obtained by correlating the corresponding frequencies of the tetrafluorides of C, Pb, Si, Ti and Ge with their respective interatomic distances. ν_2 is calculated from ν_1 , ν_3 and ν_4 using the relationship $(15) \nu_1 \nu_2 \nu_3 \nu_4 = \frac{2}{3} (1 - \frac{4}{Z})$, where F and Zr are gram atomic weights of fluorine and zirconium, respectively. The three principal moments of inertia are $I_A = I_B = I_C = 3.166 \times 10^{-38}$ g cm².

References

1. S. Lauter, Dissertation Technische Hochschule Hannover, 1948. (Cited in reference 9)
2. K. A. Sense, M. Snyder, and R. B. Filbert, Jr., J. Phys. Chem. **58**, 995 (1954).
3. K. A. Sense, C. A. Alexander, R. E. Bowman, and R. B. Filbert, Jr., J. Phys. Chem. **61**, 337 (1957).
4. S. Cantor, R. F. Newton, W. R. Grimes, and F. F. Blankenship, J. Phys. Chem. **62**, 96 (1958).
5. D. L. Hildenbrand and L. P. Theard, Aeronautics, U-1274, Ford Motor Company, 15 Mar. 1961.
6. D. L. Hildenbrand and L. P. Theard, Aeronautics, U-1274, Ford Motor Company, 15 June 1961.
7. N. P. Galkin, Y. N. Tumanov, V. I. Tarasov, and Y. D. Shishov, Russ. J. Inorg. Chem. (English Transl.) **8**, 1054 (1963).
8. P. A. Akishin, V. I. Belousov, and L. N. Sidorov, Russ. J. Inorg. Chem. (English Transl.) **8**, 1520 (1963).
9. W. Fischer, T. Petzel, and S. Lauter, Z. Anorg. Allgem. Chem. **333**, 226 (1964).
10. L. N. Sidorov, P. A. Akishin, V. B. Shol'ts, and Y. M. Kornuev, Russ. J. Phys. Chem. (English Transl.) **35**, 1146 (1965).
11. V. P. Spidonov, Vestn. Mosk. Univ. Ser. II, Khim. **23**, No. 1, 113 (1968).
12. I. N. Godnev, A. M. Aleksandrova, and I. V. Rigina, Opt. Spectry, USSR (English Transl.) **2**, 172 (1959).
13. A. Buchler, J. B. Berkowitz-Matuck, and D. H. Dugre, J. Chem. Phys. **34**, 2202 (1961).
14. M. Blander and H. W. Morgan, presented at the 138th Meeting, American Chemical Society, New York, September 1960.
15. G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, 1945, p. 182.

IODINE PENTAFLUORIDE (IF₅)

(IDEAL GAS)

Iodine Pentafluoride (IF₅)GF_W = 221.8964Point Group C_{4v}S_{298.15} = 79.96 ± 0.5 gibbs/mol

Ground State Quantum Weight = 11

ΔH_f⁰ = -198.8 ± 0.4 kcal/molGF_W = 221.8964ΔH_f⁰ = -198.8 ± 0.4 kcal/molS_{298.15} = 79.96 ± 0.5 gibbs/molGF_W = 221.8964

Ground State Quantum Weight = 11

ΔH_f⁰ = -198.8 ± 0.4 kcal/molGF_W = 221.8964

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
710 (1)	604 (1)	631 (2)
616 (1)	[257] (1)	372 (2)
318 (1)	276 (1)	190 (2)

Bond Distance: I-F(equatorial) = 1.86 Å I-F(axial) = 1.75 Å

Bond Angle: F-I-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = [4.10383 × 10⁻¹¹³] g³ cm⁶

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (1) for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF₃ and IF₅, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave ΔH_f⁰ = -210.80 ± 0.32 kcal/mol for IF₅(g) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [2.1] and -208.8 ± [2.1] kcal/mol may be obtained from calorimetric data of Woolf (2) for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3).

In particular, we estimate lower limits of ±0.8 kcal/mol for ΔH_f⁰ of HIO₃(1250 H₂O) and KIO₃(1250 H₂O) by comparison with recent data (4).ΔH_f⁰ for the ideal gas is derived from that of the liquid by use of ΔH_v⁰ = 9.96 kcal/mol at 298.15 K. ΔH_v⁰ was derived by Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF₅, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure used by Begun et al. (7) in correlation of infrared and Raman spectra of BrF₅, IF₅, ClF₅, and XeOF₄ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF₇. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (8) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun et al. (7) note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are I_A = I_B = 30.66 × 10⁻³⁹ and I_C = 43.65 × 10⁻³⁹ g cm².Vibrational frequencies are based on the assignments of Begun et al. (7) as modified by the vapor-phase Raman spectra observed by Selig (6). Location of the band center of ν₃ (4200 cm⁻¹) is difficult, so we substitute the liquid value of 190 cm⁻¹. The Raman-active fundamental ν₅ is not observed for IF₅, or any of the similar molecules, so its value is taken from the calculations (7).Osborne et al. (5) used calorimetric data at low temperatures to derive S⁰ = 57.96 ± 0.06 gibbs/mol for the liquid at 330 K. Combining this with ΔS⁰ based on their vapor pressure equation, the authors obtained S⁰ = 83.06 ± 0.20 gibbs/mol for the ideal gas at 330 K. The corresponding value from this table (89.50) is lower by 0.58 gibbs/mol. Part of this difference arises from uncertainties in ν₅, ν₃, and the product of the moments of inertia. We estimate this uncertainty at about 0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1969.
2. A. A. Woolf, J. Chem. Soc. 1951, 231 (1951).
3. ΔH_f⁰ values for H₂O(l), HIO₃(1250 H₂O) and KIO₃(1250 H₂O) are derived from U. S. Natl. Bur. Std. Tech. Note 270-3, 1968, in combination with V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
4. P. B. Howard and H. A. Skinner, J. Chem. Soc. A1967, 269 (1967); C. Wu, M. H. Birky and L. G. Hepler, J. Phys. Chem. 67, 1202 (1963).
5. D. W. Osborne, F. Schreiner, H. Selig, to be published.
6. H. Selig and H. Holzman, Israel J. Chem. 2, 417 (1969).
7. G. H. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).
8. R. M. Gavin, J. Chem. Educ. 46, 413 (1969).

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
710 (1)	604 (1)	631 (2)
616 (1)	[257] (1)	372 (2)
318 (1)	276 (1)	190 (2)

Bond Distance: I-F(equatorial) = 1.86 Å I-F(axial) = 1.75 Å

Bond Angle: F-I-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = [4.10383 × 10⁻¹¹³] g³ cm⁶

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (1) for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF₃ and IF₅, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave ΔH_f⁰ = -210.80 ± 0.32 kcal/mol for IF₅(g) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [2.1] and -208.8 ± [2.1] kcal/mol may be obtained from calorimetric data of Woolf (2) for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3).

In particular, we estimate lower limits of ±0.8 kcal/mol for ΔH_f⁰ of HIO₃(1250 H₂O) and KIO₃(1250 H₂O) by comparison with recent data (4).ΔH_f⁰ for the ideal gas is derived from that of the liquid by use of ΔH_v⁰ = 9.96 kcal/mol at 298.15 K. ΔH_v⁰ was derived by Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF₅, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure used by Begun et al. (7) in correlation of infrared and Raman spectra of BrF₅, IF₅, ClF₅, and XeOF₄ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF₇. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (8) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun et al. (7) note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are I_A = I_B = 30.66 × 10⁻³⁹ and I_C = 43.65 × 10⁻³⁹ g cm².Vibrational frequencies are based on the assignments of Begun et al. (7) as modified by the vapor-phase Raman spectra observed by Selig (6). Location of the band center of ν₃ (4200 cm⁻¹) is difficult, so we substitute the liquid value of 190 cm⁻¹. The Raman-active fundamental ν₅ is not observed for IF₅, or any of the similar molecules, so its value is taken from the calculations (7).Osborne et al. (5) used calorimetric data at low temperatures to derive S⁰ = 57.96 ± 0.06 gibbs/mol for the liquid at 330 K. Combining this with ΔS⁰ based on their vapor pressure equation, the authors obtained S⁰ = 83.06 ± 0.20 gibbs/mol for the ideal gas at 330 K. The corresponding value from this table (89.50) is lower by 0.58 gibbs/mol. Part of this difference arises from uncertainties in ν₅, ν₃, and the product of the moments of inertia. We estimate this uncertainty at about 0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1969.
2. A. A. Woolf, J. Chem. Soc. 1951, 231 (1951).
3. ΔH_f⁰ values for H₂O(l), HIO₃(1250 H₂O) and KIO₃(1250 H₂O) are derived from U. S. Natl. Bur. Std. NBS-RS-2, 1965, in combination with V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
4. P. B. Howard and H. A. Skinner, J. Chem. Soc. A1967, 269 (1967); C. Wu, M. H. Birky and L. G. Hepler, J. Phys. Chem. 67, 1202 (1963).
5. D. W. Osborne, F. Schreiner, H. Selig, to be published.
6. H. Selig and H. Holzman, Israel J. Chem. 2, 417 (1969).
7. G. H. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).
8. R. M. Gavin, J. Chem. Educ. 46, 413 (1969).

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
710 (1)	604 (1)	631 (2)
616 (1)	[257] (1)	372 (2)
318 (1)	276 (1)	190 (2)

Bond Distance: I-F(equatorial) = 1.86 Å I-F(axial) = 1.75 Å

Bond Angle: F-I-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = [4.10383 × 10⁻¹¹³] g³ cm⁶

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (1) for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF₃ and IF₅, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave ΔH_f⁰ = -210.80 ± 0.32 kcal/mol for IF₅(g) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [2.1] and -208.8 ± [2.1] kcal/mol may be obtained from calorimetric data of Woolf (2) for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3).

In particular, we estimate lower limits of ±0.8 kcal/mol for ΔH_f⁰ of HIO₃(1250 H₂O) and KIO₃(1250 H₂O) by comparison with recent data (4).ΔH_f⁰ for the ideal gas is derived from that of the liquid by use of ΔH_v⁰ = 9.96 kcal/mol at 298.15 K. ΔH_v⁰ was derived by Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF₅, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure used by Begun et al. (7) in correlation of infrared and Raman spectra of BrF₅, IF₅, ClF₅, and XeOF₄ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF₇. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (8) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun et al. (7) note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are I_A = I_B = 30.66 × 10⁻³⁹ and I_C = 43.65 × 10⁻³⁹ g cm².Vibrational frequencies are based on the assignments of Begun et al. (7) as modified by the vapor-phase Raman spectra observed by Selig (6). Location of the band center of ν₃ (4200 cm⁻¹) is difficult, so we substitute the liquid value of 190 cm⁻¹. The Raman-active fundamental ν₅ is not observed for IF₅, or any of the similar molecules, so its value is taken from the calculations (7).Osborne et al. (5) used calorimetric data at low temperatures to derive S⁰ = 57.96 ± 0.06 gibbs/mol for the liquid at 330 K. Combining this with ΔS⁰ based on their vapor pressure equation, the authors obtained S⁰ = 83.06 ± 0.20 gibbs/mol for the ideal gas at 330 K. The corresponding value from this table (89.50) is lower by 0.58 gibbs/mol. Part of this difference arises from uncertainties in ν₅, ν₃, and the product of the moments of inertia. We estimate this uncertainty at about 0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1969.
2. A. A. Woolf, J. Chem. Soc. 1951, 231 (1951).
3. ΔH_f⁰ values for H₂O(l), HIO₃(1250 H₂O) and KIO₃(1250 H₂O) are derived from U. S. Natl. Bur. Std. NBS-RS-2, 1965, in combination with V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
4. P. B. Howard and H. A. Skinner, J. Chem. Soc. A1967, 269 (1967); C. Wu, M. H. Birky and L. G. Hepler, J. Phys. Chem. 67, 1202 (1963).
5. D. W. Osborne, F. Schreiner, H. Selig, to be published.
6. H. Selig and H. Holzman, Israel J. Chem. 2, 417 (1969).
7. G. H. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).
8. R. M. Gavin, J. Chem. Educ. 46, 413 (1969).

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
710 (1)	604 (1)	631 (2)
616 (1)	[257] (1)	372 (2)
318 (1)	276 (1)	190 (2)

Bond Distance: I-F(equatorial) = 1.86 Å I-F(axial) = 1.75 Å

Bond Angle: F-I-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = [4.10383 × 10⁻¹¹³] g³ cm⁶

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (1) for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF₃ and IF₅, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave ΔH_f⁰ = -210.80 ± 0.32 kcal/mol for IF₅(g) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [2.1] and -208.8 ± [2.1] kcal/mol may be obtained from calorimetric data of Woolf (2) for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3).

In particular, we estimate lower limits of ±0.8 kcal/mol for ΔH_f⁰ of HIO₃(1250 H₂O) and KIO₃(1250 H₂O) by comparison with recent data (4).ΔH_f⁰ for the ideal gas is derived from that of the liquid by use of ΔH_v⁰ = 9.96 kcal/mol at 298.15 K. ΔH_v⁰ was derived by Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF₅, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure used by Begun et al. (7) in correlation of infrared and Raman spectra of BrF₅, IF₅, ClF₅, and XeOF₄ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF₇. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (8) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun et al. (7) note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are I_A = I_B = 30.66 × 10⁻³⁹ and I_C = 43.65 × 10⁻³⁹ g cm².Vibrational frequencies are based on the assignments of Begun et al. (7) as modified by the vapor-phase Raman spectra observed by Selig (6). Location of the band center of ν₃ (4200 cm⁻¹) is difficult, so we substitute the liquid value of 190 cm⁻¹. The Raman-active fundamental ν₅ is not observed for IF₅, or any of the similar molecules, so its value is taken from the calculations (7).Osborne et al. (5) used calorimetric data at low temperatures to derive S⁰ = 57.96 ± 0.06 gibbs/mol for the liquid at 330 K. Combining this with ΔS⁰ based on their vapor pressure equation, the authors obtained S⁰ = 83.06 ± 0.20 gibbs/mol for the ideal gas at 330 K. The corresponding value from this table (89.50) is lower by 0.58 gibbs/mol. Part of this difference arises from uncertainties in ν₅, ν₃, and the product of the moments of inertia. We estimate this uncertainty at about 0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1969.
2. A. A. Woolf, J. Chem. Soc. 1951, 231 (1951).
3. ΔH_f⁰ values for H₂O(l), HIO₃(1250 H₂O) and KIO₃(1250 H₂O) are derived from U. S. Natl. Bur. Std. NBS-RS-2, 1965, in combination with V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
4. P. B. Howard and H. A. Skinner, J. Chem. Soc. A1967, 269 (1967); C. Wu, M. H. Birky and L. G. Hepler, J. Phys. Chem. 67, 1202 (1963).
5. D. W. Osborne, F. Schreiner, H. Selig, to be published.
6. H. Selig and H. Holzman, Israel J. Chem. 2, 417 (1969).
7. G. H. Begun, W. H. Fletcher and D. F. Smith, J. Chem. Phys. 42, 2236 (1965).
8. R. M. Gavin, J. Chem. Educ. 46, 413 (1969).

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
710 (1)	604 (1)	631 (2)
616 (1)	[257] (1)	372 (2)
318 (1)	276 (1)	190 (2)

Bond Distance: I-F(equatorial) = 1.86 Å I-F(axial) = 1.75 Å

Bond Angle: F-I-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = [4.10383 × 10⁻¹¹³] g³ cm⁶

Heat of Formation

The adopted value is derived from calorimetric data of Settle et al. (1) for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF₃ and IF₅, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave ΔH_f⁰ = -210.80 ± 0.32 kcal/mol for IF₅(g) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of -208.9 ± [2.1] and -208.8 ± [2.1] kcal/mol may be obtained from calorimetric data of Woolf (2) for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data (3).

In particular, we estimate lower limits of ±0.8 kcal/mol for ΔH_f⁰ of HIO₃(1250 H₂O) and KIO₃(1250 H₂O) by comparison with recent data (4).ΔH_f⁰ for the ideal gas is derived from that of the liquid by use of ΔH_v⁰ = 9.96 kcal/mol at 298.15 K. ΔH_v⁰ was derived by Osborne et al. (5) from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF₅, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I-F distances are equal. We adopt the structure used by Begun et al. (7) in correlation of infrared and Raman spectra of BrF₅, IF₅, ClF₅, and XeOF₄ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF₇. The iodine is presumed to be in the base of the pyramid. Simplified Hückel-molecular-orbital calculations (8) predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial fluorines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun et al. (7) note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are I_A = I_B = 30.66 × 10⁻³⁹ and I_C = 43.65 × 10⁻³⁹ g cm².Vibrational frequencies are based on the assignments of Begun et al. (7) as modified by the vapor-phase Raman spectra observed by Selig (6). Location of the band center of ν₃ (4200 cm⁻¹) is difficult, so we substitute the liquid value of 190 cm⁻¹. The Raman-active fundamental ν₅ is not observed for IF₅, or any of the similar molecules, so its value is taken from the calculations (7).Osborne et al. (5) used calorimetric data at low temperatures to derive S⁰ = 57.96 ± 0.06 gibbs/mol for the liquid at 330 K. Combining this with ΔS⁰ based on their vapor pressure equation, the authors obtained S⁰ = 83.06 ± 0.20 gibbs/mol for the ideal gas at 330 K. The corresponding value from this table (89.50) is lower by 0.58 gibbs/mol. Part of this difference arises from uncertainties in ν₅, ν₃, and the product of the moments of inertia. We estimate this uncertainty at about 0.5 gibbs/mol. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1969.
2. A. A. Woolf, J. Chem. Soc. 1951, 231 (1951).
3. ΔH_f⁰ values for H₂O(l), HIO₃(1250 H₂O) and KIO₃(1250 H₂O) are derived from U. S. Natl. Bur. Std. NBS-RS-2, 1965, in combination with V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965.
4. P. B. Howard and H. A. Skinner, J. Chem. Soc. A1967, 269 (1967); C. Wu, M. H. Birky and L. G. Hepler, J. Phys. Chem. 67, 1202 (1963).

Point Group D_{3h}

$$\Delta H_f^\circ = -374.7 \pm 0.7 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -376.9 \pm 0.7 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 71.87 \pm 0.5 \text{ gibbs/mol}$$

Ground State Quantum Weight = 11

Phosphorus Pentafluoride (PF₅)

$$\text{GF}_W = 125.966$$

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	-3.950	-374.713	-374.713	INFINITE
100	10.598	55.939	96.608	-3.950	-375.658	-375.658	910.645
200	20.352	71.666	118.560	-3.950	-376.591	-376.591	264.321
298	29.941	71.866	125.966	-3.950	-376.906	-376.906	193.949
300	20.352	71.694	125.966	-3.950	-377.150	-377.150	152.731
400	23.718	78.342	142.711	-3.950	-377.747	-377.747	105.618
500	25.941	83.891	157.405	-3.950	-378.256	-378.256	74.416
600	27.416	88.760	166.400	-3.950	-378.687	-378.687	50.618
700	28.421	93.066	172.479	-3.950	-379.041	-379.041	35.012
800	29.128	96.910	177.575	-3.950	-379.359	-379.359	25.176
900	29.640	100.372	182.561	-3.950	-379.641	-379.641	18.125
1000	30.021	103.515	186.502	-3.950	-379.894	-379.894	13.146
1100	30.310	106.391	190.426	-3.950	-380.117	-380.117	9.584
1200	30.536	109.038	194.343	-3.950	-380.310	-380.310	7.000
1300	30.714	111.490	198.257	-3.950	-380.479	-380.479	5.063
1400	30.857	113.771	202.167	-3.950	-380.628	-380.628	3.612
1500	30.974	115.904	206.074	-3.950	-380.761	-380.761	2.584
1600	31.071	117.907	209.979	-3.950	-380.881	-380.881	1.825
1700	31.151	119.793	213.884	-3.950	-380.990	-380.990	1.275
1800	31.219	121.575	217.791	-3.950	-381.090	-381.090	0.885
1900	31.277	123.265	221.698	-3.950	-381.181	-381.181	0.595
2000	31.327	124.870	225.605	-3.950	-381.265	-381.265	0.374
2100	31.369	126.400	229.512	-3.950	-381.343	-381.343	0.220
2200	31.407	127.860	233.419	-3.950	-381.416	-381.416	0.137
2300	31.439	129.257	237.326	-3.950	-381.485	-381.485	0.080
2400	31.468	130.596	241.233	-3.950	-381.550	-381.550	0.040
2500	31.493	131.881	245.140	-3.950	-381.611	-381.611	0.020
2600	31.516	133.116	249.047	-3.950	-381.669	-381.669	0.010
2700	31.536	134.306	252.954	-3.950	-381.724	-381.724	0.005
2800	31.554	135.454	256.861	-3.950	-381.776	-381.776	0.002
2900	31.570	136.561	260.768	-3.950	-381.826	-381.826	0.001
3000	31.584	137.631	264.675	-3.950	-381.873	-381.873	0.000
3100	31.598	138.667	268.582	-3.950	-381.917	-381.917	0.000
3200	31.610	139.671	272.489	-3.950	-381.959	-381.959	0.000
3300	31.621	140.643	276.396	-3.950	-381.999	-381.999	0.000
3400	31.631	141.588	280.303	-3.950	-382.037	-382.037	0.000
3500	31.640	142.505	284.210	-3.950	-382.073	-382.073	0.000
3600	31.648	143.396	288.117	-3.950	-382.107	-382.107	0.000
3700	31.656	144.263	292.024	-3.950	-382.139	-382.139	0.000
3800	31.663	145.108	295.931	-3.950	-382.169	-382.169	0.000
3900	31.670	145.930	299.838	-3.950	-382.197	-382.197	0.000
4000	31.676	146.732	303.745	-3.950	-382.223	-382.223	0.000
4100	31.682	147.516	307.652	-3.950	-382.248	-382.248	0.000
4200	31.687	148.278	311.559	-3.950	-382.271	-382.271	0.000
4300	31.692	149.023	315.466	-3.950	-382.293	-382.293	0.000
4400	31.696	149.752	319.373	-3.950	-382.314	-382.314	0.000
4500	31.701	150.464	323.280	-3.950	-382.334	-382.334	0.000
4600	31.705	151.161	327.187	-3.950	-382.353	-382.353	0.000
4700	31.709	151.843	331.094	-3.950	-382.371	-382.371	0.000
4800	31.712	152.511	334.999	-3.950	-382.388	-382.388	0.000
4900	31.715	153.165	338.904	-3.950	-382.404	-382.404	0.000
5000	31.719	153.805	342.809	-3.950	-382.419	-382.419	0.000
5100	31.722	154.434	346.714	-3.950	-382.433	-382.433	0.000
5200	31.724	155.050	350.619	-3.950	-382.446	-382.446	0.000
5300	31.727	155.654	354.524	-3.950	-382.458	-382.458	0.000
5400	31.729	156.247	358.429	-3.950	-382.469	-382.469	0.000
5500	31.732	156.829	362.334	-3.950	-382.479	-382.479	0.000
5600	31.734	157.401	366.239	-3.950	-382.488	-382.488	0.000
5700	31.736	157.963	370.144	-3.950	-382.496	-382.496	0.000
5800	31.738	158.515	374.049	-3.950	-382.503	-382.503	0.000
5900	31.740	159.057	377.954	-3.950	-382.509	-382.509	0.000
6000	31.742	159.591	381.859	-3.950	-382.514	-382.514	0.000

June 30, 1963; Dec. 31, 1969

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
817 (1)	1025 (2)	
840 (1)	532.5 (2)	
946.6 (1)	179 (2)	
575.1 (1)	514 (2)	

$$\text{Bond Distance: } (P-F)_{\text{eq}} = 1.534 \pm 0.004 \text{ \AA} \quad (P-F)_{\text{ax}} = 1.577 \pm 0.005 \text{ \AA}$$

$$\text{Bond Angle: } F_{\text{eq}}-P-F_{\text{ax}} = 120^\circ \pm 0.4^\circ \quad F_{\text{eq}}-P-F_{\text{eq}} = 74.3^\circ \pm 0.4^\circ$$

$$\text{Product of Moments of Inertia: } I_A I_B I_C = 1.614 \times 10^{-113} \text{ g cm}^6$$

Heat of Formation

Gross, Hayman, and Stuart (1) measured the heat of combustion of α-white phosphorus in fluorine at 25°C. They reported a heat of formation of -381.4 ± 0.8 kcal/mol (based on α-white phosphorus standard state) calculated from their combustion studies. Similar combustion studies were performed by O'Hare and Hubbard (2). They reported a heat of formation of -380.8 ± 0.3 kcal/mol (α-white phosphorus standard state), which is in excellent agreement with the work of Gross et al. (1). An average value of -381.1 ± 0.5 kcal/mol is adopted for this tabulation. Converting to the P(red, V) standard state with a ΔH trans = 4.2 ± 0.2 kcal/mol (3), we derive, ΔH_f[°](PF₅, g) = -376.9 ± 0.7 kcal/mol.

Heat Capacity and Entropy

The molecular structure and bond lengths given above for PF₅ were recently determined by Hansen and Bartell (4) from electron-diffraction studies. These results indicate that PF₅ has a trigonal bipyramidal structure with nonequivalent axial and equatorial bonds. Wyatt et al. (5) determined rotational constants for PF₅ from a study of the infrared vibration-rotation band contour of the ν₄ (575 cm⁻¹) fundamental. Their analysis led to the following P-F bond lengths which are in excellent agreement with the electron-diffraction results: $r_{\text{ax}} = 1.534 \pm 0.024 \text{ \AA}$ and $r_{\text{eq}} = 1.581 \pm 0.025 \text{ \AA}$. Individual moments of inertia, calculated from the rotational constants given by Wyatt et al. (5) and adopted for this table, are $I_A = 2.230 \times 10^{-38} \text{ g cm}^2$ and $I_B = I_C = 2.690 \times 10^{-38} \text{ g cm}^2$. The electron diffraction data lead to a product of moments of inertia of $1.604 \times 10^{-113} \text{ g cm}^6$.

Several recent infrared and Raman studies (6, 7, and 8) have been reported for PF₅. These data are in good agreement except for the ν₇ fundamental. Griffiths et al. (6) originally assigned this fundamental to the 126 cm⁻¹ band observed in their infrared spectra. Hoskins (7) later attributed this band to one of the pure rotational lines of hydrogen fluoride, which he felt was present in the sample as an impurity. Further work by Griffiths (10) on the pressure dependence of the infrared spectra of PF₅ indicated that the missing fundamental should be assigned to the weak band at 301 cm⁻¹. Deiters and Holmes (11) recently showed that this band is not a fundamental of PF₅ but a difference band (ν₃-ν₂). Very recently, Levin (8) investigated the Raman spectra of solid phosphorus pentafluoride and assigned the ν₇ fundamental to the 179 cm⁻¹ band. Also, Beattie et al. (12) investigated the Raman spectra of PF₅ in the gas phase at 25°C and 125°C and assigned the ν₇ fundamental to 175 cm⁻¹ band which is in excellent agreement with Levin's assignment (8). The fundamental vibrational frequencies of Holmes and Lord (7) are adopted along with Levin's assignment (8) of the ν₇ fundamental (179 cm⁻¹).

References

1. P. Gross, C. Hayman, and M. C. Stuart, Trans. Faraday Soc., **62**, 2715 (1966).
2. P. A. O'Hare and W. N. Hubbard, Trans. Faraday Soc., **62**, 2709 (1966).
3. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Mich., June 30, 1961.
4. K. W. Hansen and L. S. Bartell, Inorg. Chem., **4**, 1775 (1965).
5. R. Wyatt, J. T. Roberts, R. E. Wentz, and R. M. Wilt, J. Chem. Phys., **50**, 2552 (1969).
6. J. E. Griffiths, R. F. Carter, and R. R. Holmes, J. Chem. Phys., **41**, 863 (1964).
7. L. C. Hoskins and R. C. Lord, J. Chem. Phys., **42**, 2402 (1967).
8. I. W. Levin, J. Chem. Phys., **50**, 1031 (1969).
9. L. C. Hoskins, J. Chem. Phys., **42**, 2631 (1965).
10. J. E. Griffiths, J. Chem. Phys., **42**, 2632 (1965).
11. R. M. Deiters and R. R. Holmes, J. Chem. Phys., **48**, 4796 (1968).
12. I. R. Beattie, K. M. S. Livingston, and D. J. Reynolds, J. Chem. Phys., **51**, 4269 (1969).

Molybdenum Hexafluoride (MoF₆)

(Liquid)

GFW = 209.930

MOLYBDENUM HEXAFLUORIDE (MoF₆)

(LIQUID)

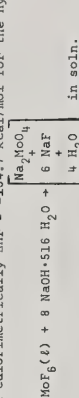
GFW = 209.930

 $S_{298.15}^{\circ} = 62.07 \pm 0.08$ gibbs/mol $\Delta H_f^{\circ} = -379.080 \pm 0.3$ kcal/mol $T_m = 290.76^{\circ}\text{K}$ $\Delta H_m^{\circ} = 1.034 \pm 0.001$ kcal/mol $T_b = 307.04^{\circ}\text{K}$ (δ + real gas, $P = 1$ atm, $f = 0.956$ atm) $\Delta H_v^{\circ} = 6.512 \pm 0.04$ kcal/mol $T_b = 308.0^{\circ}\text{K}$ (δ + ideal gas, $P = f = 1$ atm) $\Delta H_v^{\circ} = 6.562$ kcal/mol

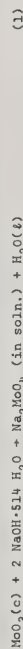
Heat of Formation

The adopted heat of formation, $\Delta H_f^{\circ}(\text{MoF}_6, l) = -379.080 \pm 0.3$ kcal/mol, is calculated from the heat of formation of the gas, $\Delta H_f^{\circ}(\text{MoF}_6, g) = -372.4 \pm 0.2$ kcal/mol (1), and the heat of vaporization, $\Delta H_v^{\circ} = 6.680 \pm 0.03$ kcal/mol at 298.15°K . The value for the heat of vaporization is obtained from a third law analysis of the vapor pressure data reported by Osborne et al. (2).

Myers and Brady (3) determined calorimetrically $\Delta H_r = -154.7$ kcal/mol for the hydrolysis reaction:



Heats of formation of Na_2MoO_4 and NaF in the final solution were determined from the following two auxiliary heat of reaction measurements:

 $\Delta H_r = -17.6$ kcal/mol $\Delta H_r = +0.09$ Kcal/mol

Combining these results with the following heat of formation data:

 $\Delta H_f^{\circ}(\text{Na}_2\text{O}_3, c) = -178.1 \pm 0.1$ kcal/mol (4) $\Delta H_f^{\circ}(\text{NaF}, c) = -137.52 \pm 0.2$ kcal/mol (5) $\Delta H_f^{\circ}(\text{NaF} \cdot 500 \text{H}_2\text{O}) = -112.12$ kcal/mol (6)

we derive $\Delta H_f(\text{Na}_2\text{MoO}_4, \text{ in soln.}) = -351.6$ kcal/mol and $\Delta H_f(\text{NaF}, \text{ in soln.}) = -137.4$ kcal/mol. These data, when combined with the results for the hydrolysis of MoF_6 , lead to $\Delta H_f^{\circ}(\text{MoF}_6, l) = -397.6$ kcal/mol. This result is not in agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity measurements for liquid MoF_6 by Osborne et al. (2) are adopted. Outside the observed range C_p was extrapolated linearly with temperature. $S_{298.15}^{\circ}$ is evaluated from the thermal data of Osborne et al. (2) and the third law of thermodynamics. They reported heat capacity data in the range $5^{\circ}\text{--}350^{\circ}\text{K}$ with $S_{5^{\circ}\text{K}} = 0.024$ gibbs/mol.

Melting Data

Melting point and heat of melting data for MoF_6 have been reported by several investigators. These results are summarized below.

Investigator	Method	Melting Point $^{\circ}\text{K}$	ΔH_m° kcal/mol
Osborne et al. (2)	Calorimetric	290.76 ± 0.02	1.034 ± 0.001
Brady et al. (2)	Calorimetric	290.7	1.059 ± 0.010
Cady and Hargreaves (8)	Vapor Pressure	290.55	$1.00 \pm 0.03^*$
Ruff and Ascher (9)	Vapor Pressure	290.65	$1.31 \pm 0.2^*$

* This value is the difference between the 2nd law heat of sublimation corrected for ΔC_p of the process and the adopted heat of vaporization calculated at 290.76°K with $(H_{290.76}^{\circ} - H_{298.15}^{\circ})$ for the vapor and liquid.

The value $\Delta H_m^{\circ}_{290.76} = 1.034 \pm 0.001$ kcal/mol from Osborne et al. (2) is adopted.

Vaporization Data

Second and third law analyses of various sets of vapor pressure data (2, 8, 9) are summarized below. Corrections for nonideality of the vapor have been calculated from the second virial coefficient equation reported by Osborne et al. (2).

Investigator	Temp. Range $^{\circ}\text{K}$	No. of Points	Boiling Point $^{\circ}\text{K}$	ΔH_v° kcal/mol
Osborne et al. (2)	291.15 - 320.15	21	307.04	2nd law* 6.690
Cady and Hargreaves (8)	290.55 - 307.15	Equation	307.15	3rd law 6.680
Ruff and Ascher (9)	290.65 - 294.85	4	308.15	6.74
* with $\Delta C_p = -11.77$ gibbs/mol				5.99

The value $\Delta H_v^{\circ}_{298} = 6.680 \pm 0.03$ ($\Delta H_v^{\circ}_{297.04} = 6.512 \pm 0.04$) kcal/mol, determined from the vapor pressure data of Osborne et al. (2), is adopted in the tabulation. The temperature at which $\Delta G_v^{\circ} = 0$ is 308.0°K and the corresponding $\Delta H_v^{\circ} = 6.562$ kcal/mol.

References

1. JANAF Thermochemical Tables, The Dow Chemical Co., Midland, Michigan, June 30, 1970.
2. D. W. Osborne, F. Schreiner, J. G. Malm, H. Selig, and L. Rochester, J. Chem. Phys., **44**, 2802 (1966).
3. O. E. Myers and A. D. Brady, J. Phys. Chem., **54**, 591 (1960).
4. Ref. 1, December 31, 1968.
5. U. S. Natl. Bur. Std. Circ. 500, 1952.
6. A. P. Brady, O. E. Myers, and J. K. Clausen, J. Phys. Chem., **64**, 588 (1960).
7. G. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961).
8. O. Ruff and E. Ascher, Z. Anorg. Allgem. Chem., **195**, 413 (1931).

June 30, 1970

Point Group O_h

$$\Delta H_f^\circ = -370.7 \pm 0.2 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -372.4 \pm 0.2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 83.76 \pm 0.50 \text{ gibbs/mol}$$

$$\text{Ground State Quantum Weight} = 1$$

Molybdenum Hexafluoride (MoF₆)

$$\text{(Ideal Gas)} \quad \text{GF}_W = 209.930$$

T, °K	C _p ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
0	-0.000	INFINITE	-	5.740	-370.714	INFINITE	INFINITE
100	16.070	59.431	105.853	-4.642	-365.385	798.548	391.981
200	23.949	73.216	86.257	-2.608	-372.325	358.711	258.024
298	28.816	83.762	83.761	-0.000	-372.400	358.711	258.024
300	28.887	83.840	83.762	-0.053	-372.400	358.711	258.024
400	33.639	100.011	87.239	6.366	-372.004	338.281	147.863
500	34.751	106.250	89.901	9.609	-371.708	331.582	120.771
600	35.478	111.665	92.432	13.323	-371.390	324.895	101.437
700	35.976	116.437	95.315	16.897	-371.066	318.950	86.950
800	36.358	120.716	98.416	20.316	-370.742	313.486	75.000
900	36.668	124.537	100.377	24.140	-370.410	308.157	66.692
1000	36.783	128.034	102.735	27.829	-370.091	303.647	59.336
1200	36.934	131.241	104.979	31.515	-369.782	299.155	53.211
1300	37.052	134.203	107.114	35.215	-369.482	295.708	48.032
1400	37.151	136.945	109.155	38.921	-369.191	292.324	43.597
1500	37.234	139.516	111.089	42.643	-368.913	289.007	39.755
1600	37.307	141.922	112.941	46.369	-368.650	285.750	36.396
1700	37.369	144.164	114.713	50.100	-368.402	282.552	33.434
1800	37.421	146.320	116.410	53.837	-368.168	279.416	30.803
1900	37.464	148.392	118.036	57.587	-367.946	276.342	28.449
2000	37.500	150.382	119.602	61.321	-367.734	273.326	26.331
2100	37.528	152.290	121.106	65.048	-367.532	270.360	24.416
2200	37.556	154.135	122.554	68.767	-367.340	267.444	22.675
2300	37.577	155.902	123.951	72.479	-367.158	264.576	21.086
2400	37.592	157.596	125.291	76.185	-366.985	261.756	19.629
2500	37.602	159.221	126.602	79.887	-366.820	258.982	18.288
2600	37.607	160.786	127.862	83.585	-366.664	256.256	17.050
2700	37.607	162.292	129.083	87.279	-366.517	253.578	15.903
2800	37.602	163.742	130.266	90.969	-366.379	250.948	14.843
2900	37.592	165.142	131.414	94.655	-366.248	248.366	13.863
3000	37.561	166.497	132.529	98.337	-366.122	245.832	12.960
3100	37.520	167.801	133.612	102.018	-366.000	243.346	12.116
3200	37.469	169.054	134.665	105.691	-365.882	240.906	11.327
3300	37.409	170.263	135.690	109.359	-365.768	238.512	10.590
3400	37.339	171.424	136.689	113.020	-365.658	236.164	9.896
3500	37.259	172.543	137.662	116.675	-365.552	233.862	9.243
3600	37.169	173.618	138.611	120.326	-365.450	231.606	8.631
3700	37.069	174.654	139.537	123.973	-365.352	229.394	8.051
3800	36.959	175.658	140.441	127.616	-365.258	227.226	7.501
3900	36.839	176.631	141.324	131.255	-365.168	225.102	6.971
4000	36.709	177.576	142.187	134.890	-365.082	223.022	6.461
4100	36.569	178.491	143.031	138.519	-365.000	221.000	5.971
4200	36.419	179.376	143.856	142.144	-364.922	219.026	5.501
4300	36.259	180.231	144.664	145.764	-364.848	217.100	5.051
4400	36.099	181.056	145.455	149.379	-364.778	215.222	4.621
4500	35.929	181.841	146.231	152.989	-364.712	213.394	4.201
4600	35.759	182.586	146.990	156.594	-364.650	211.616	3.791
4700	35.579	183.291	147.735	160.194	-364.592	209.888	3.391
4800	35.389	183.956	148.464	163.789	-364.538	208.210	2.991
4900	35.189	184.581	149.182	167.379	-364.488	206.582	2.591
5000	34.979	185.166	149.885	170.964	-364.442	205.004	2.191
5100	34.759	185.711	150.576	174.544	-364.400	203.476	1.791
5200	34.529	186.226	151.254	178.119	-364.362	201.998	1.391
5300	34.289	186.701	151.921	181.689	-364.328	200.570	0.991
5400	34.039	187.136	152.575	185.254	-364.298	199.192	0.591
5500	33.779	187.531	153.219	188.814	-364.272	197.864	0.191
5600	33.509	187.886	153.852	192.369	-364.250	196.486	-0.209
5700	33.229	188.201	154.476	195.914	-364.232	195.058	-0.609
5800	32.939	188.476	155.081	199.449	-364.218	193.580	-0.991
5900	32.639	188.711	155.681	202.964	-364.208	192.052	-1.361
6000	32.329	188.906	156.266	206.469	-364.202	190.474	-1.711

June 30, 1970

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	g , cm ⁻¹
741 (1)	262 (3)
643 (2)	312 (3)
741 (3)	122 (3)

Bond Distance: Mo-F = 1.84 ± 0.02 Å
 Bond Angle: F-Mo-F = 90°
 Product of Moments of Inertia: I_AI_BI_C = 7.771 × 10⁻¹¹³ g cm⁶
 $\sigma = 24$

Heat of Formation

Settle et al. (1) measured the heat of formation of gaseous MoF₆ by direct combination of its elements in a nickel bomb calorimeter. Their result was $\Delta H_f^\circ(\text{MoF}_6, g) = -372.4 \pm 0.2 \text{ kcal/mol}$. This value is adopted in the tabulation.

Heat Capacity and Entropy

Tanner and Duncan (2) investigated the Raman spectra of liquid MoF₆, and their results indicated that the structure of the molecule was a regular octahedron with O_h symmetry rather than an unsymmetrical structure as reported by Braune and Pinnow (3) from electron diffraction studies. The Mo-F bond length is from the electron diffraction studies of Nazarian (4). Individual moments of inertia are I_A = I_B = I_C = 4.268 × 10⁻³⁸ g cm².

Several infrared (5, 6, 7) and Raman (8, 9) studies of MoF₆ have been reported. The vibrational frequencies reported for MoF₆ from these studies are in good agreement except for the infrared and Raman inactive ν_6 vibration. Burke et al. (5) and Hellberg et al. (8) derived $\nu_6 = 234 \text{ cm}^{-1}$, while Claassen et al. (7) assigned $\nu_6 = 130 \text{ cm}^{-1}$ and Gault (6) assigned $\nu_6 = 240 \text{ cm}^{-1}$. Weinstock and Goodman (9) recently analyzed the infrared and Raman data for MoF₆ and assigned $\nu_6 = 122 \text{ cm}^{-1}$.

Osborne et al. (10) calculated $S^\circ = 62.06 \pm 0.06 \text{ gibbs/mol}$ for liquid MoF₆ at 298.15°K from their low temperature thermal data. Combining this with ΔS° , they obtained $S^\circ = 83.75 \pm 0.10 \text{ gibbs/mol}$ for the ideal gas at 298.15°K. Accepting the assignments of Weinstock and Goodman (9), we calculate $S_{298.15}^\circ = 83.76 \text{ gibbs/mol}$, which is in excellent agreement with the thermal results. The other assignments given above for ν_6 all lead to ideal gas entropies that are lower than the thermal results. Therefore, the assignments given by Weinstock and Goodman (9) are adopted here.

References

1. J. L. Settle, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, **65**, 1337 (1961).
2. K. N. Tanner and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **73**, 1164 (1951).
3. H. Braune and P. Pinnow, *Z. Physik*, **35B**, 239 (1937).
4. G. M. Nazarian, Ph.D. Thesis, California Institute of Technology, 1957.
5. T. G. Burke, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 447 (1952).
6. J. Gault, *Trans. Faraday Soc.*, **49**, 1122 (1953).
7. H. H. Claassen, H. Selig, and J. G. Malm, *J. Chem. Phys.*, **36**, 2888 (1962).
8. K. H. Hellberg, A. Müller, and O. Glensner, *Z. Naturforsch.*, **21b**, 118 (1966).
9. B. Weinstock and G. L. Goodman, *Advan. Chem. Phys.*, **9**, 169 (1965).
10. D. W. Osborne, F. Schreiner, J. G. Malm, H. Selig, and L. Rochester, *J. Chem. Phys.*, **44**, 2802 (1966).

Sulfur Hexafluoride (SF₆)

(Ideal Gas) Mol. Wt. = 146.0544

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	Log K _p
0	0.000	∞	∞	∞	∞
100	9.280	53.312	4.053	-288.460	INFINITE
200	16.505	61.798	3.234	-289.890	-282.716
298	23.224	68.713	1.968	-291.117	-275.026
300	23.329	69.857	0.043	-291.799	-266.966
400	27.852	77.237	70.689	-266.813	194.364
500	30.705	83.783	5.558	-262.632	141.181
600	32.544	88.255	75.011	-263.052	109.183
700	33.772	92.279	79.003	-263.236	87.827
800	34.624	95.239	79.003	-263.270	71.463
900	35.235	103.354	82.284	-263.270	61.463
1000	35.687	107.091	84.580	-263.270	52.173
1100	36.029	110.509	86.784	-263.270	44.752
1200	36.294	113.656	88.694	-263.270	38.490
1300	36.503	116.569	90.913	-263.270	33.645
1400	36.670	119.281	92.843	-263.270	29.383
1500	36.807	121.816	94.691	-263.270	25.736
1600	36.913	124.195	96.461	-263.270	22.580
1700	37.013	126.436	98.070	-263.270	19.824
1800	37.092	128.554	99.790	-263.270	17.404
1900	37.159	130.561	101.357	-263.270	15.316
2000	37.217	132.469	102.865	-263.270	13.586
2100	37.266	134.284	104.318	-263.270	12.224
2200	37.309	136.020	105.720	-263.270	11.130
2300	37.347	137.680	107.074	-263.270	10.262
2400	37.380	139.270	108.383	-263.270	9.594
2500	37.410	140.797	109.649	-263.270	9.043
2600	37.436	142.264	110.875	-263.270	8.594
2700	37.459	143.678	112.064	-263.270	8.257
2800	37.479	145.040	113.218	-263.270	7.931
2900	37.498	146.356	114.336	-263.270	7.615
3000	37.515	147.627	115.426	-263.270	7.308
3100	37.531	148.858	116.485	-263.270	7.012
3200	37.545	150.049	117.515	-263.270	6.726
3300	37.557	151.205	118.519	-263.270	6.450
3400	37.569	152.326	119.497	-263.270	6.184
3500	37.579	153.416	120.450	-263.270	5.928
3600	37.588	154.474	121.381	-263.270	5.684
3700	37.596	155.504	122.289	-263.270	5.450
3800	37.606	156.507	123.177	-263.270	5.226
3900	37.614	157.484	124.044	-263.270	5.012
4000	37.621	158.436	124.892	-263.270	4.808
4100	37.628	159.365	125.721	-263.270	4.614
4200	37.634	160.272	126.533	-263.270	4.430
4300	37.639	161.158	127.328	-263.270	4.256
4400	37.645	162.023	128.107	-263.270	4.092
4500	37.650	162.869	128.870	-263.270	3.938
4600	37.654	163.697	129.618	-263.270	3.794
4700	37.659	164.507	130.352	-263.270	3.660
4800	37.663	165.300	131.072	-263.270	3.536
4900	37.667	166.076	131.778	-263.270	3.422
5000	37.670	166.837	132.472	-263.270	3.318
5100	37.674	167.583	133.159	-263.270	3.224
5200	37.677	168.315	133.822	-263.270	3.140
5300	37.680	169.033	134.480	-263.270	3.066
5400	37.683	169.737	135.126	-263.270	3.002
5500	37.685	170.428	135.762	-263.270	2.948
5600	37.688	171.107	136.387	-263.270	2.904
5700	37.690	171.774	137.002	-263.270	2.870
5800	37.693	172.430	137.607	-263.270	2.846
5900	37.695	173.074	138.203	-263.270	2.832
6000	37.697	173.708	138.789	-263.270	2.828

Dec. 31, 1960 Sept. 30, 1965

SULFUR HEXAFLUORIDE (SF₆)

(IDEAL GAS)

MOL. WT. = 146.0544

Point Group O_hΔH°_f 0 = -288.46 ± 0.24 kcal. mole⁻¹S°_{298.15} = 69.713 cal. deg.⁻¹ mole⁻¹ΔH°_f 298.15 = -291.79 ± 0.24 kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
770 (1)	345 (3)
640 (2)	615 (3)
522 (3)	947 (3)

Bond Length = 1.564 Å

P-S-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = 29,400 X 10⁻¹¹⁷ g.³ cm.⁶

Heat of Formation.

P. A. G. O'Hare, J. L. Settle, and W. N. Hubbard, Preprint of Paper XIV on Fluorine Bomb Calorimetry, July, 1965, measured the enthalpy of combustion of rhombic sulfur in fluorine. Their result yields ΔH°_f 298 = -291.79 ± 0.24 kcal. mole⁻¹. P. Gross, C. Hayman, and D. L. Levi, XVIII Intern. Congr. Pure and Appl. Chem., Abstr. 1, 90 (1959), reported -289.5 kcal. mole⁻¹ also based on direct combination of the elements. O'Hare, Settle, and Hubbard mentioned a private communication from Dr. Gross indicating -289.5 kcal. mole⁻¹ may be in error due to oxygen in the fluorine used and preliminary results of a redetermination are in better agreement with -291.79 kcal. mole⁻¹. D. M. Yost and W. H. Claussen, J. Am. Chem. Soc. 55, 887 (1933) determined -282 kcal. mole⁻¹, again by direct reaction of the elements, which now appears too low. The work of O'Hare et al., loc. cit., is adopted.

Heat Capacity and Entropy.

V. C. Ewing and L. E. Sutton, Trans. Faraday Soc. 59, 124 (1963) measured the bond length adopted here by the electron diffraction technique. Earlier less accurate work by the same method by H. Braune and S. Knoke, Z. physik. Chem. 221, 297 (1933) and L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. USA 19, 68 (1933) is in agreement within experimental error. T. E. Morsy, Ber. Bunsenges Physik. Chem. 68, 277 (1964) reviewed the literature on Raman and infrared spectra. Frequencies given here differ slightly from his selection because more weight was given to the Raman frequencies of C. W. Gullikson, J. R. Nielsen, and A. T. Stair, Jr., J. Mol. Spectroscopy 1, 151 (1957). Calculated functions by Moray loc. cit. are in reasonable agreement with the present work.

A. Eucken and E. Schröder, Z. physik. Chem. 41B, 307 (1938) measured low temperature thermal data from which K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961) calculated S°₂₉₈ = 70.3 ± 0.7 cal. mole⁻¹ deg.⁻¹ which agrees within experimental error with the spectroscopic result.

The three principal moments of inertia are I_A = I_B = I_C = 3.0863 X 10⁻³⁸ g. cm.²

(LIQUID)

OPW = 297.8404

T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200	40.300	41.193	51.269	-3.973	-419.187	-382.187	-0.26-0.10
298	40.300	56.566	56.566	.000	-417.876	-380.884	285.654
300	40.300	56.565		.079	-417.648	-380.796	283.966
400	40.300	71.466		4.193	-416.697	-380.621	207.962
500	40.300	80.303		6.175	-415.669	-371.726	162.481
600	40.300	87.687		12.225	-414.726	-361.025	132.232
700	40.300	94.130		16.275	-413.850	-354.477	110.673
800	40.300	99.538		20.325	-413.031	-346.055	94.538
900	40.300	104.308		24.375	-412.251	-337.788	82.012
1000	40.300	108.375		28.425	-411.510	-329.489	72.010

$\Delta H_{298}^{\circ} = 59.564 \pm 0.2$ gibbs/mol
 $T_m = 275.2^{\circ}\text{K}$
 $T_b = 290.5^{\circ}\text{K}$

$\Delta H_{298}^{\circ} = -417.87 \pm 0.5$ kcal/mol
 $\Delta H_m^{\circ} = 0.980$ kcal/mol
 $\Delta H_v^{\circ} = 6.465 \pm 0.08$ kcal/mol

Heat of Formation.

The adopted heat of formation, -417.87 kcal/mol, is calculated from the chosen $\Delta H_{290.3}^{\circ} = 6.465 \pm 0.08$ kcal/mol with $\Delta H_{298}^{\circ}(\text{WF}_6, \text{g}) = -411.5 \pm 0.4$ kcal/mol using all JANAP functions. The value of $\Delta H_{290.3}^{\circ}$ is obtained by corrected 2nd law analysis of vapor pressure data^{6,7,8} which are given in the vaporization section of this table.

O. E. Myers and A. P. Brady¹ measured calorimetrically $\Delta H_{298}^{\circ} = -150.1$ kcal/mol for the reaction $\text{WF}_6(1) + 6 \text{ NaOH}(500\text{H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(4900\text{H}_2\text{O}) + 6 \text{ NaF}(500 \text{H}_2\text{O})$. V. I. Spitsyn and N. N. Pataukova² measured calorimetrically $\Delta H_{298}^{\circ} = -13.8$ kcal/mol for the reaction $\text{WO}_3(\text{c}) + 2 \text{ NaOH}(50\text{H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(4200\text{H}_2\text{O}) + \text{H}_2\text{O}(1)$. Based on these data and auxiliary data for $\text{NaOH}(\text{aq})$ ^{3,9}, $\text{NaF}(\text{aq})$ ^{3,10} and $\text{Na}_2\text{WO}_4(\text{aq})$ ⁴, we obtain $\Delta H_{298}^{\circ} = -136.2$ kcal/mol for $\text{WF}_6(1) + 6 \text{ NaOH}(500\text{H}_2\text{O}) \rightarrow \text{WO}_3(\text{c}) + 3 \text{ H}_2\text{O}(1) + 6 \text{ NaF}(500\text{H}_2\text{O})$. This leads to $\Delta H_{298}^{\circ}(\text{WF}_6, 1) = -416.9 \pm 1$ kcal/mol which is in good agreement with the value adopted.

Heat Capacity and Entropy.

The heat capacity, 40.5 gibbs/mol, is obtained from a graph of the Cp versus temperature curve determined calorimetrically by E. F. Westrum, Jr.⁵
 The entropy, $S_{298}^{\circ} = 59.564$ eu, is calculated from the chosen $\Delta H_{290.3}^{\circ} = 6.465$ kcal/mol with $S_{298}^{\circ}(\text{WF}_6, \text{g}) = 81.504$ eu using all JANAP functions.

Melting Data.

Melting point and heat of melting have been reported by the following investigators, and their results are summarized below. Ruff and Ascher's value, 2.40 kcal/mol, is too high because they did not know of the existence of a solid-solid transition⁵ at 264.7°K with $\Delta H^{\circ} = 2.087$ kcal/mol. Westrum's data are adopted in the tabulation.

Investigator	Method	Melting Point (°K)	ΔHm° (kcal/mol)
Westrum ⁵	Calorimetric	275.2	0.980
Ruff and Ascher ⁷	Vapor pressure	275.4	2.400*
Barber & Cady ⁸	Warming curve	275.1	0.500
Cady & Hargreaves ⁶	Vapor pressure	275.2	0.420*

*This value is the difference between the 2nd law heats of sublimation and vaporization without correction for ΔCp° for both processes.

Vaporization Data.

Second law analyses of the data^{6,7,8}, neglecting corrections for nonideality of the vapor, are summarized below. The value of $\Delta H_{298}^{\circ} = 6.37$ kcal/mol ($\Delta H_{290.3}^{\circ} = 6.465$ kcal/mol) is selected in the tabulation.

Investigator	Temp. Range (°K)	No. of Points	Boiling Point (°K)	ΔHv° ₂₉₈ ° (kcal/mol)	ΔSv° ₂₉₈ ° (eu)
Ruff and Ascher ⁷	275 - 287.5	6	290.7 ± 0.2	6.50 ± 0.12	21.70
Barber and Cady ⁸	285 - 324.5	16	290.2 ± 0.05	6.37 ± 0.01	21.94
Cady and Hargreaves ⁶	275 - 290	Equation	290.3 ± 0.05	6.12	21.09

*From second law analysis using ΔCp° = -12.4 gibbs/mol

References.

- O. E. Myers and A. P. Brady, J. Phys. Chem. **64**, 591 (1960).
- V. I. Spitsyn and N. N. Pataukova, Russ. J. Inorg. Chem. (English Transl.) **10**, 1304 (1965).
- "Thermal Properties of Aqueous Uni-univalent Electrolytes," V. B. Parker, NBS22-NBS2 Natl. Bur. Std., Washington, D.C., Apr. 1965.
- We have assumed $\Delta H_{411}^{\circ} = 0$ for $\text{Na}_2\text{WO}_4(4200\text{H}_2\text{O}) \rightarrow \text{Na}_2\text{WO}_4(4900\text{H}_2\text{O})$ based on the dilution data of H. L. Drubben and L. G. Hepler, J. Am. Chem. Soc. **80**, 3538 (1958).
- E. F. Westrum, Jr., Pure & Appl. Chem. **37**, 187 (1964); J. Chem. Ed. **39**, 443 (1962).
- O. H. Cady and G. B. Hargreaves, J. Chem. Soc., 1563 (1961).
- O. Ruff and E. Ascher, Z. Anorg. Allgem. Chem. **186**, 415 (1931).
- E. J. Barber and G. H. Cady, J. Phys. Chem. **60**, 505 (1956).
- JANAP NaOH(c) table dated Mar. 31, 1966.
- U.S. Natl. Bur. Std. Tech. Note 270-1, 1965.

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1967

Tungsten Hexafluoride (WF₆)

(Ideal Gas) GFW = 297.8404

T, °K	Cp ^a	S ^b - (G° - H° ₂₉₈)/T	kcal/mol ΔH ^c	Log Kp
0	0.000	INFINITE	-	INFINITE
100	18.220	58.272	- 409.416	- 409.416
200	23.197	71.755	- 411.358	- 397.934
300	28.446	81.504	- 411.500	- 390.140
400	31.452	86.666	- 411.500	- 390.009
500	33.508	90.354	- 411.500	- 382.856
600	34.660	93.953	- 410.427	- 375.755
700	35.412	96.256	- 410.485	- 368.706
800	35.825	97.997	- 410.485	- 361.710
900	36.289	99.090	- 410.485	- 354.787
1000	36.556	100.000	- 410.485	- 347.963
1100	36.757	100.749	- 409.482	- 341.255
1200	36.912	101.379	- 409.156	- 334.167
1300	37.033	101.897	- 408.638	- 327.351
1400	37.131	102.319	- 408.536	- 320.583
1500	37.210	102.653	- 408.285	- 313.589
1600	37.275	102.907	- 407.989	- 307.091
1700	37.329	103.087	- 407.709	- 300.374
1800	37.374	103.194	- 407.484	- 293.674
1900	37.413	103.231	- 407.236	- 286.993
2000	37.446	103.293	- 407.022	- 280.317
2100	37.475	103.334	- 406.825	- 273.684
2200	37.499	103.359	- 406.646	- 267.000
2300	37.521	103.374	- 406.485	- 260.357
2400	37.540	103.381	- 406.339	- 253.713
2500	37.557	103.384	- 406.212	- 247.080
2600	37.572	103.387	- 406.104	- 240.454
2700	37.585	103.389	- 406.013	- 233.828
2800	37.597	103.390	- 405.943	- 227.205
2900	37.608	103.391	- 405.904	- 220.584
3000	37.618	103.392	- 405.885	- 213.966
3100	37.626	103.393	- 405.877	- 207.353
3200	37.634	103.394	- 405.871	- 200.733
3300	37.641	103.395	- 405.867	- 194.106
3400	37.647	103.396	- 405.864	- 187.473
3500	37.652	103.397	- 405.862	- 180.850
3600	37.656	103.398	- 405.862	- 174.170
3700	37.660	103.399	- 405.862	- 167.486
3800	37.665	103.400	- 405.862	- 160.777
3900	37.670	103.401	- 405.862	- 154.051
4000	37.674	103.402	- 405.862	- 147.319
4100	37.678	103.403	- 405.862	- 140.584
4200	37.682	103.404	- 405.862	- 133.848
4300	37.686	103.405	- 405.862	- 127.112
4400	37.689	103.406	- 405.862	- 120.376
4500	37.692	103.407	- 405.862	- 113.640
4600	37.695	103.408	- 405.862	- 106.904
4700	37.698	103.409	- 405.862	- 100.168
4800	37.701	103.410	- 405.862	- 93.432
4900	37.704	103.411	- 405.862	- 86.696
5000	37.706	103.412	- 405.862	- 80.000
5100	37.708	103.413	- 405.862	- 73.304
5200	37.710	103.414	- 405.862	- 66.608
5300	37.712	103.415	- 405.862	- 60.000
5400	37.714	103.416	- 405.862	- 53.304
5500	37.715	103.417	- 405.862	- 46.608
5600	37.716	103.418	- 405.862	- 40.000
5700	37.718	103.419	- 405.862	- 33.304
5800	37.720	103.420	- 405.862	- 26.608
5900	37.721	103.421	- 405.862	- 20.000
6000	37.721	103.421	- 405.862	- 13.304

Sept. 30, 1962; Dec. 31, 1963; Mar. 31, 1967

TUNGSTEN HEXAFLUORIDE (WF₆)

(IDEAL GAS)

GFW = 297.8404 F₆W

Point Group O_h

ΔH_f⁰ = -409.4 ± 0.4 kcal/mol

S_{298.15} = 81.504 gibbs/mol

ΔH_f⁰_{298.15} = -411.5 ± 0.4 kcal/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies
w_i, cm⁻¹

769 (1)
256 (3)
670 (2)
712 (3)
216 (3)

Bond Distance: W-F = 1.83 Å

Bond Angle: F-W-F = 90°

Product of the Moments of Inertia: I_AI_BI_C = 7.54576 x 10⁻¹¹³ g³ cm⁶

Heat of Formation

P. A. G. O'Hare and W. N. Hubbard, J. Phys. Chem. **70**, 3353 (1966), determined the heat of formation, ΔH_f⁰₂₉₈(WF₆g) = -411.5 ± 0.4 kcal/mol, by combustion of tungsten in fluorine in a bomb calorimeter. This value is adopted in the tabulation.

Heat Capacity and Entropy

The molecular configuration and vibrational frequencies were obtained from the infrared and Raman spectroscopic studies by J. Gaunt¹, T. G. Burke, D. F. Smith and A. H. Nielsen²; K. Tanner and A. B. P. Duncan³.
The bond distance was reported by H. H. Claassen⁴, based on the preliminary result of V. Schomaker, M. Kimura and B. Weinstein⁵ who determined the bond distance by electron diffraction. J. Gaunt⁶ derived W-F = 1.89 Å from correlations with other hexafluorides and a valence force constant calculation. The three principal moments of inertia are I_A = I_B = I_C = 4.22572 x 10⁻³⁸ g cm².

References

1. J. Gaunt, Trans. Faraday Soc. **49**, 1122 (1953).
2. T. G. Burke, D. F. Smith and A. H. Nielsen, J. Chem. Phys. **20**, 447 (1952).
3. K. H. Tanner and A. B. P. Duncan, J. Am. Chem. Soc. **73**, 1164 (1951).
4. H. H. Claassen, J. Chem. Phys. **30**, 968 (1959).
5. V. Schomaker, M. Kimura and B. Weinstein, Proceedings of 2nd U.N. International Conference on Peaceful Uses of Atomic Energy, Geneva, **28**, 125, (1958).
6. J. Gaunt, Trans. Faraday Soc. **50**, 546 (1954).

Point Group D_{5h}

$$\Delta H_f^\circ = -226.35 \pm 0.6 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -229.7 \pm 0.6 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 83.08 \pm 0.3 \text{ gibbs/mol}$$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}	ω_e, cm^{-1}	ω_e, cm^{-1}
676 (1)	746 (2)	510 (2)
636 (1)	425 (2)	352 (2)
670 (1)	257 (2)	310 (2)
365 (1)		[340] (2)

$$\text{Bond Distance: I-F(equatorial)} = 1.86 \text{ \AA} \quad \text{I-F(axial)} = 1.76 \text{ \AA}$$

$$\text{Bond Angle: F(eq)-I-F(ax)} = 90^\circ \quad \text{F(eq)-I-F(eq)} = 72^\circ$$

$$\text{Product of the Moments of Inertia: } I_{AB}^2 C = 1.1965 \times 10^{-112} \text{ g}^3 \text{ cm}^6$$

Heat of Formation

Settle et al. (1) derived $\Delta H_f^\circ = -229.7 \pm 0.6 \text{ kcal/mol}$ for IF₇(g) at 298.15 K from treatment of their calorimetric data on combustion of iodine in fluorine. The combustion products, consisting of mixtures of IF₅ and IF₃, were expanded, treated to remove excess fluorine, and then hydrolyzed. The solutions were analyzed for iodate and the sum of iodate plus periodate. Since the recovery of iodine was not complete (about 70 to 98%), it was necessary to try various assumptions about the form of the unrecovered iodine. Consistent results were obtained only by assigning the unrecovered iodine to IF₇, the less volatile product. This treatment indicated that IF₇ was formed in yields ranging from about 1 to 70%.

ΔH_f° for the reaction IF₇(g) + IF₅(g) + F₂(g) may be checked via equilibrium data (2). Using six points read from Fig. 2 of Bernstein and Katz, we obtain $\Delta H_f^\circ(3\text{rd law}) = 29.36 \pm 0.2 \text{ kcal/mol}$ and $\Delta H_f^\circ(2\text{nd law}) = 29.53 \pm 0.7 \text{ kcal/mol}$, both at 298.15 K. The entropy test, $\Delta S_f^\circ(2\text{nd law}) - \Delta S_f^\circ(\text{JANAF Functions}) = 0.3 \pm 1.4 \text{ gibbs/mol}$, indicates consistency with the JANAF functions. Combination of $\Delta H_f^\circ(3\text{rd law})$ with ΔH_f° for IF₅(g) yields $\Delta H_f^\circ(\text{IF}_7, g) = -230.2 \pm 0.6 \text{ kcal/mol}$. In deriving the uncertainty, we assume that $\Delta H_f^\circ(3\text{rd law})$ is uncertain by $\pm 0.5 \text{ kcal/mol}$ due to an estimated uncertainty of about 1.0 gibbs/mol in the JANAF value of ΔS_f° at 500 K.

Heat Capacity and Entropy

Recent evidence favors D_{5h} symmetry and a pentagonal bipyramidal structure for the heptafluoride. Claassen et al. (3) review the earlier debate about structures of lower symmetry. They provide convincing evidence of D_{5h} symmetry from the first observation of Raman spectra of the vapor state and re-examination of the infrared spectra. Their data-including five fundamentals in Raman (two polarized), five fundamentals in infrared, no coincidences between Raman and infrared, and one fundamental inactive--are consistent only with D_{5h} symmetry. This is confirmed by Falconer et al. (4) who interpret their electric-deflection experiments as indicating a symmetry-forbidden dipole moment. Extended Huckel-molecular-orbital calculations (5) also predict D_{5h} symmetry. The adopted structural parameters are from our approximate analysis of the electron-diffraction data of Thompson and Bartell (6). The authors gave a radial distribution curve and suggested only a gross (unrefined) structure because of the probable presence of a fluorocarbon impurity in their sample. Principal moments of inertia are $I_A = I_B = 46.83 \times 10^{-39} \text{ g cm}^2$ and $I_C = 84.57 \times 10^{-39} \text{ g cm}^2$.

Observed vibrational fundamentals are from Claassen et al. (3). The inactive fundamental is estimated from the calculations of Khanna (7).

References

1. J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare and W. N. Hubbard, presented at the 23rd Annual Calorimetry Conference, Midland, Mich., August, 1968.
2. R. B. Bernstein and J. J. Katz, J. Phys. Chem. **56**, 885 (1952).
3. H. H. Claassen, E. L. Gasner and H. Seelig, J. Chem. Phys. **52**, 1803 (1968).
4. W. E. Falconer, A. Büchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **48**, 312 (1968).
5. R. L. Oakland and E. Duffey, J. Chem. Phys. **45**, 19 (1967).
6. H. B. Thompson and L. S. Bartell, Trans. Amer. Crystallogr. Ass. **2**, 190 (1966).
7. R. K. Khanna, J. Mol. Spectrosc. **9**, 134 (1962).

Mar. 31, 1962; Mar. 31, 1963; Dec. 31, 1963; June 30, 1966; Dec. 31, 1969

Iodine Heptafluoride (IF₇)

GEW = 259.8932

(Ideal Gas)

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔG _f ^o	Log K _p
0	0.000	INFINITE		5,610	-226.348	-226.348	INFINITE
100	12.467	59.083	106.243	4,716	-219.187	-219.187	479.033
200	24.797	65.817	85.817	3,826	-209.076	-209.076	229.076
300	32.134	63.065	63.064	3,000	-199.776	-199.776	146.441
400	32.235	63.264	63.085	2,266	-192.701	-192.701	105.403
500	36.323	63.175	62.406	1,588	-187.534	-187.534	78.038
600	38.645	61.553	60.555	1,000	-184.894	-184.894	60.838
800	40.057	58.733	58.739	520	-182.022	-182.022	40.838
1000	41.569	56.491	56.256	308	-180.293	-180.293	39.419
1200	42.001	54.414	54.227	185	-179.568	-179.568	37.419
1400	42.315	52.456	52.071	107	-178.852	-178.852	35.419
1600	42.552	50.601	50.784	62	-178.136	-178.136	33.419
1800	42.746	48.841	48.927	35	-177.420	-177.420	31.419
2000	42.900	47.168	47.111	20	-176.704	-176.704	29.419
2200	43.158	45.560	45.544	11	-176.027	-176.027	27.419
2400	43.274	44.002	44.002	6	-175.340	-175.340	25.419
2600	43.319	42.483	42.483	3	-174.653	-174.653	23.419
2800	43.358	41.000	41.000	1	-173.966	-173.966	21.419
3000	43.357	39.557	39.557	0	-173.279	-173.279	19.419
3200	43.357	38.150	38.150	0	-172.592	-172.592	17.419
3400	43.357	36.780	36.780	0	-171.905	-171.905	15.419
3600	43.357	35.440	35.440	0	-171.218	-171.218	13.419
3800	43.357	34.130	34.130	0	-170.531	-170.531	11.419
4000	43.357	32.850	32.850	0	-169.844	-169.844	9.419
4200	43.357	31.600	31.600	0	-169.157	-169.157	7.419
4400	43.357	30.380	30.380	0	-168.470	-168.470	5.419
4600	43.357	29.190	29.190	0	-167.783	-167.783	3.419
4800	43.357	28.030	28.030	0	-167.096	-167.096	1.419
5000	43.357	26.900	26.900	0	-166.409	-166.409	0.419
5200	43.357	25.800	25.800	0	-165.722	-165.722	-1.581
5400	43.357	24.730	24.730	0	-165.035	-165.035	-3.581
5600	43.357	23.690	23.690	0	-164.348	-164.348	-5.581
5800	43.357	22.680	22.680	0	-163.661	-163.661	-7.581
6000	43.357	21.700	21.700	0	-162.974	-162.974	-9.581
6200	43.357	20.750	20.750	0	-162.287	-162.287	-11.581
6400	43.357	19.830	19.830	0	-161.600	-161.600	-13.581
6600	43.357	18.940	18.940	0	-160.913	-160.913	-15.581
6800	43.357	18.080	18.080	0	-160.226	-160.226	-17.581
7000	43.357	17.250	17.250	0	-159.539	-159.539	-19.581
7200	43.357	16.450	16.450	0	-158.852	-158.852	-21.581
7400	43.357	15.680	15.680	0	-158.165	-158.165	-23.581
7600	43.357	14.940	14.940	0	-157.478	-157.478	-25.581
7800	43.357	14.230	14.230	0	-156.791	-156.791	-27.581
8000	43.357	13.550	13.550	0	-156.104	-156.104	-29.581
8200	43.357	12.900	12.900	0	-155.417	-155.417	-31.581
8400	43.357	12.280	12.280	0	-154.730	-154.730	-33.581
8600	43.357	11.690	11.690	0	-154.043	-154.043	-35.581
8800	43.357	11.130	11.130	0	-153.356	-153.356	-37.581
9000	43.357	10.590	10.590	0	-152.669	-152.669	-39.581
9200	43.357	10.070	10.070	0	-151.982	-151.982	-41.581
9400	43.357	9.570	9.570	0	-151.295	-151.295	-43.581
9600	43.357	9.090	9.090	0	-150.608	-150.608	-45.581
9800	43.357	8.630	8.630	0	-149.921	-149.921	-47.581
10000	43.357	8.190	8.190	0	-149.234	-149.234	-49.581

Iron (Fe)

(Reference State) At. Wt. = 55.85

T. °K.	C _p	S° (cal. mole ⁻¹ deg. ⁻¹)	S° - (F° - H ₂₉₈ °)/T (kcal. mole ⁻¹)	H° - H ₂₉₈ ° ΔH _f °	ΔF _f °	Log K _p
0	∞.000	∞.000	INFINITE	- 1.075	∞.000	INFINITE
100	2.680	1.464	11.190	∞.972	∞.000	∞.000
200	5.133	4.302	7.053	∞.950	∞.000	∞.000
298	5.989	6.529	6.529	∞.000	∞.000	∞.000
300	6.000	6.564	6.539	∞.011	∞.000	∞.000
400	6.500	8.363	6.771	∞.000	∞.000	∞.000
500	7.020	9.868	7.243	1.312	∞.000	∞.000
600	7.580	11.197	7.793	2.042	∞.000	∞.000
700	8.240	12.412	8.367	3.231	∞.000	∞.000
800	8.980	13.526	8.966	4.800	∞.000	∞.000
900	10.480	14.718	9.523	4.678	∞.000	∞.000
1000	13.560	15.934	10.102	5.847	∞.000	∞.000
1100	10.230	17.249	10.697	7.207	∞.000	∞.000
1200	10.400	18.516	11.291	9.300	∞.000	∞.000
1300	8.310	18.915	11.291	9.300	∞.000	∞.000
1400	8.460	19.537	12.471	10.032	∞.000	∞.000
1500	8.610	20.125	12.869	10.885	∞.000	∞.000
1600	8.760	20.686	13.340	11.746	∞.000	∞.000
1800	10.860	21.906	13.791	12.769	∞.000	∞.000
1900	10.860	22.046	13.791	12.769	∞.000	∞.000
2000	10.580	24.534	14.748	18.539	∞.000	∞.000
2100	10.620	25.595	15.731	20.713	∞.000	∞.000
2200	10.700	26.556	16.431	22.845	∞.000	∞.000
2300	10.740	27.020	17.055	23.917	∞.000	∞.000
2400	10.780	27.460	17.462	24.998	∞.000	∞.000
2500	10.820	27.884	17.855	26.073	∞.000	∞.000
2600	10.900	28.688	18.600	28.245	∞.000	∞.000
2800	10.940	29.071	18.945	29.317	∞.000	∞.000
3000	10.980	29.443	19.298	30.433	∞.000	∞.000
3100	11.020	29.804	19.631	31.511	∞.000	∞.000
3200	6.488	26.856	20.406	115.502	∞.000	∞.000
3300	6.488	26.856	20.406	115.502	∞.000	∞.000
3400	6.565	57.063	22.551	117.360	∞.000	∞.000
3500	6.644	57.260	23.440	118.020	∞.000	∞.000
3600	6.724	57.446	24.480	118.689	∞.000	∞.000
3700	6.809	57.616	24.724	120.050	∞.000	∞.000
3800	6.897	57.997	27.037	120.743	∞.000	∞.000
3900	6.974	57.997	27.037	121.444	∞.000	∞.000
4000	7.061	58.174	27.813	121.444	∞.000	∞.000
4100	7.151	58.350	28.546	122.145	∞.000	∞.000
4200	7.245	58.528	29.000	122.847	∞.000	∞.000
4300	7.335	58.698	29.000	123.547	∞.000	∞.000
4400	7.430	58.864	30.405	124.242	∞.000	∞.000
4500	7.527	59.032	31.235	125.000	∞.000	∞.000
4600	7.625	59.199	31.861	125.847	∞.000	∞.000
4700	7.726	59.378	32.068	126.592	∞.000	∞.000
4800	7.828	59.559	32.831	127.342	∞.000	∞.000
4900	7.928	59.690	33.431	128.180	∞.000	∞.000
5000	8.032	59.851	34.046	128.978	∞.000	∞.000
5100	8.136	60.011	34.563	129.786	∞.000	∞.000
5200	8.240	60.178	35.090	130.594	∞.000	∞.000
5300	8.345	60.348	35.629	131.402	∞.000	∞.000
5400	8.450	60.485	35.990	132.274	∞.000	∞.000
5500	8.555	60.641	36.437	133.124	∞.000	∞.000
5600	8.660	60.706	36.870	133.986	∞.000	∞.000
5700	3.794	60.920	37.291	134.850	∞.000	∞.000
5800	8.668	61.104	37.761	135.758	∞.000	∞.000
5900	8.970	61.256	38.089	136.630	∞.000	∞.000
6000	9.072	61.408	38.486	137.532	∞.000	∞.000

Mar. 31, 1965

Fe

IRON (Fe)

AT. WT. = 55.85

(REFERENCE STATE)

0 to 1184°K. Crystal alpha
 1184 to 1665°K. Crystal gamma
 1665 to 1809°K. Crystal delta
 1809 to 3145°K. Liquid
 3145 to 8000°K. Ideal Monatomic gas

See crystal, liquid and monatomic gas for details.

Fe

(Crystal) At. Wt. = 55.85

AT. WT. = 55.85

(CRYSTAL)

IRON (Fe)

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔF _f °	Log K _p
0	•000	INFINITE	1.075	•000	•000	INFINITE
100	2.880	11.100	•972	•000	•000	•001
200	5.133	4.302	•540	•000	•000	•000
298	5.989	6.529	•000	•000	•000	•000
300	6.000	6.566	•011	•000	•000	•000
400	6.500	8.363	•637	•000	•000	•000
500	7.020	9.868	1.312	•000	•000	•000
600	7.580	11.197	2.042	•000	•000	•000
700	8.240	12.312	2.847	•000	•000	•000
800	9.170	13.569	3.660	•000	•000	•000
900	10.480	14.718	4.523	•000	•000	•000
1000	13.560	15.934	5.832	•000	•000	•000
1100	10.230	17.240	10.407	•000	•000	•000
1200	8.160	18.256	11.754	•000	•000	•000
1300	8.310	18.915	11.844	•000	•000	•000
1400	8.460	19.537	12.371	•000	•000	•000
1500	8.610	20.125	12.869	•000	•000	•000
1600	8.760	20.686	13.340	•000	•000	•000
1700	8.920	21.396	13.790	•000	•000	•000
1800	10.000	21.963	14.230	•000	•000	•000
1900	10.761	22.308	14.651	•000	•000	•021
2000	10.300	23.031	15.057	•000	•000	•042
2100	10.610	23.538	15.449	•000	•000	•062
2200	10.519	24.025	15.828	•000	•000	•080
2300	10.598	24.495	16.194	•000	•000	•096
2400	10.658	24.947	16.550	•000	•000	•110
2500	10.698	25.381	16.894	•000	•000	•124

$\Delta H_{f,0}^{\circ} = 0$ kcal. mole⁻¹
 $\Delta H_{f,298.15}^{\circ} = 0$ kcal. mole⁻¹
 $\Delta H_{f,298.15}^{\circ} = 0.225$ kcal. mole⁻¹
 $\Delta H_{f,298.15}^{\circ} = 0.260$ kcal. mole⁻¹
 $\Delta H_{f,298.15}^{\circ} = 3.630$ kcal. mole⁻¹
 $\Delta H_{f,298.15}^{\circ} = 99.5 \pm 0.4$ kcal. mole⁻¹

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The heat capacity below 298°K. was obtained by smoothing graphically the data of G. Duyckaerts, *Physica*, 6, 401 (1939) and W. H. Keesom and B. Kurrelmeyer, *Physica*, 6, 633 (1939) over the range 1° - 20°K.; P. E. Simon and R. C. Swain, *Z. Physik. Chem.* 28B, 189 (1935) (30-220°K.), A. Bucken and H. Werth, *Z. Anorg. Chem.* 188, 152 (1930) (17-206°K.) and K. K. Kelley, *J. Chem. Phys.* 11, 16 (1943) (55-295°K.). This data on integration yielded $S_{298.15}^{\circ} = 6.529$ starting with $S_1^{\circ} = 0.0003$ cal. deg⁻¹ mole⁻¹. The heat capacity and enthalpy data above room temperature are extensive and the heat capacities and enthalpies chosen by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" John Wiley and Sons, Inc., New York 1963, were adopted here. These values have a sharp peak in the heat capacity curve at the Curie point* and through this region follow closely the work of P. R. Fallister, *J. Iron Steel Inst.* 167, 87 (1949). This data has recently been corroborated using a pulse heating technique by D. C. Wallace, P. H. Stiles and G. C. Danielson, *J. App. Phys.* 31, 168 (1960). It should be noted that there is some disagreement between the heat capacities chosen and the enthalpies measured by P. D. Anderson and R. Hultgren, *Trans. Met. Soc. AIME*, 224, 842 (1962). The measured values lie consistently above the chosen enthalpies in the range 298-900°K. by from 30 to 60 calories, however the chosen values are considered to be the more reliable. The δ -iron heat capacities adopted here have recently been substantiated confirmed by W. A. Dench and O. Kubashchewski, *J. Iron Steel Inst.* (London) 201, 140 (1963).

Transition Data.

The enthalpies of the α - γ transition at 1184°K. and the δ - γ transition at 1665°K. were also taken from Hultgren et al. loc. cit.

Melting Data.

The temperature and heat of melting were those adopted by Hultgren et al. loc. cit.

Heat of Sublimation.

The value adopted is from a critical second and third law analysis of the data of 14 investigators over gamma-iron and liquid iron. See the Fe(g) table for details.

*See W. P. Giauque, G. E. Brodale, R. A. Fisher and E. W. Hornung, *J. Chem. Phys.* 42, 1 (1965) for the definition of "perit".

Iron (Fe)

(Liquid) At. Wt. = 55.85

T, °K	C _p (cal. mole ⁻¹ deg.°K ⁻¹)	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ (kcal. mole ⁻¹)	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298	5.985	8.195	•000	3.138	2.641	- 1.916
300	6.000	8.232	•011	3.138	2.638	- 1.922
400	6.500	8.637	•617	3.138	2.632	- 1.950
500	7.020	11.534	1.312	3.138	2.505	- 1.606
600	7.580	12.663	2.042	3.138	2.138	- .779
700	8.240	14.078	3.034	3.138	1.972	- .616
800	9.170	15.235	4.699	3.138	1.805	- .493
900	10.460	16.384	7.199	3.138	1.639	- .399
1000	13.560	17.600	11.688	3.138	1.472	- .332
1100	10.230	18.916	12.364	3.138	1.304	- .259
1200	10.260	19.761	12.945	2.947	1.141	- .208
1300	10.300	20.584	13.502	3.152	.982	- .165
1400	10.340	21.388	14.035	3.345	.826	- .126
1500	10.380	22.067	14.547	3.526	.671	- .090
1600	10.420	22.734	15.038	3.699	.522	- .058
1700	10.460	23.387	15.509	3.868	.377	- .028
1800	10.500	23.966	15.963	4.025	.235	- .002
1900	10.540	24.475	16.399	•000	.099	•000
2000	10.580	24.917	16.819	•000	•000	•000
2100	10.620	25.294	17.225	•000	•000	•000
2200	10.660	25.604	17.617	•000	•000	•000
2300	10.700	25.854	17.995	•000	•000	•000
2400	10.740	26.142	18.359	•000	•000	•000
2500	10.780	27.459	18.717	•000	•000	•000
2600	10.820	27.881	19.062	•000	•000	•000
2700	10.860	28.292	19.386	•000	•000	•000
2800	10.900	28.687	19.721	•000	•000	•000
2900	10.940	29.067	20.067	•000	•000	•000
3000	10.980	29.442	20.334	•000	•000	•000
3100	11.020	29.801	20.643	•000	•000	•000
3200	11.060	30.153	20.995	•000	•000	•000
3300	11.100	30.494	21.220	83.425	1.448	- .099
3400	11.140	30.826	21.420	82.862	4.092	- .271
3500	11.180	31.150	21.708	82.047	9.338	- .453
3600	11.220	31.465	22.033	81.596	11.946	- .725
3700	11.260	31.774	22.292	81.148	14.537	- .859
3800	11.300	32.074	22.546	80.705	17.114	- .984
3900	11.340	32.366	22.795	80.260	19.678	- 1.100
4000	11.380	32.656	23.037	79.812	22.240	- 1.215
4100	11.420	32.937	23.275	79.402	24.791	- 1.321
4200	11.460	33.213	23.506	78.978	27.324	- 1.422
4300	11.500	33.483	23.737	78.559	29.852	- 1.517
4400	11.540	33.748	23.962	78.136	32.375	- 1.608
4500	11.580	34.008	24.182	77.717	34.871	- 1.693

IRON (Fe)

(LIQUID)

AT. WT. = 55.85

$$S_{298.15}^{\circ} = 8.195 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1809^{\circ}\text{K.}$$

$$T_b = 3145.4^{\circ}\text{K.}$$

$$\Delta H_f^{\circ} 298.15 = 3.138 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 3.620 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = 83.679 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The $\Delta H_f^{\circ} 298.15$ was obtained from that of the crystal by adding ΔH_m and the difference between $H_{1809} - H_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was that chosen by R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" John Wiley and Sons, Inc., New York (1963).

Melting Data.

See Fe(c) for details.

Vaporization Data.

The boiling point was calculated from the adopted thermodynamic functions and the chosen heat of sublimation at 298°K. so that the free energy function calculated by integration of the crystal liquid data or by statistical methods from the gas phase were equal at the boiling point.

(Ideal Gas) At. Wt. = 55.85

IRON, MONATOMIC (Fe)

(IDEAL GAS)

AT. WT. = 55.85

Ground State Configuration $5D_4$ $\Delta H_f^\circ = 98.9 \pm 0.4$ kcal. mole $^{-1}$
 $S_{298.15}^\circ = 43.112$ cal. mole $^{-1}$ deg $^{-1}$ $\Delta H_f^\circ = 99.5 \pm 0.4$ kcal. mole $^{-1}$

Electronic Levels and Multiplicities

E , cm $^{-1}$	g_i	E , cm $^{-1}$	g_i	E , cm $^{-1}$	g_i
0	9	12561	7	19913	5
416	7	12569	5	20020	3
704	5	12589	7	19330	13
978	3	17550	7	43022	412
6928	11	17527	3	47182	427
7377	9	18378	5	47182	427
13653	3	20641	9	57165	405
20874	7	19553	3	53782	433
20038	1	21039	5	57421	482
19551	11	21949	27		
19553	5	22928	49		
19757	7	23143	146		

Heat of Formation.

The heat of formation is the heat of sublimation at 298°K. which was obtained by second and third law analysis of the following vapor pressure data.

Method	Points	Ref.	$\Delta H_{298.15}^\circ$ 2nd law kcal. mole $^{-1}$	$\Delta H_{298.15}^\circ$ 3rd law kcal. mole $^{-1}$	Drift in 3rd law cal. deg $^{-1}$ mole $^{-1}$
Boiling	1	1	—	105.6	—
Boiling	2	2	—	88.1	—
Transport	1	3	—	101.4	—
Langmuir	1	4	—	99.5	—
Langmuir	20	5*	100.0 \pm 1.1	97.3	-0.2 \pm 0.6
Langmuir	6	6	98.4 \pm 1.6	98.0	-0.6 \pm 1.2
Langmuir	12	7	101.6 \pm 1.8	98.0	-1.1 \pm 1.3
Langmuir	9	8*	99.4 \pm 1.0	99.8	0.3 \pm 0.7
Alloy activities	4	9	101.7 \pm 13.5	99.1	-4.6 \pm 6.5
Knudsen	12	11*	108.4 \pm 1.0	98.8	-7.9 \pm 0.8
Langmuir	12	12	105.9 \pm 1.2	97.2	-5.9 \pm 0.9
Isotope Exchange	10	13*	95.6 \pm 5.2	97.3	1.0 \pm 3.6
Knudsen	—	14**	99.9	99.0	-0.6
Knudsen	—	15**	98.6	101.0	1.5 \pm 0.3
Langmuir	4	16	94.5 \pm 0.5	98.8	—

*1 point rejected in statistical test. **Data from equations.

- 1 - O. Ruff and W. Bornmann, Z. Anorg. Chem. **89**, 365 (1914) [2723°K.]
- 2 - H. C. Greenwood and M. S. B. Fellow, Proc. Roy. Soc. **83A**, 483 (1910) [2723°K.]
- 3 - E. T. Turkogian and L. E. Leake, Trans. Met. Soc. AIME, **218**, 1136 (1960) [1873°K.]
- 4 - L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. **69**, 798 (1946) [1873°K.]
- 5 - J. P. Morris, O. R. Zellars, S. L. Payne and R. L. Kipp, U.S.B.M. Report Invest. 5364 (1957) [1810-1869°K.]
- 6 - A. L. Marehall, R. W. Dornie, and P. J. Norton, J. Am. Chem. Soc. **59**, 1161 (1937) [1317-1579°K.]
- 7 - Ref. 6 with temperatures increased by 11 degrees suggested by Ref. 8 [1328-1590°K.]
- 8 - J. W. Edwards, H. L. Johnston and W. E. Dittmar, J. Am. Chem. Soc. **76**, 4729 (1951) [1389-1519°K.]
- 9 - R. Spieser, A. J. Jacobs and J. W. Sprenak, Trans. Met. Soc. AIME, **215**, 185 (1959) [1725-1926°K.]
- 10 - Yu. V. Kornev, Dokl. Akad. Nauk. SSSR, **93**, 467 (1953) [1464-1623°K.]
- 11 - V. D. Burlikov, Vis. Metallov i Metalloved. **50** (1957) (cast specimen) [1292-1525°K.]
- 12 - Ref. 11 using evaporated specimens on different substrates [1302-1505°K.]
- 13 - I. I. Ivanov - Thesis - Inst. of Metallurgy, Acad. Sci. USSR (1957) [1260-1620°K.]
- 14 - K. M. Nyles and A. T. Aldred, J. Phys. Chem. **68**, 64 (1964) [1450-1650°K.]
- 15 - E. Z. Vintalokin, Dokl. Akad. Nauk. SSSR, **117**, 632 (1957) [1400-1600°K.]
- 16 - H. A. Jones, I. Langmuir and G. M. J. Meckay, Phys. Rev. **90**, 201 (1957) [1270-1580°K.]

The adopted value of 99.5 kcal. mole $^{-1}$ is based mainly on the work of Refs. 5, 8 and 14, which have the best drift analysis and agreement between second and third law.

Heat Capacities and Entropies.

The electronic levels were taken from C. E. Moore, Natl. Bur. Standards Circ. 467 (1949). Levels above 20,000 cm $^{-1}$ were averaged.

Iron Dihydroxide (Fe(OH)₂)

(Crystal) GFW = 89.86174



QFW = 89.86174

IRON DIHYDROXIDE (Fe(OH)₂) (CRYSTAL)

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0°							
100							
200							
298	23.200	21.040	21.000	•000	-137.200	-117.599	86.203
300	23.220	21.144	21.000	•043	-137.194	-117.478	85.583
400	24.400	27.987	21.925	2.424	-136.844	-110.958	80.625
500	25.520	33.552	23.711	4.721	-136.452	-104.250	75.690
600	26.600	38.302	25.756	7.527	-136.031	-98.186	71.764
700	27.600	42.480	27.853	10.239	-135.588	-91.912	68.696
800	28.430	46.222	29.919	13.042	-135.157	-85.705	66.413
900	29.050	49.608	31.921	15.918	-134.763	-79.545	64.316
1000	29.490	52.693	33.847	18.846	-134.357	-73.422	62.046
1100	29.760	55.517	35.690	21.810	-134.533	-67.305	60.372
1200	29.900	58.113	37.452	24.793	-134.295	-61.209	59.148
1300	29.960	60.509	39.135	27.787	-133.725	-55.142	58.270
1400	29.980	62.750	40.742	30.784	-133.185	-49.117	57.667
1500	30.000	64.799	42.277	33.783	-132.676	-43.129	57.284

ΔHf° = Unknown

ΔHf°_{298.15} = -137.2 ± 0.7 kcal/mol

ΔHm° = Unknown

ΔHs°_{298.15} = 58.2 kcal/mol

Heat of Formation.

The heat of combustion of Fe(OH)₂(c), according to the chemical reaction Fe(OH)₂(c) + 1/4 O₂(g) = 1/2 Fe₂O₃(c) + H₂O(l), was determined to be -29.8 ± 0.65 kcal/mol by R. Fricke and S. Rühl, Z. anorg. allgem. chem. 251, 414 (1943). From this data the heat of formation (ΔHf°_{298.15}) was evaluated to be -137.2 ± 0.7 kcal/mol, which was adopted here.

The enthalpy changes for the following three reactions were determined by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882 - 1886:

Reaction	ΔHr° ₂₉₈ , kcal/mol
1. FeCl ₂ (c) = FeCl ₂ (400 H ₂ O)	-17.9
2. FeCl ₂ (200 H ₂ O) + H ₂ SO ₄ (200 H ₂ O) = FeSO ₄ (200 H ₂ O) + 2 HCl(100 H ₂ O)	-3.6
3. FeSO ₄ (aq.) + 2KOH(aq.) = Fe(OH) ₂ (c) + K ₂ SO ₄ (aq.)	-6.34

Using ΔHr°_{298.15} = -81.7 kcal/mol for FeCl₂(c) and those for the other compounds in aqueous solution (assuming aq. = 200 H₂O in Reaction 3) obtained from D.D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, National Bureau of Standards, 1965, the heat of formation (298.15°K) for Fe(OH)₂(c) was derived as -135.8 kcal/mol which agrees reasonably with the adopted value.

Heat Capacity and Entropy.

The heat capacities, 298.15 - 700°K, and S°_{298.15} were estimated by comparison with those for FeCl₂(c), CaCl₂(c) and Ca(OH)₂(c). The Cp values above 700°K were obtained by graphical extrapolation of the Cp curve plotted using the above Cp values.

Heat of Sublimation.

The value of ΔHs°_{298.15} was calculated as the difference between ΔHf°_{298.15} for Fe(OH)₂(g) and Fe(OH)₂(c).

GFW = 89.86174

IRON DIHYDROXIDE (Fe(OH)₂)

(IDEAL GAS)

OPW = 89.86174

Point Group [C_{2h}]
 $S_{298.15}^\circ = [67.58] \text{ gibbs/mol}$
 $\Delta H_f^\circ = [-77.2 \pm 0.5] \text{ kcal/mol}$
 $\Delta H_f^{298.15} = [-79.0 \pm 0.5] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[5]
[700]	[10]
[2500]	[5]
[4000]	[5]

Vibrational Frequencies and Degeneracies

ω_j, cm^{-1}	ω_j, cm^{-1}	ω_j, cm^{-1}
[2300] (1)	[450] (1)	[800] (1)
[750] (1)	[320] (1)	[700] (1)
[400] (1)	[2600] (1)	[570] (1)

Bond Distance: Fe-O = [1.8] Å

Bond Angle: O-Fe-O = [105]°

Product of the Moments of Inertia: $I_{AB}I_C = [9.388 \times 10^{-116}] \text{ g}^3 \text{ cm}^6$

Heat of Formation.

The equilibrium constants, at temperatures between 1300 and 1460°C, for the chemical reaction $\text{Fe}(c) + 2\text{H}_2\text{O}(g) = \text{Fe}(\text{OH})_2(g) + \text{H}_2(g)$, were determined by G. R. Belton and P. D. Richardson, Trans. Faraday Soc. 58, 1562 (1962). Using these data, the enthalpy change ($\Delta H_{298.15}^\circ$) of the reaction is evaluated to be 35.53 ± 3.0 and 35.57 kcal/mol by the second and third law method, respectively. Based on the third law value for $\Delta H_{298.15}^\circ$, the heat of formation ($\Delta H_{298.15}^\circ$) for $\text{Fe}(\text{OH})_2(g)$ is calculated to be $-79 \pm 0.5 \text{ kcal/mol}$.

Heat Capacity and Entropy.

The molecular structure is assumed to be the same as that for $\text{B}(\text{OH})_2(g)$. The Fe-O bond distance is taken from $\text{FeO}(g)$. The O-H bond distance and Fe-O-H bond angle are estimated from those for $\text{H}_2\text{O}(g)$. The vibrational frequencies, and electronic levels and quantum weights are obtained by comparison with those for $\text{B}(\text{OH})_2(g)$ and $\text{FeCl}_2(g)$, respectively. These values are adjusted to give reasonable second and third law agreements. The three principal moments of inertia are: $I_A = 2.658 \times 10^{-40}$, $I_B = 1.864 \times 10^{-36}$ and $I_C = 1.890 \times 10^{-36} \text{ g cm}^2$.

T, °K	Cp°	S°	-(G°-H°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	8.787	0.000	INFINITE	3.396	-77.222	-77.222	INFINITE
100	46.182	54.182	54.182	-2.386	-77.968	-77.968	167.542
200	13.193	61.525	69.027	-1.501	-78.604	-78.604	82.066
298	17.090	67.577	67.577	0.000	-79.000	-79.000	53.363
300	17.145	67.683	67.683	0.032	-79.005	-79.005	53.363
400	19.362	72.953	68.281	1.869	-79.199	-79.199	38.956
500	20.585	77.416	69.673	3.871	-79.302	-79.302	30.296
600	21.907	81.248	71.281	5.973	-79.385	-79.385	24.516
700	22.059	82.593	72.593	8.144	-79.422	-79.422	20.279
800	22.568	87.573	76.601	10.377	-79.422	-79.422	17.279
900	23.057	90.261	76.194	12.661	-79.480	-79.480	14.659
1000	23.485	92.714	77.725	14.989	-80.214	-80.214	12.916
1100	23.864	94.970	79.182	17.256	-80.787	-80.787	11.316
1200	24.196	97.058	80.595	19.750	-81.132	-81.132	9.977
1300	24.419	99.002	81.937	22.485	-81.127	-81.127	8.840
1400	24.643	100.820	83.221	25.339	-81.130	-81.130	7.866
1500	24.833	102.527	84.452	27.713	-81.146	-81.146	7.021
1600	24.993	104.135	85.632	29.604	-81.179	-81.179	6.283
1700	25.128	105.654	86.762	31.111	-81.171	-81.171	5.647
1800	25.242	107.084	87.856	32.429	-81.075	-81.075	5.047
1900	25.339	108.461	88.904	33.558	-85.524	-85.524	4.503
2000	25.420	109.763	89.915	34.606	-85.757	-85.757	4.010
2100	25.490	111.005	90.890	42.242	-86.000	-86.000	3.563
2200	25.548	112.192	91.825	47.913	-86.522	-86.522	2.783
2300	25.598	113.329	92.742	47.913	-86.801	-86.801	2.440
2400	25.641	114.420	93.622	49.713	-87.094	-87.094	2.123
2500	25.677	115.467	94.475	52.479	-87.397	-87.397	1.830
2600	25.707	116.475	95.302	55.048	-87.715	-87.715	1.530
2700	25.734	117.445	96.093	57.313	-88.043	-88.043	1.303
2800	25.756	118.382	96.883	60.195	-88.384	-88.384	1.066
2900	25.775	119.286	97.640	62.772	-88.739	-88.739	0.843
3000	25.792	120.160	98.377	65.350	-89.104	-89.104	0.634
3100	25.806	121.006	99.089	67.930	-89.482	-89.482	0.439
3200	25.818	121.825	99.781	70.511	-89.873	-89.873	0.262
3300	25.828	122.620	100.470	73.093	-90.282	-90.282	0.109
3400	25.837	123.391	101.133	75.677	-90.709	-90.709	0.035
3500	25.844	124.140	101.780	78.261	-91.156	-91.156	0.010
3600	25.851	124.868	102.411	80.845	-91.623	-91.623	0.000
3700	25.856	125.576	103.026	83.429	-92.110	-92.110	0.000
3800	25.861	126.266	103.619	86.017	-92.617	-92.617	0.000
3900	25.865	126.938	104.219	88.603	-93.143	-93.143	0.000
4000	25.868	127.593	104.796	91.190	-93.683	-93.683	0.000
4100	25.871	128.232	105.359	93.777	-94.230	-94.230	0.000
4200	25.873	128.856	105.914	96.361	-94.796	-94.796	0.000
4300	25.875	129.466	106.452	98.944	-95.372	-95.372	0.000
4400	25.877	130.059	106.982	101.539	-95.970	-95.970	0.000
4500	25.878	130.641	107.501	104.127	-96.583	-96.583	0.000
4600	25.879	131.209	108.011	106.714	-97.210	-97.210	0.000
4700	25.880	131.763	108.500	109.300	-97.852	-97.852	0.000
4800	25.881	132.311	109.000	111.900	-98.506	-98.506	0.000
4900	25.881	132.844	109.481	114.478	-99.173	-99.173	0.000
5000	25.881	133.367	109.954	117.057	-99.853	-99.853	0.000
5100	25.881	133.880	110.418	119.655	-100.540	-100.540	0.000
5200	25.881	134.375	110.873	122.283	-101.243	-101.243	0.000
5300	25.881	134.855	111.232	124.941	-101.962	-101.962	0.000
5400	25.881	135.359	111.763	127.619	-102.694	-102.694	0.000
5500	25.881	135.834	112.166	130.007	-103.439	-103.439	0.000
5600	25.881	136.300	112.623	132.595	-104.196	-104.196	0.000
5700	25.881	136.750	113.045	135.377	-104.966	-104.966	0.000
5800	25.880	137.208	113.425	137.771	-105.749	-105.749	0.000
5900	25.879	137.651	113.661	140.359	-106.511	-106.511	0.000
6000	25.879	138.086	114.261	142.947	-107.260	-107.260	0.000

June 30, 1966; Dec. 31, 1966

Iron Trihydroxide (Fe(OH)₃)

(Crystal) GFW = 106.86911

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	24.300	25.000	25.000	•000	-199.000	-168.634	123.612
300	24.400	25.151	25.000	+045	-199.005	-168.446	122.713
400	28.200	32.714	26.006	2.683	-199.100	-158.238	86.457
500	31.000	39.312	28.021	5.645	-198.958	-148.034	64.706
600	33.600	45.205	30.403	8.882	-198.634	-137.877	50.222
700	35.400	50.523	32.904	12.333	-198.192	-127.784	39.896
800	37.000	55.357	35.413	15.956	-197.663	-117.762	32.171
900	38.300	59.792	37.879	19.723	-197.191	-107.799	26.177
1000	39.400	63.867	40.277	23.610	-196.779	-97.891	21.394
1100	40.250	67.684	42.598	27.594	-196.517	-88.010	17.486
1200	40.900	71.215	44.838	31.653	-195.994	-78.174	14.237
1300	41.400	74.509	46.995	35.769	-195.103	-68.391	11.498
1400	41.750	77.591	49.071	39.927	-194.210	-58.678	9.160
1500	42.000	80.480	51.070	44.115	-193.331	-49.026	7.143

IRON TRYDROXIDE (Fe(OH)₃)

(CRYSTAL)

GFW = 106.86911

ΔH _f ^o = Unknown	
ΔH _f ^o _{298.15} = -199 ± 3 kcal/mol	
ΔH _m ^o = Unknown	
S _{298.15} ^o = [25 ± 2] gibbs/mol	
T _m = Unknown	

Heat of Formation.

P. Schindler, W. Michaelis and W. Peitmecht, *Helv. Chim. Acta*, **46**, 444 (1963), investigated the solubility of aged Fe(OH)₃ precipitates by determining the Fe⁺⁺⁺ and H⁺ ion concentration of solution in contact with the solid phase. The ion concentration was measured by the EMF method at the constant ionic strength 3M NaClO₄ (solution). The precipitates were investigated by X-ray and electron microscope methods. The equilibrium constant was derived as log [Fe⁺⁺⁺] [H⁺]⁻³ = log K = 3.55 ± 0.1 for amorphous inactive hydroxide at 25°C. From these data the quantity log K_a = -39.1 ± 0.2 was evaluated where K_a is the solubility product of Fe(OH)₃. The Gibbs energy change (ΔH_f^o_{298.15}) of the reaction Fe(OH)₃(c) = Fe⁺⁺⁺(aq) + 3OH⁻(aq) was calculated to be 53.34 ± 0.27 kcal/mol. Using S_{298.15}^o = 70.1 and -2.57 gibbs/mol for Fe⁺⁺⁺(aq) and OH⁻(aq), respectively, and an estimated S_{298.15}^o(Fe(OH)₃, c) = 25 gibbs/mol, the enthalpy change (ΔH_f^o_{298.15}) of the reaction is calculated to be 22.69 kcal/mol, according to the relationship ΔH = ΔG + TΔS. The entropy values for Fe⁺⁺⁺ and OH⁻ ions were obtained from "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952, and NBS Technical Note 270-1 by D. D. Wagman and co-workers, 1965, respectively. Based on ΔH_f^o_{298.15}(Fe⁺⁺⁺, aq) = -11.4 and ΔH_f^o_{298.15}(OH⁻, aq) = -54.97 kcal/mol, taken from the same sources, the heat of formation (ΔH_f^o_{298.15}) for Fe(OH)₃(c) was evaluated to be -199 ± 3 kcal/mol, which was adopted here.

The divergent values for solubility product (SP) of Fe(OH)₃ found in the literature may be due not only to the various forms of precipitate, but also to the tendency to form colloidal solutions. The SP values for Fe(OH)₃ were also reported by Evans and Pryor, *J. Chem. Soc.* **5157** (1949); Kriukor and Aseevetsch, *Z. Elektrochem.* **59**, 884 (1955); Ruff and Hirsch, *Z. Anorg. Chem.* **146**, 338 (1925); Britton, *J. Chem. Soc.* **2148** (1925); and Jellinek and Gordon, *Z. Phys. Chem.* **112**, 207 (1924).

The enthalpy changes (ΔH_f^o_{298.15}) for the reactions: (1) FeCl₃(aq) + 3NaOH(aq) = Fe(OH)₃(c) + 3NaCl(aq) and (2) FeCl₃(c) = FeCl₃(aq) were determined to be -24.50 and -31.66 kcal/mol, respectively, by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882 - 1886. Assuming the aqueous solutions all contain 200 mol of H₂O, the heat of formation (ΔH_f^o_{298.15}) for Fe(OH)₃ was calculated as -196.9 kcal/mol from Reactions (1) and (2). The ΔH_f^o_{298.15} values for NaOH(aq) and NaCl(aq) were obtained from V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-2, National Bureau of Standards, 1965, and JANAP ΔH_f^o_{298.15} values for NaOH(c) and NaCl(c).

Heat Capacity and Entropy.

The heat capacities, S_{298.15} - 1000°K, were estimated by comparison with those for B₂O₃(c), Fe₂O₃(c) and B(OH)₃(c). The Cp values above 1000°K were obtained by graphical extrapolation. The S_{298.15}^o(Fe(OH)₃, c) value was estimated by comparison with that for B(OH)₃(c).

Iron Diodide (FeI₂)

(Crystal) GFW = 309.6558

IRON DIODIDE (FeI₂)

(CRYSTAL)

GFW = 309.6558

FeI₂

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0							
100							
200							
298	20.000	40.000	40.000	•000	- 25•000	- 26•703	19•574
300							
400	20.000	40.124	40.000	•037	- 24.998	- 26.716	19.461
500	20.000	40.266	40.000	2.040	- 28.793	- 27.161	18.840
600	20.120	50.368	42.270	4.049	- 38.982	- 25.793	11.274
700	20.178	54.042	43.935	6.064	- 36.594	- 23.194	8.449
800	22.800	57.588	45.633	8.368	- 37.978	- 20.673	6.454
900	26.500	62.217	47.352	12.534	- 37.978	- 18.670	4.865
1000	32.700	67.562	50.708	16.833	- 35.224	- 13.713	2.997
1100	33.745	70.716	52.385	20.144	- 34.175	- 11.607	2.306
1200	34.000	73.685	54.037	23.554	- 32.857	- 9.619	1.752
1300	34.000	76.407	55.668	27.000	- 31.186	- 7.740	1.318
1400	34.000	78.907	57.195	30.554	- 29.540	- 6.008	0.938
1500	34.000	81.252	58.749	33.754	- 27.906	- 4.386	•639

 $\Delta H_f^\circ = \text{Unknown}$ $\Delta H_{298.15}^\circ = -25 \pm 4 \text{ kcal/mol}$ $\Delta H^\circ = 0.2 \text{ kcal/mol}$ $\Delta H_m^\circ = [10.7] \text{ kcal/mol}$ $\Delta H_{298.15}^\circ \text{ (to monomer)} = [46] \text{ kcal/mol}$ $\Delta H_{298.15}^\circ \text{ (to dimer)} = [52] \text{ kcal/mol}$

Heat of Formation.

The chemical equilibrium of the decomposition of $\text{FeI}_2(\text{c})$, $771.15 - 858.15^\circ\text{K}$, has been studied by W. E. Zaugg and N. W. Gregory, *J. Phys. Chem.* **70**, 486 (1966). Using the reported partial pressures for $\text{I}_2(\text{g})$, the enthalpy change ($\Delta H_{298.15}^\circ$) for the reaction $\text{FeI}_2(\text{c}) = \text{Fe}(\text{c}) + \text{I}_2(\text{g})$ was evaluated by both the second and third law methods to be 39.79 ± 1.0 and $39.69 \pm 0.3 \text{ kcal/mol}$, respectively. Based on the third law $\Delta H_{298.15}^\circ$ value, the heat of formation ($\Delta H_{298.15}^\circ$) for $\text{FeI}_2(\text{c})$ was calculated as -25 kcal/mol which was adopted here.

The enthalpy change for the reaction $\text{FeI}_2(\text{c}) = \text{Fe}^{++}(\text{aq}) + 2 \text{I}^-(\text{aq})$ was determined to be $-19.48 \pm 0.03 \text{ kcal/mol}$ by P. Paoletti, A. Sabatini and A. Vacca, *Trans. Faraday Soc.* **61**, 2417 (1965), using a solution calorimetric method. Adopting $\Delta H_{298.15}^\circ = -21.3$ and -13.9 kcal/mol for $\text{Fe}^{++}(\text{aq})$ and $\text{I}^-(\text{aq})$, respectively, the value of $\Delta H_{298.15}^\circ$ (FeI_2, c) was derived as $-28.22 \pm 1 \text{ kcal/mol}$. The value of $\Delta H_{298.15}^\circ (\text{I}^-, \text{aq})$ was taken from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Part 1, Technical Note 270-1, National Bureau of Standards, 1955. The value of $\Delta H_{298.15}^\circ (\text{Fe}^{++}, \text{aq})$ was derived from heats of solution and formation for $\text{FeCl}_2(\text{c})$.

The heats of solution of $\text{Fe}(\text{c})$, $\text{I}_2(\text{c})$ and $\text{FeI}_2(\text{c})$ in aqueous $\text{Br}_2\text{-KBr}$ solution were measured by W. Hieber and A. Moerner, *Z. Elektrochem.* **40**, 287 (1934), using an ice calorimeter. From the results obtained the heat of formation for $\text{FeI}_2(\text{c})$ was reported as -30.1 kcal/mol .

Heat Capacity and Entropy.

The heat capacities, $343.15 - 773.15^\circ\text{K}$, were measured by P. L. Oetting and N. W. Gregory, *J. Phys. Chem.* **65**, 173 (1961). The C_p values at temperatures below 343.15 and above 773.15°K were estimated by graphical extrapolation. The low temperature heat capacities, $11-130^\circ\text{K}$, were determined by O. Miljutin and E. A. Parfenova, *Phys. Trans. Ukrain, Acad. Sci.* **5**, 81 (1940). These data appear to be inadequate for the derivation of the entropy at 298.15°K . The value of $S_{298.15}$ adopted was calculated from the entropy change, $\Delta S_{298.15}^\circ = 28.7 \text{ eu}$, for the decomposition reaction $\text{FeI}_2(\text{c}) = \text{Fe}(\text{c}) + \text{I}_2(\text{g})$, obtained by the second law analysis of the equilibrium pressure data reported by W. E. Zaugg and N. W. Gregory, *J. Phys. Chem.* **70**, 486 (1966).

Transition Data.

A minor transition in the vicinity of 370°C ($360-385^\circ\text{C}$) has been reported by P. L. Oetting and N. W. Gregory, *loc. cit.* Subsequent studies by T. J. Wydeven, Ph. D. Thesis, University of Washington, Seattle, Wash., 1964, have shown the magnitude of the transition to be sensitive to trace amounts of impurities, but the nature of the transition has not been clearly established. A magnetic transition at 10°K was reported by H. Bizotte, C. Terrier and E. Tsal, *Compt. rend.* **245**, 507 (1957). The ΔH° value was evaluated from the heat capacity - temperature plot given by P. L. Oetting and N. W. Gregory, *loc. cit.*

Melting Data.

T_m was reported by W. Fischer and R. Gwehn, *Z. anorg. allgem. Chem.* **222**, 303 (1935). ΔH_m° was estimated by comparison with that for $\text{FeBr}_2(\text{c})$.

Heat of Sublimation.

$\Delta H_{298.15}^\circ$ (to monomer) is calculated as the difference between $\Delta H_{298.15}^\circ$ for $\text{FeI}_2(\text{g})$ and $\text{FeI}_2(\text{c})$. $\Delta H_{298.15}^\circ$ (to dimer) was calculated as the difference between those for $\text{Fe}_2\text{I}_4(\text{g})$ and $2 \text{FeI}_2(\text{c})$.

FeI₂

Sept. 30, 1966

Iron Diodide (FeI₂)

(Liquid) GFW = 309.6558

FeI₂

GFW = 309.6558

IRON DIODIDE (FeI₂) (LIQUID)

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	27.000	46.720	46.720	0.000	-16.966	-20.676	15.156
300	27.000	46.887	46.720	0.050	-16.954	-20.658	15.079
400	27.000	54.654	47.779	2.750	-20.052	-21.628	14.405
500	27.000	60.679	49.779	5.450	-20.550	-21.517	14.405
600	27.000	65.602	52.018	8.150	-28.477	-20.013	7.290
700	27.000	69.764	54.264	10.850	-27.465	-18.684	5.833
800	27.000	73.248	56.512	13.550	-26.453	-17.351	4.376
900	27.000	76.248	58.760	16.250	-25.441	-16.018	2.919
1000	27.000	79.394	60.444	18.950	-25.076	-15.417	2.469
1100	27.000	81.967	62.285	21.650	-24.658	-14.467	2.874
1200	27.000	84.317	64.025	24.350	-24.030	-13.574	2.477
1300	27.000	86.476	65.728	27.050	-23.213	-12.683	1.872
1400	27.000	88.276	67.228	29.750	-22.179	-11.793	1.645
1500	27.000	90.341	68.708	32.450	-21.179	-10.862	1.456
1600	27.000	92.084	70.115	35.150	-20.262	-10.085	1.297
1700	27.000	93.721	71.456	37.850	-19.453	-9.364	1.160
1800	27.000	95.161	72.736	40.550	-18.684	-8.664	1.020
1900	27.000	96.724	73.960	43.250	-17.957	-8.027	0.897
2000	27.000	98.109	75.134	45.950	-17.262	-7.407	0.797

ΔH°_{298.15} = [16.966] kcal/mol

ΔH° = [10.7] kcal/mol

ΔH° = [25.0] kcal/mol

S°_{298.15} = [46.720] gibbs/mol

T_m = 860 ± 2° K

T_b = [1366] °K

Heat of Formation.

The heat of formation (ΔH°_{298.15}) was obtained from ΔH°_{298.15} (c) by adding ΔH° and the difference between H° - H°_{298.15} for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was assumed to be constant in the temperature range from 298.15 to 2000°K. The value of Cp was calculated on an assumption that Cp = 9.0 gibbs/g-atom for FeI₂(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Vaporization Data.

T_b is the temperature at which the vapor pressure of FeI₂(g) and Fe₂I₄(g) over FeI₂(l) equals one atmosphere. The value of ΔH° is derived from the vapor composition and the heats of vaporization of FeI₂(l) to monomer and dimer at T_b.

Iron Dioxide (FeI₂)
(Ideal Gas)

GFW = 309.6558

IRON DIODIDE (FeI₂)

(IDEAL GAS)

QPW = 309.6558

FeI₂

T, °K Cp° S° (-C°-H°₃₉₈)^o H°-H°₃₉₈ ΔH° kcal/mol ΔG° Log Kp

0	0.000	INFINITE	-	3.864	21.365	21.365	INFINITE
100	12.687	68.365	96.158	- 2.770	21.618	21.618	- 35.811
200	16.172	77.769	84.851	- 2.412	21.866	21.866	- 12.268
300	18.545	83.530	89.530	- 2.000	22.126	22.126	- 6.631
400	20.819	88.119	93.119	- 1.533	22.392	22.392	- 4.537
500	22.998	91.619	96.619	- 1.023	22.663	22.663	- 3.151
600	25.098	94.119	99.119	- 0.464	22.939	22.939	- 2.278
700	27.122	95.619	100.619	- 0.000	23.219	23.219	- 1.782
800	29.065	97.119	102.119	0.464	23.503	23.503	- 1.582
900	30.822	98.619	103.619	0.949	23.791	23.791	- 1.465
1000	32.398	100.119	105.119	1.444	24.083	24.083	- 1.400
1100	33.798	101.619	106.619	1.944	24.380	24.380	- 1.375
1200	35.022	103.119	108.119	2.444	24.682	24.682	- 1.382
1300	36.072	104.619	109.619	2.944	24.989	24.989	- 1.408
1400	36.958	106.119	111.119	3.444	25.301	25.301	- 1.452
1500	37.692	107.619	112.619	3.944	25.618	25.618	- 1.500
1600	38.282	109.119	114.119	4.444	25.940	25.940	- 1.550
1700	38.732	110.619	115.619	4.944	26.267	26.267	- 1.600
1800	39.052	112.119	117.119	5.444	26.600	26.600	- 1.650
1900	39.252	113.619	118.619	5.944	26.938	26.938	- 1.700
2000	39.332	115.119	120.119	6.444	27.281	27.281	- 1.749
2100	39.292	116.619	121.619	6.944	27.629	27.629	- 1.792
2200	39.132	118.119	123.119	7.444	27.982	27.982	- 1.828
2300	38.852	119.619	124.619	7.944	28.340	28.340	- 1.858
2400	38.452	121.119	126.119	8.444	28.703	28.703	- 1.875
2500	37.932	122.619	127.619	8.944	29.071	29.071	- 1.878
2600	37.292	124.119	129.119	9.444	29.444	29.444	- 1.868
2700	36.532	125.619	130.619	9.944	29.822	29.822	- 1.845
2800	35.652	127.119	132.119	10.444	30.205	30.205	- 1.808
2900	34.652	128.619	133.619	10.944	30.593	30.593	- 1.758
3000	33.532	130.119	135.119	11.444	30.986	30.986	- 1.695
3100	32.292	131.619	136.619	11.944	31.384	31.384	- 1.618
3200	30.932	133.119	138.119	12.444	31.787	31.787	- 1.528
3300	29.452	134.619	139.619	12.944	32.195	32.195	- 1.425
3400	27.852	136.119	141.119	13.444	32.608	32.608	- 1.308
3500	26.132	137.619	142.619	13.944	33.026	33.026	- 1.178
3600	24.292	139.119	144.119	14.444	33.449	33.449	- 1.035
3700	22.332	140.619	145.619	14.944	33.877	33.877	- 0.878
3800	20.252	142.119	147.119	15.444	34.310	34.310	- 0.708
3900	18.052	143.619	148.619	15.944	34.748	34.748	- 0.525
4000	15.732	145.119	150.119	16.444	35.191	35.191	- 0.328
4100	13.292	146.619	151.619	16.944	35.639	35.639	- 0.118
4200	10.732	148.119	153.119	17.444	36.092	36.092	0.095
4300	8.052	149.619	154.619	17.944	36.550	36.550	0.358
4400	5.252	151.119	156.119	18.444	37.013	37.013	0.685
4500	2.332	152.619	157.619	18.944	37.481	37.481	1.085
4600	- 0.708	154.119	159.119	19.444	37.954	37.954	1.558
4700	- 3.652	155.619	160.619	19.944	38.432	38.432	2.095
4800	- 6.492	157.119	162.119	20.444	38.915	38.915	2.698
4900	- 9.232	158.619	163.619	20.944	39.403	39.403	3.368
5000	- 11.872	160.119	165.119	21.444	39.896	39.896	4.105
5100	- 14.412	161.619	166.619	21.944	40.394	40.394	4.900
5200	- 16.852	163.119	168.119	22.444	40.897	40.897	5.753
5300	- 19.192	164.619	169.619	22.944	41.405	41.405	6.665
5400	- 21.432	166.119	171.119	23.444	41.918	41.918	7.638
5500	- 23.572	167.619	172.619	23.944	42.436	42.436	8.672
5600	- 25.612	169.119	174.119	24.444	42.959	42.959	9.768
5700	- 27.552	170.619	175.619	24.944	43.487	43.487	10.928
5800	- 29.392	172.119	177.119	25.444	44.020	44.020	12.153
5900	- 31.132	173.619	178.619	25.944	44.558	44.558	13.445
6000	- 32.772	175.119	180.119	26.444	45.101	45.101	14.805

Sept. 30, 1965

Point Group [D_{oh}]
S_{298.15} = [83.5] gibbs/mol
ΔH_f^o = [21.4 ± 3] kcal/mol
ΔH_f^o_{298.15} = [21.0 ± 3] kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	[10]
[4200]	[10]
[6800]	[5]

Vibrational Frequencies and Degeneracies

ω _i , cm ⁻¹	
[140] (1)	
[32] (2)	
[280] (1)	

Bond Distance: Fe - I = [2.43] Å

Bond Angle: I - Fe - I = [180]°

Rotational Constant: B₀ = [0.0124] cm⁻¹

σ = 2

Heat of Formation

The chemical equilibria for the reactions: (A) FeI₂(g) = FeI₂(g), (B) FeI₂(1) = FeI₂(g), and (C) Fe(c) + 2I(g) = FeI₂(g), have been studied by several investigators. Based on the equilibrium pressures reported, the corresponding enthalpy changes were evaluated by both the second and third law methods. The results obtained are presented in the table below. Using the third law ΔH_{298.15} values, the heats of formation for FeI₂(g) were calculated. The adopted value for ΔH_{298.15}(FeI₂, g) is 21.0 ± 3 kcal/mol. The disagreement between the acts of second and third law ΔH_{298.15} values listed in the table may be due to the presence of dimer, Fe₂I₄(g), which was not accounted for in deriving the partial pressure of FeI₂(g). The data obtained from Schoonmaker et al. was adjusted for the presence of dimer.

Investigator	Reaction	Temperature, °K	Method	Second Law Value	Third Law Value	Drift kcal/mol
Schäfer and Hones ¹	(A)	790.15 - 850.15	Transpiration	41.61	46.58	+ 5.78
	(B)	874.15 - 959.15	Transpiration	43.56	35.58	- 8.75
Schoonmaker et al. ²	(A)	714	Mass Spectrometric	-	46.78	- 21.78
Sine and Gregory ³	(A)	670.0 - 740.0	Torsion - Effusion	45.13	45.70	0.85
Zaugg and Gregory ⁴	(C)	865.15 - 1023.15	Transpiration	-32.53	-28.99	3.75
						22.1

¹The vapor pressure data used for evaluation were those adjusted by V. E. Zaugg and N. W. Gregory, J. Phys. Chem. **70**, 490 (1966).

²H. Schäfer and W. J. Hones, Z. Anorg. Allgem. Chem. **286**, 82 (1956).

³R. C. Schoonmaker, A. H. Friedman and P. R. Porter, J. Chem. Phys. **31**, 1586 (1959).

⁴R. J. Sine and N. W. Gregory, J. Phys. Chem. **64**, 86 (1960). The vapor pressure equation used for calculation is log P_{mm} = -(9760/T) + 11.82. In the original paper, the term A = 960 should be 9760.

⁵W. E. Zaugg and N. W. Gregory, J. Phys. Chem. **70**, 490 (1966).

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The Fe-I bond distance was estimated by L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **53**, 111 (1963). The vibrational frequencies were estimated so that the derived Gibbs energy functions yielded second and third law ΔH_{298.15} values in reasonable agreement (see the above table). The electronic levels and quantum weights were estimated from those for FeI₂(g) reported by C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966). The moment of inertia is 2.4884 x 10⁻³⁷ g cm².

FeI₂

Wustite (Fe_{0.947}O)
(Crystal)

Mol. Wt. = 68.88651

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	5.577	2.938	23.548	-2.262	-63.846	INFINITE
200	10.577	3.719	14.793	-2.061	-62.178	135.884
298	11.500	4.764	13.764	-1.005	-60.289	65.888
300	11.516	13.835	13.764	-0.021	-58.595	42.949
400	12.041	17.224	14.223	1.201	-58.564	42.662
500	12.392	19.950	15.104	2.423	-56.608	31.092
600	12.674	22.235	16.107	3.476	-55.309	24.174
700	12.923	24.207	17.127	4.946	-53.752	19.378
800	13.155	25.948	18.123	6.260	-50.710	15.404
900	13.377	27.510	19.080	7.587	-49.201	11.947
1000	13.593	28.931	19.996	8.936	-47.666	10.421
1100	13.805	30.237	20.868	10.305	-46.160	9.167
1200	14.013	31.447	21.700	11.606	-44.683	8.119
1300	14.220	32.577	22.493	13.108	-43.017	7.233
1400	14.426	33.638	23.252	14.540	-41.470	6.473
1500	14.630	34.640	23.978	15.993	-39.938	5.819
1600	14.834	35.591	24.674	17.466	-38.421	5.248
1700	15.036	36.500	25.344	18.960	-36.921	4.745
1800	15.130	37.357	25.987	20.466	-35.439	4.285
1900	15.224	38.178	26.607	21.984	-33.971	3.878
2000	15.300	38.961	27.206	23.510	-32.032	3.500
2100	15.353	39.700	27.783	25.043	-30.343	3.158
2200	15.400	40.424	28.342	26.581	-28.847	2.847
2300	15.440	41.109	28.882	28.123	-26.978	2.568
2400	15.473	41.767	29.405	29.669	-25.301	2.304
2500	15.500	42.399	29.912	31.217	-23.425	2.065

June 30, 1965

WUSTITE (Fe_{0.947}O)

(CRYSTAL)

MOL. WT. = 68.88651

$$\Delta H_f^0 = -63.65 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -63.64 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 7.49 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 13.764 \pm 0.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1650^\circ\text{K.}$$

Heat of Formation.

The chemical equilibria in the Fe-C-O and Fe-H-O systems have been studied by many investigators. Using the reported equilibrium constants for the following two reactions (1) $\text{Fe}_0.947\text{O}(c) + \text{CO}(g) = 0.947\text{Fe}(c) + \text{CO}_2(g)$ and (2) $\text{Fe}_0.947\text{O}(c,1) + \text{H}_2(g) = 0.947\text{Fe}(c) + \text{H}_2\text{O}(g)$, the corresponding enthalpy changes (ΔH_f^0) were evaluated by both the second and third law methods. Based on the third law values for ΔH_f^0 , the ΔH_f^0 298.15 (Wüstite, c) values were also calculated. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	ΔH_f^0 298.15 kcal. mole ⁻¹
Eastman ¹	(1)	873.2-1273.2	-3.80 ± 0.01	-4.01	-63.63
Eastman - Evans ²	(1)	873.2-1273.2	-4.02 ± 0.01	-4.03	-63.61
Eastman ¹	(2)	873.2-1273.2	6.50 ± 0.12	5.90	-65.70
Eastman - Evans ²	(2)	873.2-1273.2	5.81 ± 0.01	5.07	-62.86
Emmett - Schultz ³	(2)	873.2-1273.2	5.95 ± 0.07	5.82	-63.62
Britzke et al. ⁴	(2)	1123.2-1498.2	-2.25 ± 0.03	4.26	-62.06
Joninry - Murphy ⁵	(2)	1360.0-1646.0	5.01 ± 0.61	6.01	-65.81
Chipman - Marshall ⁶	(2)	1438.2-1635.2	5.03 ± 0.34	5.85	-62.83
Joninry - Murphy ⁵	(2)	1653.2-1787.2	-2.61 ± 0.77	-0.02	-61.87
Britzke et al. ⁴	(3)	1698.0-1700.0	—	0.87	-62.72
		1123.0-1473.0	-129.08 ± 0.18	-126.28	-65.14

¹ E. D. Eastman, *J. Am. Chem. Soc.* **44**, 975 (1922).

² E. D. Eastman and R. M. Evans, *J. Am. Chem. Soc.* **46**, 888 (1924). The K_p value at 1273.2°K. for reaction (1) is rejected by a statistical criterion.

³ P. H. Emmett and J. F. Schultz, *J. Am. Chem. Soc.* **52**, 4268 (1930).

⁴ E. V. Britzke, A. F. Kapustinsky and N. I. Schastkina, *Z. anorg. allgem. Chem.* **219**, 287 (1934). The K_p value at 1123°K. for reaction (3) is rejected by a statistical criterion.

⁵ W. E. Joninry and D. W. Murphy, *Ind. Eng. Chem.* **23**, 384 (1931). The K_p values at 1530 and 1645°K. are rejected by a statistical criterion.

⁶ J. Chipman and S. Marshall, *J. Am. Chem. Soc.* **62**, 299 (1940).

Britzke et al. also determined the equilibrium pressures for the reaction (3) $1.894 \text{ Fe}(c) + \text{O}_2(g) = 2\text{Fe}_0.947 \text{O}(c)$. The corresponding ΔH_f^0 298.15 for Wüstite was evaluated based on the third law value for ΔH_f^0 298.15. The adopted value of ΔH_f^0 298.15 (Wüstite, c) is the weighted average of the ΔH_f^0 298.15 listed in the above table.

Heat Capacity and Entropy.

The low temperature (54.37-298.16°K.) heat capacities (C_p) were measured by S. S. Todd and K. R. Bonnickson, *J. Am. Chem. Soc.* **73**, 3894 (1951). The high temperature (298-1650°K.) heat capacities were determined by J. P. Coughlin, E. G. King and K. R. Bonnickson, *J. Am. Chem. Soc.* **73**, 3891 (1951). The two sets of C_p data were plotted and joined smoothly at 298°K. The C_p values above 1650°K. were obtained by graphical extrapolation. The low temperature (70.7-279.8°K.) C_p 's were also reported by R. W. Millar, *J. Am. Chem. Soc.* **51**, 215 (1929). $S_{298.15}^0$ was derived from the low temperature heat capacities, based on $S_{52}^0 = 0.696 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, S. S. Todd and K. R. Bonnickson, loc. cit. added 0.41 e.u., the amount calculated for completely random distribution of the vacant Fe spaces in the Wüstite lattice. However, the free energy functions derived from $S_{52}^0 = 0.696 \text{ e.u.}$ give better agreement between second and third law values for ΔH_f^0 than those derived from $S_{52}^0 = 1.11 \text{ e.u.}$ Therefore the value 0.41 e.u. was not added here.

Melting Data.

T_m and ΔH_m^0 were taken from J. P. Coughlin, E. G. King and K. R. Bonnickson, et al. T_m was reported as 1372°C. (1645°K.) by L. S. Darken and R. W. Durr, *J. Am. Chem. Soc.* **68**, 798 (1946) and as 1569°C. (1642°K.) by J. Chipman and S. Marshall, loc. cit.

Fe_{0.947}O

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100						
200						
298	11.930	14.520	0.000	65.020	60.097	44.050
300	11.950	14.594	0.022	65.015	60.067	43.757
400	12.390	18.094	1.240	64.779	58.454	31.936
500	12.760	20.898	2.467	64.562	56.897	24.868
600	13.120	23.257	3.762	64.375	55.382	20.172
700	13.420	25.103	5.119	64.226	53.896	16.826
800	13.680	26.510	6.548	64.107	52.447	14.172
900	13.930	27.640	8.041	64.013	50.964	12.375
1000	14.190	30.222	10.599	64.003	49.495	10.817
1100	14.366	31.984	12.663	64.068	47.991	9.535
1200	14.500	32.825	14.277	64.005	46.494	8.464
1300	14.600	33.127	15.483	64.000	44.994	7.583
1400	14.680	33.239	16.319	64.366	43.453	6.783
1500	14.751	36.167	25.093	64.167	41.968	6.114
1600	15.200	37.150	25.616	63.932	40.496	5.531
1700	15.449	38.082	26.510	64.010	39.033	5.018
1800	15.520	38.608	27.278	64.000	37.584	4.568
1900	15.720	39.819	27.821	67.642	36.021	4.132
2000	15.850	40.625	28.441	67.380	34.266	3.744

June 30, 1965

FeO

$S_{298.15}^o = [14.52] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = \text{Unknown}$
 $\Delta H_f^o 298.15 = [-65.02] \text{ kcal. mole}^{-1}$
 $\Delta H_m^o = [5.75] \text{ kcal. mole}^{-1}$
 $\Delta H_g^o 298.15 = [121.62] \text{ kcal. mole}^{-1}$
 $T_m = [1650]^{\circ}\text{K.}$

Heat of Formation.

The value of $\Delta H_f^o 298.15$ for FeO(c) was derived based on an assumption that at 1650°K., $\Delta H_f^o(\text{FeO, c}) = \Delta H_f^o(\text{FeO, l})$. From the value $\Delta H_f^o 1650(\text{FeO, c}) = -59.77 \text{ kcal. mole}^{-1}$, $\Delta H_f^o 1650(\text{FeO, c})$ was calculated to be $-63.97 \text{ kcal. mole}^{-1}$, yielding $\Delta H_f^o 298.15(\text{FeO, c}) = -65.02 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The C_p values were estimated assuming $C_p(\text{FeO, c}) = C_p(\text{Wüstite, c}) + 0.053 C_p(\text{Fe, c})$. The C_p values obtained were plotted. The adopted C_p points were taken from the smoothed C_p curve. $S_{298.15}^o$ for FeO(c) was calculated as $S^o(\text{FeO, c}) = S^o(\text{Wüstite, c}) + 0.053 S^o(\text{Fe, c}) + \Delta S^o(\text{mixing})$ where ΔS^o is the entropy of mixing (0.41 cal. deg.⁻¹ mole⁻¹).

Melting Data.

T_m is assumed to be the same as that for Wüstite. The difference between $\Delta H_f^o 1650$ for FeO(l) and FeO(c) is ΔH_m^o .

Heat of Sublimation.

$\Delta H_g^o 298.15$ is calculated as the difference between $\Delta H_f^o 298.15$ for FeO(g) and FeO(c).

Iron Oxide (FeO)

Mol. Wt. = 71.8464

FeO

IRON OXIDE (FeO) (LIQUID)

MOL. WT. = 71.8464

T, °K	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
0							
100							
200							
298	11.500	18.029	18.029	0.000	-59.642	-55.765	40.875
300	11.516	18.100	18.029	0.021	-59.638	-55.761	40.606
400	12.041	21.489	18.488	1.201	-59.440	-54.473	29.761
500	12.392	24.215	19.370	2.423	-59.259	-53.252	23.275
600	12.674	26.500	20.373	3.676	-59.113	-52.065	18.864
700	12.921	28.421	21.386	4.891	-59.001	-50.905	15.891
800	13.155	30.214	22.366	6.240	-58.924	-49.785	13.595
900	13.377	31.776	23.346	7.587	-58.874	-48.588	11.798
1000	13.593	33.196	24.261	8.936	-58.852	-47.418	10.363
1100	13.800	34.502	25.133	10.306	-58.856	-46.210	9.181
1200	14.000	35.725	25.960	11.596	-58.886	-45.062	8.251
1300	14.200	36.875	26.750	12.816	-58.946	-43.968	7.561
1400	14.400	37.958	27.509	13.966	-59.036	-42.922	7.009
1500	14.600	38.978	28.241	15.046	-59.156	-41.922	6.541
1600	14.800	39.941	28.956	16.056	-59.306	-40.966	6.146
1700	15.000	40.849	29.646	17.006	-59.486	-40.056	5.809
1800	15.200	41.709	30.316	17.906	-59.696	-39.186	5.521
1900	15.400	42.529	31.026	18.756	-59.936	-38.356	5.271
2000	15.600	43.309	31.776	19.556	-60.206	-37.566	5.051
2100	15.800	44.049	32.476	20.306	-60.506	-36.816	4.851
2200	16.000	44.749	33.156	21.006	-60.836	-36.106	4.671
2300	16.200	45.409	33.806	21.656	-61.196	-35.436	4.501
2400	16.400	46.029	34.426	22.256	-61.586	-34.806	4.341
2500	16.600	46.609	35.006	22.806	-62.006	-34.216	4.191
2600	16.800	47.149	35.546	23.306	-62.456	-33.666	4.051
2700	17.000	47.649	36.046	23.756	-62.936	-33.156	3.921
2800	17.200	48.109	36.506	24.156	-63.446	-32.686	3.801
2900	17.400	48.529	36.926	24.506	-63.986	-32.256	3.691
3000	17.600	48.909	37.306	24.806	-64.556	-31.866	3.591
3100	17.800	49.249	37.646	25.056	-65.156	-31.516	3.501
3200	18.000	49.549	37.946	25.256	-65.786	-31.206	3.421
3300	18.200	49.809	38.206	25.406	-66.446	-30.936	3.351
3400	18.400	50.029	38.426	25.506	-67.136	-30.706	3.291
3500	18.600	50.209	38.606	25.556	-67.856	-30.516	3.241
3600	18.800	50.349	38.746	25.556	-68.606	-30.366	3.191
3700	19.000	50.449	38.846	25.506	-69.386	-30.256	3.151
3800	19.200	50.509	38.906	25.406	-70.196	-30.186	3.111
3900	19.400	50.529	38.926	25.256	-71.036	-30.156	3.071
4000	19.600	50.509	38.906	25.056	-71.906	-30.166	3.031
4100	19.800	50.449	38.846	24.806	-72.806	-30.216	3.001
4200	20.000	50.349	38.746	24.506	-73.736	-30.306	2.971
4300	20.200	50.209	38.606	24.156	-74.696	-30.436	2.941
4400	20.400	50.029	38.426	23.756	-75.686	-30.606	2.911
4500	20.600	49.809	38.206	23.306	-76.706	-30.816	2.881
4600	20.800	49.549	37.946	22.806	-77.756	-31.066	2.851
4700	21.000	49.249	37.646	22.256	-78.836	-31.356	2.821
4800	21.200	48.909	37.306	21.656	-79.946	-31.686	2.791
4900	21.400	48.529	36.926	21.006	-81.086	-32.056	2.761
5000	21.600	48.109	36.506	20.306	-82.256	-32.466	2.731

$S_{298.15}^{\circ} = 18.029$ cal. deg⁻¹ mole⁻¹
 $T_m = [1650]^{\circ}\text{K}$.
 $T_d = [3687]^{\circ}\text{K}$.

Heat of Formation.
 $\Delta H_f^{\circ} 298.15 = [-59.642]$ kcal. mole⁻¹
 $\Delta H_m^{\circ} = [5.75]$ kcal. mole⁻¹

The heat of formation ($\Delta H_f^{\circ} 298.15$) was evaluated based on an assumption that the heat of melting of wüstite, $\Delta H_m^{\circ} = 7.49$ kcal. mole⁻¹, represents the enthalpy change of the reaction $\text{FeO}_{0.947}(\text{c}) = 0.947 \text{FeO}(\text{l}) + \frac{0.053}{2} \text{O}_2(\text{g})$. In other words, during melting the wüstite releases $\text{O}_2(\text{g})$ and converts to $\text{FeO}(\text{l})$.

Heat Capacity and Entropy.

The enthalpy changes ($H_f^{\circ} - H_{298.15}^{\circ}$) of liquid iron oxide were determined by J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3591 (1951). The C_p (FeO , l) was derived as 16.3 cal. deg⁻¹ mole⁻¹. This value was adopted as the heat capacity for $\text{FeO}(\text{l})$ up to 4000°K. A glass transition temperature was assumed at 1100°K. $S_{298.15}^{\circ}$ (FeO , l) was calculated based on an assumption that the entropy of melting of wüstite represents also the entropy change of the reaction, $\text{FeO}_{0.947}(\text{c}) = 0.947 \text{FeO}(\text{l}) + \frac{0.053}{2} \text{O}_2(\text{g})$. From the entropy of melting, $\Delta S_m^{\circ} 1650 = 4.539$ e.u., the value $S_{298.15}^{\circ}$ (FeO , l) = 18.029 e.u. was derived.

Melting Data.

The melting point (T_m) for wüstite ($\text{FeO}_{0.947}$, c) has been reported by many investigators. However, the composition of the liquid state of wüstite was not identified. An assumption was made that during melting the reaction $\text{FeO}_{0.947}(\text{c}) = 0.947 \text{FeO}(\text{l}) + \frac{0.053}{2} \text{O}_2(\text{g})$ occurs. Hence the related thermodynamic properties were derived.

Decomposition Temperature.

T_d is the temperature at which ΔF_f° equals zero.

IRON OXIDE (FeO)

(IDEAL GAS)

GFW = 71.8464

Ground State Configuration [5s]
 $\Delta H_f^\circ = 80 \pm 5 \text{ kcal/mol}$ $S_{298.15}^\circ = [57.8] \text{ gibbs/mol}$
 $\Delta H_f^\circ = 80 \pm 5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ , cm ⁻¹	S_e
0	[10]
[10000]	[10]
[16000]	[5]

 $\omega_e x_e = 5.0 \text{ cm}^{-1}$
 $\sigma = 1$ $\omega_e = 880.0 \text{ cm}^{-1}$
 $\omega_e x_e = [0.00293] \text{ cm}^{-1}$
 $\tau_e = [1.8] \text{ \AA}$

Heat of Formation

The heat of formation for FeO(g) is not well established at the present time. The values of ΔH_f° (FeO, g) derived from the following reactions: (1) FeO(g) = Fe(g) + O(g), (2) FeO(g) = Fe(g) + 1/2 O₂(g), and (3) FeO(l) = FeO(g), are not in agreement. There are three D^o (Fe-O) values reported for reaction (1). The enthalpy change for reaction (2) was evaluated based on the partial pressure data ($P_{\text{FeO}}/P_{\text{Fe}} = 0.2$ at 1600°C, measured by Washburn⁴, using a mass spectrometric method, U. S. Atomic Energy Commission, UCRL-10991, August 1963, and $P_{\text{O}_2} = 1.66 \times 10^{-6}$ atm reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 796 (1946). The enthalpy value for reaction (3) was calculated based on the reported value, $\Delta H_f^\circ = 96.096 \text{ kcal/mol}$ determined by Burtsev, Karasev and Samarin⁵. The results obtained are presented as follows. The value of ΔH_f° for FeO(g) adopted is $80 \pm 5 \text{ kcal/mol}$.

Investigator	Reaction	Method	ΔH_f° , kcal/mol	ΔH_f° , kcal/mol
1. Herzberg (1950)	(1)	Spectroscopic	111.9	47.2
2. Gaydon (1953)	(1)	Spectroscopic	93.4 ± 23.1	65.7 ± 23.1
3. Lagerqvist and Huldt (1953)	(1)	Spectroscopic	99.0 ± 11.6	80.1 ± 11.6
4. Washburn et al. (1963)	(2)	Spectroscopic	99.3 ± 5	59.8 ± 5
5. Burtsev et al. (1964)	(3)	transpiration	111.8	52.2

1. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950.

2. A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

3. A. Lagerqvist and L. Huldt, Z. Naturforsch. 8d, 483 (1953). D^o was derived from atomic spectra of Fe produced by acetylene-air flame method.

4. J. Washburn, UCRL 10991, August 1963, obtained from L. Brewer, private communication, October 18, 1966.

5. V. T. Burtsev, R. A. Karasev and A. M. Samarin, Fiz.-Khim. Osnovy Proizv. Stal', Akad. Nauk SSSR, Inst. Met., Tr. 5-01 (Shestol) Konf., Moscow, 366 (1961); published in 1964.

Heat Capacity and Entropy

Since the ground state configuration is due to Fe⁺⁺ in a ligand field, it was assumed to be the same as that of FeCl₂(g) reported by C. W. Decock and D. M. Gruen, J. Chem. Phys. 44, 4387 (1966). The electronic levels and quantum weights were estimated by comparison with those of FeCl₂(g). The values of ω_e and $\omega_e x_e$ were taken from G. Herzberg, loc. cit. The bond distance was calculated according to the method suggested by K. M. Osgood, Proc. Phys. Soc. (London) 86, 456 (1966), assuming FeO(g) as a polar molecule. The value of B_e was calculated by use of the relationship: $B_e = (2.79976 \times 10^{-39}) / I$ where I is the moment of inertia of FeO(g). The value of α_e was derived from ω_e , $\omega_e x_e$ and B_e by the method suggested by G. Herzberg, loc. cit. The principal moment of inertia is $6.6899 \times 10^{-39} \text{ g cm}^2$.

June 30, 1965; Sept. 30, 1966



Iron Sulfate (FeSO₄)

(Crystal)

GFW = 151.9086

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.000	0.000	INFINITE	-	-219.730	-219.730	INFINITE
100	10.534	10.223	46.561	3.634	-221.011	-213.311	466.191
200	18.845	20.319	30.966	2.429	-221.713	-205.305	224.347
298	24.040	28.909	28.909	0.000	-222.000	-197.176	144.534
300	24.140	29.038	28.910	0.015	-222.002	-197.022	143.531
400	30.810	36.596	20.904	2.652	-222.542	-188.668	103.083
500	30.810	43.085	31.698	5.593	-222.676	-180.178	78.756
600	32.990	48.904	34.257	8.788	-222.378	-171.685	62.536
700	34.570	54.113	36.728	12.170	-222.313	-165.037	52.222
800	35.510	58.664	38.618	15.299	-222.443	-158.665	42.627
900	36.160	62.693	41.618	19.299	-222.543	-152.615	35.498
1000	37.160	66.943	43.960	22.963	-222.611	-146.392	29.808
1100	37.710	70.511	46.213	26.727	-222.663	-140.629	25.159
1200	38.200	73.813	48.377	30.523	-222.700	-135.226	21.022
1300	38.640	76.964	50.464	34.250	-222.726	-130.235	18.028
1400	39.040	79.979	52.464	38.250	-222.743	-125.631	15.241
1500	39.420	82.873	54.356	42.173	-222.759	-121.391	12.835
1600	39.780	85.629	56.136	46.133	-222.770	-117.498	10.737
1700	40.120	87.451	57.804	50.159	-222.776	-113.923	9.025
1800	40.440	89.219	59.369	54.259	-222.778	-110.643	7.629
1900	40.780	91.020	61.308	58.219	-222.778	-107.643	6.482
2000	41.100	92.850	62.893	62.313	-222.778	-104.943	5.542

IRON SULFATE (FeSO₄)

(CRYSTAL)

GFW = 151.9086

$\Delta H^\circ_0 = -219.7 \pm 2 \text{ kcal/mol}$
 $\Delta H^\circ_{298.15} = -222.0 \pm 2 \text{ kcal/mol}$
 $S^\circ_{298.15} = 28.91 \pm 0.3 \text{ gibbs/mol}$
 $T_d = 944^\circ\text{K}$

Heat of Formation.

The enthalpy change for the reaction $\text{FeSO}_4(c) = \text{FeSO}_4(110 \text{ H}_2\text{O})$ was determined to be -14.9 kcal/mol by R. de Forcrand, Comp. rend. 158, 20 (1914). Using $\Delta H^\circ_{298.85} = -235.85 \text{ kcal/mol}$ for $\text{FeSO}_4(110 \text{ H}_2\text{O})$, the heat of formation (298.15°K) for $\text{FeSO}_4(c)$ was calculated as -221 kcal/mol . The value of $\Delta H^\circ_{298.15}(\text{FeSO}_4, c)$ was estimated based on $\Delta H^\circ_{298.15} = 235.9 \text{ kcal/mol}$ for $\text{FeSO}_4(200 \text{ H}_2\text{O})$ and $2\text{HCl}(100 \text{ H}_2\text{O})$ which was derived from the enthalpy change for the reaction $\text{FeCl}_2(200 \text{ H}_2\text{O}) + \text{H}_2\text{SO}_4(200 \text{ H}_2\text{O}) = \text{FeSO}_4(200 \text{ H}_2\text{O}) + 2\text{HCl}(100 \text{ H}_2\text{O})$ measured by J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882-1886. See the $\text{Fe}(\text{OH})_2(c)$ table for details.

The decomposition pressures of $\text{FeSO}_4(c)$ at different temperatures were investigated by J. D'Ans and E. Greulich. Using their reported partial pressures for $\text{SO}_3(g)$ and $\text{SO}_2(g)$, the enthalpy change for the reaction $2 \text{FeSO}_4(c) = \text{Fe}_2\text{O}_3(c) + \text{SO}_3(g) + \text{SO}_2(g)$ was evaluated by both the second and third law methods. The results obtained are presented in the following table.

Investigator	Temperature, °K	Second Law Value	Third Law Value	$\Delta H^\circ_{298.15}$ kcal/mol
1. J. D'Ans (1905)	753.15 - 908.15	83.2 ± 4.6	82.7 ± 1.1	-222.7
2. E. Greulich (1927)	887.15 - 971.15	84.8 ± 8.8	80.1 ± 1.4	-221.5
3. B. Neumann and G. Heintke (1937)	835.15 - 862.15	72.4 ± 5.4	75.3 ± 0.5	-219.1

1. J. D'Ans, Dissertation, Darmstadt, 1905. Data quoted by B. Neumann and G. Heintke, loc. cit.
2. E. Greulich, Z. anorg. Chem. 169, 197 (1927). Only the last seven high temperature points were adopted for evaluation.
3. B. Neumann and G. Heintke, Z. Elektrochem. 43, 246 (1937), based on the last 18 high temperature points adopted.

The decomposition pressures assumed for the same reaction have been determined by B. Neumann and G. Heintke. From their data the partial pressures for $\text{SO}_3(g)$ and $\text{SO}_2(g)$ were evaluated. Using the derived $\text{SO}_3(g)$ and $\text{SO}_2(g)$ partial pressures, the corresponding enthalpy changes for the reaction were calculated by both the second and third law methods. The results obtained are also listed in the same table.

The value of $\Delta H^\circ_{298.15}$ for $\text{FeSO}_4(c)$ is selected as $-222 \pm 2 \text{ kcal/mol}$.

Heat Capacity and Entropy.

The low temperature heat capacities, $53.0-294.9^\circ\text{K}$, were determined by O. E. Moore and K. K. Kelley, J. Am. Chem. Soc., 64, 2949 (1942). Based on $S^\circ_{50.12} = 2.10 \text{ eu}$, the value of $S^\circ_{298.15}(\text{FeSO}_4, c)$ was reported to be $25.71 \pm 0.2 \text{ eu}$. Using the free energy functions for $\text{FeSO}_4(c)$ based on this $S^\circ_{298.15}$ value, to evaluate the vapor pressure data for Reaction (1), the second and third law values of $\Delta H^\circ_{298.15}$ were derived as 72.36 ± 7.60 and $86.51 \pm 1.26 \text{ kcal/mol}$, respectively. Since the report by Moore and Kelley, loc. cit., did not mention the magnetic entropy contribution, an attempt was made to add $3.20 (= R \ln 5)$ eu to $S^\circ_{298.15}(\text{FeSO}_4, c)$ and re-evaluate the decomposition pressure data. The results obtained were better than before (see the paragraph on "Heat of Formation," for details). Therefore the value, $S^\circ_{298.15} = 25.71 + 3.2 = 28.91 \text{ eu}$ for $\text{FeSO}_4(c)$, was adopted. The heat capacities above 294.9°K were estimated by comparison with those for $\text{MnSO}_4(c)$. The high temperature heat capacities, $870.3-1082.3^\circ\text{K}$, were determined by J. C. Southard and C. H. Shomate, J. Am. Chem. Soc. 64, 1770 (1942). The two sets of data were joined smoothly at 298.15°K by use of Shomate-function plot.

Temperature of Decomposition.

T_d is the temperature at which the vapor pressure of the gaseous decomposition products equals one atmosphere, which was obtained by graphical interpolation of the decomposition pressure data on $\text{FeSO}_4(c)$, reported by E. Greulich, loc. cit.



Iron Dioxide, Dimeric (Fe_2I_4)
(Ideal Gas) GFW = 619.3116

IRON DIOXIDE, DIMERIC (Fe_2I_4) (IDEAL GAS) OPW = 619.3116 Fe_2I_4

T, °K	Cp ^a	S ^b	gibbs/mol -(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	8.133	2.325	2.325	INFINITE
100	28.554	96.669	157.341	6.067	2.727	- 3.731	8.154
200	30.887	117.422	132.723	3.060	2.534	- 10.151	11.093
298	31.577	129.865	129.865	.000	2.000	- 16.274	11.929
300	31.382	130.059	129.865	.058	1.988	- 16.387	11.938
400	31.561	139.115	131.099	3.206	6.460	- 22.134	12.083
500	31.666	146.168	133.433	6.367	27.695	- 24.034	10.505
600	31.699	151.042	136.051	9.595	27.781	- 23.297	8.486
700	31.744	156.832	138.680	12.707	27.985	- 22.535	6.936
800	31.797	161.074	141.220	15.884	28.346	- 21.734	5.637
900	31.861	164.823	143.638	19.066	28.924	- 20.875	5.069
1000	31.939	168.184	145.927	22.256	29.858	- 19.936	4.457
1100	32.029	171.232	148.091	25.455	31.223	- 18.868	3.749
1200	32.129	174.023	150.138	28.663	32.159	- 17.715	3.226
1300	32.235	176.599	152.075	31.881	32.405	- 16.500	2.774
1400	32.343	178.992	153.914	35.110	32.678	- 15.265	2.383
1500	32.450	181.227	155.661	38.349	32.971	- 14.015	2.042
1600	32.554	183.325	157.325	41.600	33.285	- 12.738	1.740
1700	32.653	185.301	158.913	44.860	33.628	- 11.433	1.470
1800	32.744	187.170	160.431	48.130	34.000	- 10.076	1.223
1900	32.826	188.944	161.886	51.408	34.400	- 8.731	.957
2000	32.900	190.628	163.281	54.695	34.833	- 7.401	.710
2100	32.964	192.235	164.627	57.998	35.300	- 6.097	.483
2200	33.019	193.770	165.912	61.287	35.800	- 4.837	.273
2300	33.065	195.239	167.156	64.556	36.333	- 3.620	.079
2400	33.102	196.647	168.355	67.800	36.900	- 2.442	.012
2500	33.131	197.999	169.514	71.021	37.500	- 1.301	.000
2600	33.152	199.299	170.635	74.226	38.133	- .205	.000
2700	33.167	200.550	171.720	77.400	38.800	7.140	.578
2800	33.175	201.756	172.771	80.550	39.500	11.250	.851
2900	33.178	202.921	173.791	83.677	40.233	15.400	.976
3000	33.176	204.045	174.781	86.784	41.000	19.600	1.056
3100	33.169	205.133	175.742	89.870	41.800	23.833	1.096
3200	33.159	206.186	176.672	92.938	42.633	28.100	1.096
3300	33.146	207.206	177.587	95.980	43.500	32.400	1.056
3400	33.130	208.195	178.473	98.997	44.400	36.733	1.000
3500	33.112	209.156	179.336	101.957	45.333	41.100	.928
3600	33.092	210.088	180.177	104.869	46.300	45.533	.851
3700	33.068	210.994	181.000	107.720	47.300	50.000	.773
3800	33.048	211.876	181.799	110.520	48.333	54.500	.696
3900	33.024	212.734	182.581	113.267	49.400	59.033	.620
4000	33.000	213.570	183.345	116.000	50.500	63.600	.543
4100	32.975	214.385	184.093	118.720	51.633	68.200	.466
4200	32.950	215.176	184.820	121.430	52.800	72.833	.389
4300	32.925	215.954	185.538	124.120	54.000	77.500	.312
4400	32.900	216.711	186.238	126.800	55.233	82.200	.235
4500	32.874	217.450	186.924	129.467	56.500	86.933	.158
4600	32.849	218.172	187.595	132.120	57.800	91.700	.081
4700	32.824	218.876	188.250	134.760	59.133	96.500	.004
4800	32.800	219.569	188.890	137.380	60.500	101.333	.000
4900	32.776	220.245	189.531	140.000	61.900	106.200	.000
5000	32.752	220.907	190.152	142.600	63.333	111.100	.000
5100	32.729	221.555	190.762	145.180	64.800	116.033	.000
5200	32.704	222.193	191.356	147.750	66.300	121.000	.000
5300	32.680	222.813	191.936	150.300	67.833	126.000	.000
5400	32.656	223.424	192.525	152.830	69.400	131.033	.000
5500	32.631	224.023	193.092	155.350	71.000	136.100	.000
5600	32.606	224.611	193.650	157.860	72.633	141.200	.000
5700	32.581	225.186	194.196	160.350	74.300	146.333	.000
5800	32.556	225.755	194.727	162.830	76.000	151.500	.000
5900	32.531	226.312	195.258	165.290	77.733	156.700	.000
6000	32.506	226.859	195.790	167.740	79.500	162.000	.000

Sept. 30, 1966

Point Group [D_{2h}]
 $S_{298.15}^\circ = 129.9 \text{ gibbs/mol}$
 $\Delta H_f^\circ = 2.3 \pm 5 \text{ kcal/mol}$
 $\Delta H_f^\circ = 2.3 \pm 5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

ϵ, cm^{-1}	g_i
0	[5]
[4200]	[5]
[6800]	[5]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}	ω, cm^{-1}
[100] (1)	[70] (1)	[80] (2)
[50] (1)	[90] (1)	[20] (2)
[95] (1)	[105] (1)	[160] (2)

Bond Distance: Fe - I = [2.43] Å

Bond Angle: I - Fe - I_{bridge} = [135]°

I_{bridge} - Fe - I_{bridge} = [90]°

Product of the Moments of Inertia: $I_A I_B I_C = 8.7771 \times 10^{-110} \text{ kg}^3 \text{ cm}^6$

Heat of Formation.

The chemical equilibrium of the interaction of Fe(c) and I(g) has been studied by a transpiration method by W. E. Zaugg and N. W. Gregory, J. Phys. Chem. **70**, 490 (1966). Using the reported equilibrium constants in the temperature range from 591 to 751°K, the enthalpy change ($\Delta H_{298.15}^\circ$) of the reaction $2\text{Fe}(c) + 4 \text{I}(g) = \text{Fe}_2\text{I}_4(g)$ was evaluated by both the second and third law method to be -85.3 and -103.75 kcal/mol, respectively. The corresponding values of the heat of formation ($\Delta H_{298.15}^\circ$) for $\text{Fe}_2\text{I}_4(g)$ were calculated as +16.9 and -1.6 kcal/mol.

Mass spectrometric and Knudsen effusion techniques have been used to study the vaporization of $\text{FeI}_2(c)$ by R. C. Schoonmaker, A. H. Friedman and R. P. Porter, J. Chem. Phys. **31**, 1988 (1959). Using the reported vapor pressure, $P = 1.21 \times 10^{-6}$ atm. at 714°K for $\text{Fe}_2\text{I}_4(g)$, the enthalpy change ($\Delta H_{298.15}^\circ$) for the reaction $2 \text{FeI}_2(c) = \text{Fe}_2\text{I}_4(g)$ was evaluated by the third law method as 52.8 kcal/mol, yielding $\Delta H_{298.15}^\circ = 2.8$ kcal/mol for $\text{Fe}_2\text{I}_4(g)$.

The adopted value of $\Delta H_{298.15}^\circ$ for $\text{Fe}_2\text{I}_4(g)$ is 2.0 ± 5 kcal/mol.

Heat Capacity and Entropy.

The molecular structure was assumed to be the same as that assumed for $\text{Fe}_2\text{Br}_4(g)$. The Fe-I bond distance was estimated from that in $\text{FeI}_2(g)$ molecule. Four vibrational frequencies (ν_i), i.e. 1 = 2, 4, 5 and 6, were estimated by comparison with those for $\text{K}_2\text{I}_2(g)$, calculated by J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960). The other frequency values were estimated from those for $\text{FeI}_2(g)$. The electronic levels and quantum weights were estimated from those for $\text{FeI}_2(g)$. The three principal moments of inertia are: $I_A = 1.2442 \times 10^{-57}$, $I_B = 7.7996 \times 10^{-57}$ and $I_C = 9.0439 \times 10^{-57} \text{ g cm}^2$.

Fe_2I_4

Hematite (Fe₂O₃)

(Crystal) Mol. Wt. = 159.6922

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	7.528	3.492	38.192	3.719	-195.757	-195.757	INFINITE
200	18.300	12.256	22.976	3.470	-196.783	-196.783	416.560
298	24.800	20.889	20.889	2.144	-197.321	-184.182	201.255
300	24.900	21.043	20.889	∞	-197.300	-177.719	130.265
400	28.710	28.752	21.015	2.735	-197.296	-171.598	129.374
500	31.500	35.469	23.968	5.750	-196.925	-171.081	93.470
600	33.740	41.413	26.390	9.014	-196.356	-164.681	71.979
700	35.750	46.753	28.410	12.504	-195.685	-158.409	57.697
800	37.615	51.679	31.446	16.171	-194.904	-152.203	46.553
900	39.792	56.248	33.968	20.051	-194.099	-146.248	34.055
1000	36.000	60.440	36.415	24.025	-193.079	-134.363	29.364
1100	33.652	63.760	38.795	27.505	-193.608	-128.461	25.522
1200	31.998	69.409	43.098	34.270	-192.872	-122.240	22.316
1300	31.998	69.409	43.098	34.270	-192.872	-116.728	19.285
1400	34.174	71.935	45.022	37.578	-192.938	-110.728	17.279
1500	34.350	74.299	46.866	41.105	-192.524	-104.672	15.279
1600	34.552	76.522	48.679	44.550	-192.132	-99.040	13.528
1700	34.762	78.611	50.376	47.902	-191.767	-93.566	12.084
1800	34.950	82.457	53.559	54.982	-191.385	-88.208	10.341
1900	35.083	84.263	55.051	58.484	-190.946	-81.208	9.341
2000	35.200	85.008	56.485	61.998	-190.309	-74.994	8.195
2100	35.300	87.048	59.525	65.523	-189.309	-68.773	7.157
2200	35.383	89.219	59.194	69.058	-189.255	-62.755	6.354
2300	35.450	90.726	60.477	72.599	-189.241	-56.748	5.354
2400	35.500	92.175	61.716	76.147	-189.237	-50.133	4.565
2500					-189.237	-43.922	3.899

HEMATITE (Fe₂O₃) (CRYSTAL)Fe₂O₃

MOL. WT. = 159.6922

$$\Delta H_f^{\circ} 0 = -195.8 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -197.3 \pm 0.3 \text{ kcal. mole}^{-1}$$

$$S^{\circ} 298.15 = 20.889 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_d = 1755^{\circ}\text{K.}$$

Heat of Formation.

The chemical equilibria for the reaction $4\text{Fe}_2\text{O}_3(\text{c}) + \text{O}_2(\text{g}) = 6\text{Fe}_2\text{O}_3(\text{c})$ have been studied by several investigators. From the reported data the corresponding values of $\Delta H_f^{\circ} 298.15$ and $\Delta H_f^{\circ} 298.15$ (Fe_2O_3 , c) were evaluated. The results obtained are given as follows.

Investigator	Temperature, °K.	Second Law Value	Third Law Value	$\Delta H_f^{\circ} 298.15^{\circ}$ kcal. mole ⁻¹
Tretyskov and Khomyakov ¹	1373-1728	-106.32 ± 0.19	-111.05	-197.11
Schmahl ²	1583-1683	-123.95 ± 1.37	-112.94	-197.42
Smitten ³	1373-1673	-117.68 ± 0.38	-114.25	-197.64
Darkey and Gurry ⁴	1725	-110.29	—	-196.98

*Calculation based on the third law values for $\Delta H_f^{\circ} 298.15$.

1 Y.D. Tretyskov and K. G. Khomyakov, Russ. J. Inorg. Chem. **7**, 628 (1962).

2 N. G. Schmahl, Z. Elektrochem. **47**, 821 (1941).

3 J. Smitten, J. Am. Chem. Soc. **79**, 4877 (1957).

4 L. S. Darkey and R. W. Gurry, J. Am. Chem. Soc. **68**, 799 (1946). $\Delta H_f^{\circ} 298.15$ was calculated based on $\Delta H_f^{\circ} 1725 = -54.5 \text{ kcal. mole}^{-1}$.

The value of $\Delta H_f^{\circ} 298.15$ adopted for $\text{Fe}_2\text{O}_3(\text{c})$ is the weighted average of the $\Delta H_f^{\circ} 298.15$ values listed in the above table.

Heat Capacity and Entropy.

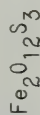
The low temperature (5.58-345.42°K.) heat capacities were determined by P. Gronvold and E. P. Westrum, Jr., J. Am. Chem. Soc. **81**, 1780 (1959). The high temperature (298-1750°K.) C_p values were obtained from J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. **73**, 3891 (1951). The two sets of data were plotted and joined smoothly at 298°K. The C_p values above 1750°K. were obtained by graphical extrapolation. The heat capacities of $\text{Fe}_2\text{O}_3(\text{c})$ have also been reported by G. G. Brown and C. C. Furnas, Trans. Am. Inst. Chem. Eng. **18**, 309 (1926), 0-650°K., and G. S. Parks and K. K. Kelley, J. Phys. Chem. **50**, 47 (1946), 96-289°K. $S^{\circ} 298.15$ for $\text{Fe}_2\text{O}_3(\text{c})$ was derived from the smoothed C_p data, based on $S^{\circ} = 0.0003 \text{ e.u.}$ J. P. Coughlin, E. G. King and K. R. Bonnickson, loc. cit. measured the heat-content for hematite and found two anomalies, presumably of magnetic nature, at about 950 and 1050°K., respectively. Both appear to involve maxima in the heat-capacity curves rather than isothermal heats of transformation. The complex magnetic properties at low temperatures were discussed by P. Gronvold and E. P. Westrum, Jr., loc. cit. No heat capacity anomaly was observed at the magnetic transition about 250°K. The Curie points of the antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$ were reported by A. Aharoni, E. H. Frei and M. Schieber, Phys. Rev. **127**, 439 (1962) and J. Lieke and A. C. D. Chakrader, Phys. Rev. Letters, **13**, 866 (1965).

Temperature of Decomposition.

T_d is the temperature at which $\Delta H_f^{\circ} = 0$ for the reaction $6\text{Fe}_2\text{O}_3(\text{c}) = 4\text{Fe}_3\text{O}_4(\text{c}) + \text{O}_2(\text{g})$. In other words, $\text{Fe}_2\text{O}_3(\text{c})$ decomposes into $\text{Fe}_3\text{O}_4(\text{c})$ and $\text{O}_2(\text{g})$ at 1755°K.

Fe₂O₃

Diiron Trisulfate ($\text{Fe}_2(\text{SO}_4)_3$)
(Crystal) GFW = 399.8788



(CRYSTAL)

DIIRON TRISULFATE ($\text{Fe}_2(\text{SO}_4)_3$)

OFW = 399.8788

T, °K	Cp°	S°	-(G°-H°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100	63.270	73.500		0.000	-617.350	-340.882	396.477
200	63.540	73.892	73.501	.117	-617.363	-340.408	393.686
300	63.580	73.970	76.117	6.981	-619.314	-314.024	281.178
400	63.590	74.000	81.067	14.721	-620.124	-286.343	213.434
500	63.590	74.000	86.830	23.130	-620.276	-261.962	168.270
600	63.590	74.000	90.990	32.031	-620.021	-243.521	135.976
700	63.590	74.000	93.990	41.287	-618.764	-213.004	112.827
800	63.590	74.000	96.090	50.794	-617.407	-182.362	92.850
900	63.590	74.000	97.810	60.492	-616.308	-151.860	76.899
1000	63.590	74.000	99.230	70.346	-615.567	-121.449	63.866
1100	100.540	101.687	124.740	80.337	-614.322	-91.136	51.023
1200	101.700	103.205	130.205	90.450	-612.332	-60.947	39.869
1300	102.750	104.686	135.648	100.672	-610.313	-30.919	29.048
1400	103.750	106.129	140.982	110.968	-608.263	-1.038	18.291
1500	104.700	107.530	146.219	121.421	-606.184	171.287	23.397
1600	105.600	108.890	151.361	131.936	-604.058	141.657	18.211
1700	106.480	109.990	156.453	142.561	-601.719	112.124	13.614
1800	107.330	110.940	161.774	153.432	-600.102	82.326	9.470
1900	108.180	111.750	167.246	164.607	-600.192	52.610	5.749
2000							

June 30, 1966

$S_{298.15}^\circ = [73.5 \pm 2] \text{ gibbs/mol}$
 $T_D = 1451^\circ\text{K}$
 $\Delta H_{298.15}^\circ = -617.35 \pm 0.40 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = \text{Unknown}$

Heat of Formation.

The enthalpy change ($\Delta H_{298.15}^\circ$) for the chemical reaction $\text{Fe}_2\text{O}_3(\text{c}) + 3\text{H}_2\text{SO}_4(14.855 \text{ H}_2\text{O}) = \text{Fe}_2(\text{SO}_4)_3(\text{c}) + 3\text{H}_2\text{O}(1)$ was measured to be $8.54 \pm 0.18 \text{ kcal/mol}$ by solution calorimetry by R. Barany and L. H. Jermol, U. S. Bur. Mines RI 6687, 1965. Using $\Delta H_{298.15}^\circ = -211.178 \text{ kcal/mol}$ for $\text{H}_2\text{SO}_4(14.855 \text{ H}_2\text{O})$ and -68.315 kcal/mol for $\text{H}_2\text{O}(1)$, obtained from "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, by D. D. Wagman and coworkers, National Bureau of Standards, 1965, and -197.3 kcal/mol for $\text{Fe}_2\text{O}_3(\text{c})$, the heat of formation ($\Delta H_{298.15}^\circ$) for $\text{Fe}_2(\text{SO}_4)_3(\text{c})$ was evaluated as $-617.35 \pm 0.40 \text{ kcal/mol}$ which was adopted here.

The equilibrium pressures for the decomposition of $\text{Fe}_2(\text{SO}_4)_3(\text{c})$ have been determined by several investigators at different temperatures. The chemical reactions involved are: (1) $\text{Fe}_2(\text{SO}_4)_3(\text{c}) = \text{Fe}_2\text{O}_3(\text{c}) + 3\text{SO}_3(\text{g})$ and (2) $\text{SO}_3(\text{g}) = \text{SO}_2(\text{g}) + 0.5 \text{ O}_2(\text{g})$. However, the measured pressure of the chemical equilibrium is the total pressure of three partial pressures, namely, P_{SO_3} , P_{SO_2} , and P_{O_2} . In order to calculate the enthalpy change of Reaction (1), the partial pressures of $\text{SO}_3(\text{g})$ were evaluated from the total vapor pressure data at each temperature. Based on the derived values for P_{SO_3} , the $\Delta H_{298.15}^\circ$ value for Reaction (1) was calculated by both the second and third law methods. The results obtained are presented in the following table. The $\Delta H_{298.15}^\circ$ ($\text{Fe}_2(\text{SO}_4)_3$, c) values were derived, using the third law $\Delta H_{298.15}^\circ$. These determinations were not given any weight.

Investigator	Temperature, °K	Second Law Value	Third Law Value	Drift	$\Delta H_{298.15}^\circ$, kcal/mol
1. Keppeler and D'Ans (1908)	753.15 - 1013.15	136.8 ± 0.5	139.9 ± 0.5	3.4 ± 0.6	-821.0
2. Wöhler, et al. (1908)	826.15 - 980.15	114.2 ± 6.2	133.1 ± 2.3	19.2 ± 6.9	-614.2
3. Bodenstein and Suzuki (1910)	903.65 - 997.15	140.7 ± 6.8	139.1 ± 1.3	-1.2 ± 7.1	-820.2
4. Wöhler and Grunzweig (1913)	909.15 - 994.15	155.1 ± 1.3	135.5 ± 1.3	-20.4 ± 1.4	-616.6
5. Neumann and Heintke (1937)	793.15 - 973.15	136.4 ± 2.3	136.2 ± 1.2	-1.2 ± 2.6	-617.3
6. Warner and Ingraham (1960)	903.15 - 997.15	133.9 ± 2.6	135.4 ± 0.5	1.7 ± 2.7	-616.5

1. G. Keppeler and J. D'Ans, Z. physik. Chem. 62, 89 (1908).
2. L. Wöhler, M. Püddemann and P. Wöhler, Ber. Deut. Chem. Gesell. 41, 703 (1908).
3. M. Bodenstein and T. Suzuki, Z. Elektrochem. 16, 912 (1910).
4. L. Wöhler and M. Grunzweig, Ber. Deut. Chem. Gesell. 43, 1587 (1913).
5. B. Neumann and G. Heintke, Z. Elektrochem. 43, 246 (1937).
6. N. A. Warner and T. R. Ingraham, Can. J. Chem. 38, 2196 (1960).

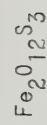
The decomposition pressures of $\text{Fe}_2(\text{SO}_4)_3(\text{c})$ have also been investigated by M. Grunzweig, Ph. D. dissertation, Darmstadt, Germany, 1913, 793-994 K; R. F. Blanks, Ph. D. dissertation, University of Melbourne, Australia, 1961, 845 - 976° K; and T. R. Ingraham, Internal Rept. EMT-63-17, Department of Mines and Technical Surveys, Ottawa, Canada, 1963, 856-995°K. These data together with some of the data mentioned previously were critically reviewed by H. H. Kellogg, Trans. AIME, 230, 1622 (1964).

Heat Capacity and Entropy.

The heat capacities were estimated by comparison with those for $\text{FeSO}_4(\text{c})$, assuming their average specific heats, gibbs/g, to be the same. The value of $S_{298.15}^\circ$ was estimated so that the second and third law $\Delta H_{298.15}^\circ$ values, derived from decomposition pressure data, are in reasonable agreement.

Temperature of Decomposition.

T_D is the temperature at which the total pressure of the gaseous products equals one atmosphere, which was obtained by graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham, loc. cit.



Magnetite (Fe₃O₄)
(Crystal)

Mol. wt. = 231.5386

Fe₃O₄

MOL. WT. = 231.5386

(CRYSTAL)

MAONETITE (Fe₃O₄)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	+∞	+∞	+∞	+∞	-266.398	-266.398	INFINITE
100	13.464	6.599	60.756	5.416	-267.676	-259.592	567.410
200	27.476	12.772	34.772	3.511	-268.017	-251.258	274.658
298	34.770	16.699	34.770	3.511	-268.017	-243.191	178.225
300	35.300	34.938	34.770	3.511	-267.894	-243.038	177.044
400	40.900	45.878	36.174	3.881	-267.378	-234.820	128.294
500	45.980	55.555	39.100	8.228	-266.518	-226.772	99.117
600	50.800	64.364	42.586	13.067	-265.370	-218.926	79.760
700	55.620	72.557	46.289	18.888	-263.981	-211.290	65.963
800	60.440	80.299	50.060	24.191	-262.378	-203.874	55.695
900	65.260	87.696	53.834	30.476	-260.649	-196.661	47.754
1000	68.000	92.751	57.677	37.276	-260.874	-189.541	41.422
1100	68.000	97.328	60.895	44.076	-261.077	-182.336	36.225
1200	68.000	101.504	64.108	49.876	-261.362	-175.096	31.868
1300	68.000	105.347	67.134	54.676	-261.745	-167.849	28.217
1400	68.000	108.904	69.992	58.476	-261.190	-160.646	25.077
1500	68.000	112.215	72.668	61.276	-260.691	-153.483	22.361
1600	68.000	115.311	75.266	64.076	-260.252	-146.350	19.989
1700	68.000	118.223	77.708	66.876	-260.741	-139.227	17.898
1800	68.000	120.967	80.036	73.676	-260.592	-132.079	16.036
1900	68.000	123.567	82.259	78.476	-260.522	-124.930	14.306
2000	68.000	126.024	84.386	83.276	-260.522	-117.881	12.744
2100	68.000	128.364	86.425	89.076	-272.071	-109.853	11.328
2200	68.000	130.599	88.383	92.876	-272.287	-101.077	10.041
2300	68.000	132.733	90.265	97.676	-272.523	-93.296	8.865
2400	68.000	134.776	92.077	102.476	-272.783	-85.497	7.785
2500	68.000	136.735	93.825	107.276	-273.067	-77.685	6.791
2600	68.000	138.618	95.512	112.076	-273.371	-69.867	5.873
2700	68.000	140.429	97.142	116.876	-273.699	-62.033	5.021
2800	68.000	142.175	98.719	121.676	-274.049	-54.185	4.229
2900	68.000	143.859	100.247	126.476	-274.421	-46.325	3.491
3000	68.000	145.486	101.728	131.276	-274.815	-38.448	2.801

June 30, 1965

$\Delta H_f^0 = -266.4 \pm 0.2$ kcal. mole⁻¹
 $\Delta H_f^{298.15} = -267.9 \pm 0.2$ kcal. mole⁻¹
 $\Delta H_m^0 = 33.0 \pm 2.0$ kcal. mole⁻¹
 $T_m = 1870 \pm 2^\circ\text{K.}$

Heat of Formation.

The equilibrium constants for the following four reactions, i.e. (1) $3\text{Fe}(c) + 4\text{H}_2\text{O}(g) = \text{Fe}_3\text{O}_4(c) + 4\text{H}_2(g)$; (2) $\text{Fe}_3\text{O}_4(c) + \text{H}_2(g) = 3\text{FeO}(c) + \text{CO}_2(g)$; and (4) $2\text{Fe}_3\text{O}_4(c) = 6\text{FeO}(c) + \text{O}_2(g)$, have been studied by several investigators. Using their reported equilibrium data, the corresponding enthalpy changes ($\Delta H_f^{298.15}$) were evaluated by both the second and third law methods. Based on the third law value for $\Delta H_f^{298.15}$, the respective $\Delta H_f^{298.15}$ values for $\text{Fe}_3\text{O}_4(c)$ were also derived. The results obtained are presented as follows.

Investigator	Reaction	Temperature, °K.	Second Law Value	Third Law Value	$\Delta H_f^{298.15}$ kcal. mole ⁻¹
Prickett, et al. ¹	(1)	633.2-823.2	-29.68 ± 1.30	-36.91	-268.10
Eastman ²	(2)	873.2-1273.2	22.41 ± 0.03	19.29	-268.01
Eastman and Evans ³	(2)	973.2-1273.2	21.56 ± 0.07	18.54	-267.26
Emmett and Shultz ⁴	(2)	973.2-1073.2	—	19.18	-267.90
Eastman ²	(3)	873.2-1273.2	11.87 ± 0.03	9.38	-267.93
Eastman and Evans ³	(3)	973.2-1273.2	11.63 ± 0.03	9.38	-267.94
Salmon ⁵	(4)	1473.2-1673.2	—	153.73	-267.79

1 R. Prickett, K. Walter and W. Lehnert, Z. Elektrochem. 47, 487 (1941). The two $\Delta H_f^{298.15}$ values listed are the average values of three separate results derived from three sets of experimental data.

2 E. D. Eastman, J. Am. Chem. Soc. 44, 975 (1922).

3 E. D. Eastman and R. M. Evans, J. Am. Chem. Soc. 46, 888 (1924).

4 P. H. Emmett and J. P. Schultz, J. Am. Chem. Soc. 52, 4268 (1930).

5 O. N. Salmon, J. Phys. Chem. 65, 550 (1961).

The enthalpy change of the reaction $\text{Fe}_3\text{O}_4(c) + 0.8215 \text{Fe}(c) + 0.5787 \text{O}_2(g) = 0.5895 \text{Fe}_3\text{O}_4(c)$ has been determined by O. L. Humphrey, E. G. King and K. K. Kelley, U. S. Bur. Mines RI 4870 (1952). Based on $\Delta H_f^{298.15} = -93.46$ kcal. mole⁻¹ (average of two separate values derived from two experimental determinations) and $\Delta H_f^{298.15}$ (Wüster, c) = -63.64 kcal. mole⁻¹, the value of $\Delta H_f^{298.15}(\text{Fe}_3\text{O}_4, c)$ was calculated as -266.5 kcal. mole⁻¹. The enthalpy change, $\Delta H_f^{298.15} = 4.33$ kcal. mole⁻¹, for the reaction $3\text{Fe}(c) + 4\text{CO}_2(g) = \text{Fe}_3\text{O}_4(c) + 4\text{CO}(g)$ was reported by L. S. Darken and R. W. Gurry, J. Am. Chem. Soc. 68, 798 (1946). The corresponding $\Delta H_f^{298.15}(\text{Fe}_3\text{O}_4, c)$ was evaluated as -266.22 kcal. mole⁻¹. The adopted value of $\Delta H_f^{298.15}$ for $\text{Fe}_3\text{O}_4(c)$ is selected as -267.9 ± 0.2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The low temperature (60.5-299.7°K.) heat capacities were reported by R. W. Millar, J. Am. Chem. Soc. 51, 215 (1929). The high temperature (298-1800°K.) heat capacities were obtained from J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Am. Chem. Soc. 73, 3891 (1951). These two sets of data were plotted and joined smoothly at 298°K. The C_p values above 1800°K. were obtained by graphical extrapolation. Heat capacities (90-295°K.) for $\text{Fe}_3\text{O}_4(c)$ were also reported by O. S. Parks and K. K. Kelley, J. Phys. Chem. 50, 47 (1946). $S_{298.15}^\circ(\text{Fe}_3\text{O}_4, c)$ was derived from the smoothed C_p data mentioned previously, using $S_{44.7}^\circ = 0.969$ e.u. J. P. Coughlin, E. G. King and K. R. Bonnickson, loc. cit. measured the heat-content for magnetite and found a magnetic anomaly around 880°K., corresponding to a maximum in heat capacity. A maximum heat capacity of 37.1 cal. deg.⁻¹ mole⁻¹ at 114.15°K. was also reported by R. W. Millar, loc. cit.

Melting Data.

T_m and ΔH_m^0 were obtained from L. S. Darken and R. W. Gurry, loc. cit.

Fe₃O₄

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	4.968	0.000	INFINITE	1.481	51.631	INFINITE	INFINITE
100	4.968	21.965	31.809	1.984	50.771	-110.954	-
200	4.968	25.408	27.447	2.488	51.943	-54.322	-
298	4.968	27.392	27.392	2.988	52.100	-48.565	-35.612
300	4.968	27.423	27.392	2.992	52.103	-48.563	-35.617
400	4.968	28.852	27.587	3.506	52.253	-47.361	-25.876
500	4.968	29.961	27.955	4.003	52.400	-46.121	-20.158
600	4.968	30.867	28.367	4.500	52.547	-44.851	-16.236
700	4.968	31.632	28.780	5.000	52.692	-43.558	-13.199
800	4.968	32.296	29.179	5.493	52.836	-42.242	-11.539
900	4.968	32.881	29.559	5.990	52.977	-40.910	-9.934
1000	4.968	33.404	29.917	6.487	53.115	-39.562	-8.646
1100	4.968	33.878	30.256	6.984	53.250	-38.200	-7.589
1200	4.968	34.310	30.576	7.481	53.379	-36.826	-6.707
1300	4.968	34.708	30.879	7.978	53.503	-35.441	-5.958
1400	4.968	35.076	31.166	8.474	53.623	-34.048	-5.315
1500	4.968	35.419	31.438	8.971	53.737	-32.645	-4.756
1600	4.968	35.739	31.697	9.468	53.845	-31.236	-4.266
1700	4.968	36.041	31.944	9.965	53.948	-29.819	-3.839
1800	4.968	36.325	32.179	10.461	54.046	-28.396	-3.448
1900	4.968	36.593	32.405	10.958	54.140	-26.970	-3.102
2000	4.968	36.848	32.621	11.455	54.230	-25.538	-2.790
2100	4.968	37.090	32.828	11.952	54.314	-24.102	-2.508
2200	4.968	37.322	33.027	12.449	54.398	-22.659	-2.247
2300	4.968	37.542	33.216	12.946	54.472	-21.217	-2.016
2400	4.968	37.754	33.403	13.442	54.546	-19.769	-1.800
2500	4.968	37.957	33.581	13.939	54.615	-18.316	-1.601
2600	4.968	38.152	33.753	14.436	54.682	-16.864	-1.417
2700	4.968	38.339	33.919	14.933	54.745	-15.409	-1.247
2800	4.968	38.520	34.081	15.430	54.806	-13.949	-1.089
2900	4.968	38.694	34.237	15.926	54.863	-12.491	-0.941
3000	4.968	38.862	34.388	16.423	54.918	-11.030	-0.803
3100	4.968	39.025	34.535	16.920	54.971	-9.565	-0.674
3200	4.968	39.183	34.678	17.417	55.021	-8.099	-0.554
3300	4.968	39.336	34.817	17.914	55.068	-6.632	-0.439
3400	4.968	39.484	34.952	18.410	55.113	-5.164	-0.332
3500	4.968	39.628	35.083	18.907	55.156	-3.695	-0.231
3600	4.968	39.768	35.212	19.404	55.196	-2.224	-0.135
3700	4.968	39.904	35.337	19.901	55.233	-0.753	-0.042
3800	4.968	40.037	35.459	20.398	55.269	0.722	0.042
3900	4.968	40.166	35.578	20.895	55.302	2.196	0.123
4000	4.968	40.292	35.694	21.391	55.333	3.671	0.201
4100	4.968	40.415	35.808	21.888	55.362	5.144	0.274
4200	4.968	40.534	35.929	22.385	55.389	6.612	0.346
4300	4.968	40.651	36.047	22.882	55.412	8.080	0.412
4400	4.968	40.765	36.164	23.379	55.435	9.545	0.476
4500	4.968	40.877	36.278	23.875	55.454	11.006	0.537
4600	4.968	40.986	36.390	24.372	55.473	12.463	0.595
4700	4.968	41.093	36.500	24.869	55.489	13.918	0.650
4800	4.968	41.198	36.608	25.366	55.503	15.372	0.705
4900	4.968	41.300	36.714	25.863	55.515	16.826	0.757
5000	4.968	41.400	36.728	26.359	55.525	18.279	0.806
5100	4.968	41.499	36.831	26.856	55.534	19.728	0.854
5200	4.968	41.595	36.932	27.353	55.541	21.174	0.900
5300	4.968	41.690	37.031	27.850	55.545	22.618	0.946
5400	4.968	41.783	37.089	28.347	55.548	24.061	0.986
5500	4.968	41.874	37.175	28.844	55.550	25.504	1.027
5600	4.968	41.963	37.260	29.340	55.549	26.946	1.066
5700	4.968	42.051	37.343	29.837	55.547	28.387	1.106
5800	4.968	42.138	37.425	30.334	55.543	29.828	1.141
5900	4.968	42.223	37.506	30.831	55.537	31.269	1.177
6000	4.968	42.306	37.585	31.328	55.530	32.710	1.211

Dec. 31, 1960; Sept. 30, 1965

Ground State Configuration $s_{1/2}$
 $S_{298.15}^{\circ} = 27.392 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} = 51.631 \pm 0.001 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = 52.100 \pm 0.001 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

E_i , cm. ⁻¹	E_i
0.000	2
82258.907	2
82258.942	2
82259.272	4
97492.198	2
97492.208	2
97492.306	4
97492.342	6

Heat of Formation.

The heat of formation was calculated from $D_0^{\circ}(\text{H}_2) = 36113.0 \pm 0.3 \text{ cm.}^{-1}$, reported by G. Herzberg and A. Monfils, *J. of Molecular Spectroscopy* 5, 482 (1960). This value was measured more precisely than the value $D_0^{\circ}(\text{H}_2) = 36116 \pm 6 \text{ cm.}^{-1}$ by H. Baulier, *Z. Phys. Chem. B29*, 315 (1935).

Heat Capacity and Entropy.

Electronic levels taken from C. E. Moore, *Natl. Bur. Standards (U. S.) Circ. 467* (1949).

Proton (H⁺)

(Ideal Gas)

GFW = 1.00742

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o /T)	H ^o - H ^o ₂₉₈	ΔH ^o kcal/mol	ΔG ^o	Log K _p
100	4.968	26.012	26.012	0.000	367.186	-265.790
200	4.968	26.043	26.012	0.009	367.198	-264.130
300	4.968	26.077	26.012	0.506	367.184	-262.201
400	4.968	26.111	26.012	1.003	368.489	-259.972
500	4.968	26.145	26.012	1.500	367.188	-257.105
600	4.968	26.179	26.012	2.000	369.772	-253.145
700	4.968	26.213	26.012	2.493	370.415	-248.438
800	4.968	26.247	26.012	2.990	371.053	-243.185
900	4.968	26.281	26.012	3.487	371.688	-237.168
1000	4.968	26.315	26.012	3.984	372.319	-230.777
1100	4.968	26.349	26.012	4.480	372.945	-224.008
1200	4.968	26.383	26.012	4.977	373.566	-216.878
1300	4.968	26.417	26.012	5.474	374.183	-209.389
1400	4.968	26.451	26.012	5.971	374.794	-201.542
1500	4.968	26.485	26.012	6.467	375.400	-193.337
1600	4.968	26.519	26.012	6.964	376.000	-184.776
1700	4.968	26.553	26.012	7.461	376.593	-175.860
1800	4.968	26.587	26.012	7.958	377.180	-166.589
1900	4.968	26.621	26.012	8.455	377.760	-156.960
2000	4.968	26.655	26.012	8.951	378.340	-146.983
2100	4.968	26.689	26.012	9.448	378.920	-136.658
2200	4.968	26.723	26.012	9.945	379.503	-125.984
2300	4.968	26.757	26.012	10.442	380.073	-114.961
2400	4.968	26.791	26.012	10.939	380.640	-103.589
2500	4.968	26.825	26.012	11.435	381.203	-91.868
2600	4.968	26.859	26.012	11.932	381.764	-79.797
2700	4.968	26.893	26.012	12.429	382.321	-67.376
2800	4.968	26.927	26.012	12.926	382.875	-54.605
2900	4.968	26.961	26.012	13.423	383.427	-41.484
3000	4.968	26.995	26.012	13.919	383.976	-28.013
3100	4.968	27.029	26.012	14.416	384.523	-14.192
3200	4.968	27.063	26.012	14.913	385.067	-0.021
3300	4.968	27.097	26.012	15.410	385.609	13.445
3400	4.968	27.131	26.012	15.907	386.148	26.476
3500	4.968	27.165	26.012	16.403	386.685	39.107
3600	4.968	27.199	26.012	16.900	387.220	51.338
3700	4.968	27.233	26.012	17.397	387.752	63.169
3800	4.968	27.267	26.012	17.894	388.282	74.600
3900	4.968	27.301	26.012	18.390	388.809	85.631
4000	4.968	27.335	26.012	18.887	389.335	96.262
4100	4.968	27.369	26.012	19.384	389.858	106.493
4200	4.968	27.403	26.012	19.881	390.379	116.324
4300	4.968	27.437	26.012	20.378	390.899	125.755
4400	4.968	27.471	26.012	20.874	391.414	134.786
4500	4.968	27.505	26.012	21.369	391.930	143.417
4600	4.968	27.539	26.012	21.866	392.443	151.648
4700	4.968	27.573	26.012	22.363	392.954	159.479
4800	4.968	27.607	26.012	22.860	393.463	166.910
4900	4.968	27.641	26.012	23.358	393.969	173.941
5000	4.968	27.675	26.012	23.855	394.475	180.572
5100	4.968	27.709	26.012	24.352	394.978	186.803
5200	4.968	27.743	26.012	24.849	395.480	192.634
5300	4.968	27.777	26.012	25.346	395.980	198.065
5400	4.968	27.811	26.012	25.842	396.478	203.096
5500	4.968	27.845	26.012	26.339	396.974	207.727
5600	4.968	27.879	26.012	26.836	397.468	211.958
5700	4.968	27.913	26.012	27.333	397.961	215.789
5800	4.968	27.947	26.012	27.830	398.453	219.220
5900	4.968	27.981	26.012	28.326	398.942	222.251
6000	4.968	28.015	26.012	28.823	399.434	224.882

June 30, 1966

PROTON (H⁺)

(IDEAL GAS)

GFW = 1.00742

ΔH_{f,0}^o = 365.236 ± 0.01 kcal/molΔH_{f,298.15}^o = 367.186 ± 0.01 kcal/molS_{298.15}^o = 26.012 gibbs/mol

Heat of Formation.

The heat of formation was calculated from the equation $H(g) \rightarrow H^+(g) + e^-$ with the JANAP auxiliary data for $H(g)$, using an ionization potential = 13.598 eV (313.605 kcal/mol) for $H(g)$ obtained from C. W. Beckett, National Bureau of Standards Report 8628, Jan. 1, 1965.

Heat Capacity and Entropy.

Calculated by assuming the proton to be an ideal monatomic gas. The enthalpy between 298° and 0°K is 1.481 kcal/mol as for all unexcited monatomic gases.

H⁺H⁺

Hydrogen Uninegative Ion (H^-)
(Ideal Gas) At. Wt. = 1.00852

H^-

AT. WT. = 1.00852

(IDEAL GAS)

HYDROGEN UNINEGATIVE ION (H^-)

Ground State Configuration $1s_0$
 $S^{\circ}_{298.15} = 26.015 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^{\circ}_f 0 = 34.2 \pm 0.5 \text{ kcal. mole}^{-1}$
 $\Delta H^{\circ}_f 298.15 = 33.2 \pm 0.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon_{1 \text{ cm}^{-1}}$	ϵ_1
0	1

Heat of Formation.

The heat of formation was calculated from the equation: $H(g) + e^- \rightarrow H^-(g)$ with the JANAF auxiliary value for $H(g)$ (this supplement), using an I.P. = $6.083098 \times 10^5 \text{ cm}^{-1}$ (.754 e.v. or 17.39 kcal/mole) for $H^-(g)$ obtained from C. L. Pekeris, Phys. Rev. **125**, 1470 (1962). The I.P. value for $H^-(g)$ reported by C. W. Scherr and R. E. Knight, Rev. Mod. Phys. **35**, 436 (1963) is in agreement with the value of Pekeris.

Heat Capacity and Entropy.

The electronic levels and quantum weights were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, U. S. National Bureau of Standards Circular 467, June 15, 1949, by assuming that the extra electron would produce an electronic configuration similar to that of the next higher atomic numbered element, in this case Helium. The electronic levels above $1 \times 10^5 \text{ cm}^{-1}$ were omitted because their contribution is negligible below 6000°K. The H°_{298} value at 0°K. is -1.481 kcal/mole.

Sept. 30, 1965

H^-

T. °K.	C_p°	$S^{\circ} - (F^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	ΔH°_f	ΔF°_f	Log K_p
100	4.968	26.015	0.000	33.200	31.583	-23.150
200	4.968	26.015	0.009	33.194	31.574	-23.000
300	4.968	26.015	0.009	33.194	31.574	-23.000
400	4.968	26.015	0.009	33.194	31.574	-23.000
500	4.968	26.015	0.009	33.194	31.574	-23.000
600	4.968	26.015	0.009	33.194	31.574	-23.000
700	4.968	26.015	0.009	33.194	31.574	-23.000
800	4.968	26.015	0.009	33.194	31.574	-23.000
900	4.968	26.015	0.009	33.194	31.574	-23.000
1000	4.968	26.015	0.009	33.194	31.574	-23.000
1100	4.968	26.015	0.009	33.194	31.574	-23.000
1200	4.968	26.015	0.009	33.194	31.574	-23.000
1300	4.968	26.015	0.009	33.194	31.574	-23.000
1400	4.968	26.015	0.009	33.194	31.574	-23.000
1500	4.968	26.015	0.009	33.194	31.574	-23.000
1600	4.968	26.015	0.009	33.194	31.574	-23.000
1700	4.968	26.015	0.009	33.194	31.574	-23.000
1800	4.968	26.015	0.009	33.194	31.574	-23.000
1900	4.968	26.015	0.009	33.194	31.574	-23.000
2000	4.968	26.015	0.009	33.194	31.574	-23.000
2100	4.968	26.015	0.009	33.194	31.574	-23.000
2200	4.968	26.015	0.009	33.194	31.574	-23.000
2300	4.968	26.015	0.009	33.194	31.574	-23.000
2400	4.968	26.015	0.009	33.194	31.574	-23.000
2500	4.968	26.015	0.009	33.194	31.574	-23.000
2600	4.968	26.015	0.009	33.194	31.574	-23.000
2700	4.968	26.015	0.009	33.194	31.574	-23.000
2800	4.968	26.015	0.009	33.194	31.574	-23.000
2900	4.968	26.015	0.009	33.194	31.574	-23.000
3000	4.968	26.015	0.009	33.194	31.574	-23.000
3100	4.968	26.015	0.009	33.194	31.574	-23.000
3200	4.968	26.015	0.009	33.194	31.574	-23.000
3300	4.968	26.015	0.009	33.194	31.574	-23.000
3400	4.968	26.015	0.009	33.194	31.574	-23.000
3500	4.968	26.015	0.009	33.194	31.574	-23.000
3600	4.968	26.015	0.009	33.194	31.574	-23.000
3700	4.968	26.015	0.009	33.194	31.574	-23.000
3800	4.968	26.015	0.009	33.194	31.574	-23.000
3900	4.968	26.015	0.009	33.194	31.574	-23.000
4000	4.968	26.015	0.009	33.194	31.574	-23.000
4100	4.968	26.015	0.009	33.194	31.574	-23.000
4200	4.968	26.015	0.009	33.194	31.574	-23.000
4300	4.968	26.015	0.009	33.194	31.574	-23.000
4400	4.968	26.015	0.009	33.194	31.574	-23.000
4500	4.968	26.015	0.009	33.194	31.574	-23.000
4600	4.968	26.015	0.009	33.194	31.574	-23.000
4700	4.968	26.015	0.009	33.194	31.574	-23.000
4800	4.968	26.015	0.009	33.194	31.574	-23.000
4900	4.968	26.015	0.009	33.194	31.574	-23.000
5000	4.968	26.015	0.009	33.194	31.574	-23.000
5100	4.968	26.015	0.009	33.194	31.574	-23.000
5200	4.968	26.015	0.009	33.194	31.574	-23.000
5300	4.968	26.015	0.009	33.194	31.574	-23.000
5400	4.968	26.015	0.009	33.194	31.574	-23.000
5500	4.968	26.015	0.009	33.194	31.574	-23.000
5600	4.968	26.015	0.009	33.194	31.574	-23.000
5700	4.968	26.015	0.009	33.194	31.574	-23.000
5800	4.968	26.015	0.009	33.194	31.574	-23.000
5900	4.968	26.015	0.009	33.194	31.574	-23.000
6000	4.968	26.015	0.009	33.194	31.574	-23.000

Mercury Monohydride (HgH)

(Ideal Gas) Mol. Wt. = 201.618

T, °K.	C _p	S° - (F° - H ₂₉₈)/T	H° - H ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	INFINITE	-2.082	58.163	58.163	INFINITE
100	6.653	46.000	2.082	58.066	58.066	-12.708
200	6.999	58.746	1.391	57.984	57.984	-12.708
298	7.181	52.486	0.000	57.000	51.421	-37.693
300	7.186	52.530	-0.13	56.995	51.387	-37.434
400	7.309	54.640	52.772	56.721	49.560	-27.077
500	7.845	56.353	53.322	56.487	47.798	-20.891
600	8.140	57.810	53.951	56.288	46.078	-16.783
700	8.386	59.084	54.595	56.142	44.509	-14.349
800	8.588	60.217	55.228	56.048	43.088	-12.707
900	8.757	61.238	55.840	45.958	41.803	-11.429
1000	8.899	62.169	56.427	44.761	40.659	-10.407
1100	9.022	63.023	56.989	43.587	39.646	-9.569
1200	9.130	63.813	57.525	42.436	38.759	-8.871
1300	9.227	64.547	58.037	41.308	37.900	-8.279
1400	9.314	65.234	58.527	40.193	37.071	-7.771
1500	9.395	65.880	58.996	40.096	36.278	-7.331
1600	9.471	66.488	59.445	40.026	35.518	-6.945
1700	9.541	67.065	59.877	40.000	34.788	-6.604
1800	9.609	67.612	60.291	40.000	34.088	-6.300
1900	9.673	68.133	60.690	40.000	33.413	-6.028
2000	9.735	68.631	61.075	40.000	32.761	-5.783
2100	9.796	69.108	61.446	40.000	32.131	-5.560
2200	9.854	69.565	61.805	40.000	31.523	-5.358
2300	9.911	70.004	62.152	40.000	30.937	-5.173
2400	9.967	70.427	62.488	40.000	30.373	-5.003
2500	10.022	70.835	62.814	40.000	29.831	-4.846
2600	10.076	71.229	63.130	40.000	29.311	-4.702
2700	10.130	71.610	63.437	40.000	28.813	-4.567
2800	10.182	71.980	63.736	40.000	28.337	-4.442
2900	10.235	72.338	64.026	40.000	27.883	-4.326
3000	10.286	72.686	64.309	40.000	27.451	-4.217
3100	10.338	73.024	64.585	40.000	27.042	-4.114
3200	10.388	73.353	64.853	40.000	26.655	-4.018
3300	10.439	73.673	65.116	40.000	26.290	-3.928
3400	10.489	73.986	65.372	40.000	25.946	-3.843
3500	10.539	74.290	65.623	40.000	25.623	-3.762
3600	10.589	74.588	65.868	40.000	25.321	-3.686
3700	10.638	74.879	66.107	40.000	25.039	-3.614
3800	10.688	75.163	66.342	40.000	24.776	-3.545
3900	10.737	75.441	66.572	40.000	24.532	-3.480
4000	10.786	75.714	66.797	40.000	24.306	-3.417
4100	10.835	75.981	67.018	40.000	24.098	-3.358
4200	10.884	76.243	67.234	40.000	23.906	-3.301
4300	10.932	76.499	67.447	40.000	23.729	-3.247
4400	10.981	76.751	67.655	40.000	23.566	-3.195
4500	11.029	76.998	67.860	40.000	23.416	-3.146
4600	11.078	77.241	68.061	40.000	23.278	-3.098
4700	11.126	77.480	68.259	40.000	23.151	-3.052
4800	11.174	77.715	68.454	40.000	23.034	-3.008
4900	11.222	77.946	68.645	40.000	22.927	-2.966
5000	11.270	78.173	68.833	40.000	22.830	-2.925
5100	11.318	78.397	69.019	40.000	22.742	-2.885
5200	11.366	78.617	69.201	40.000	22.664	-2.848
5300	11.414	78.834	69.381	40.000	22.595	-2.812
5400	11.462	79.048	69.558	40.000	22.534	-2.776
5500	11.510	79.258	69.732	40.000	22.480	-2.742
5600	11.558	79.466	69.904	40.000	22.431	-2.709
5700	11.605	79.671	70.074	40.000	22.386	-2.677
5800	11.653	79.873	70.241	40.000	22.344	-2.646
5900	11.701	80.073	70.406	40.000	22.305	-2.616
6000	11.748	80.270	70.569	40.000	22.272	-2.587

June 30, 1963

HHg

(Ideal Gas) (HgH)

MOL. WT. = 201.618

Ground State Configuration [$2\Sigma^+$]
 $\Delta H_f^\circ = 59 \pm 4$ kcal. mole⁻¹
 $S_{298.15}^\circ = [52.486]$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^\circ = 57 \pm 4$ kcal. mole⁻¹

Electronic Levels and Multiplicities

$$\frac{\epsilon_1 \text{ cm.}^{-1}}{0} \quad \frac{g_1}{[2]}$$

$$\omega_e x_e = 1387 \text{ cm.}^{-1}$$

$$\omega_e = 83.01 \text{ cm.}^{-1}$$

$$\sigma = 1$$

$$\alpha_e = 0.312 \text{ cm.}^{-1}$$

$$r_e = 1.74 \text{ \AA}$$

$$B_e = 5.549 \text{ cm.}^{-1}$$

Heat of Formation.

The heat of formation was calculated from D_0 , 8.671 kcal. mole⁻¹, taken from G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Company, Inc., New York (1950).

Heat Capacity and Entropy.

Molecular constants were taken from G. Herzberg, loc. cit.

HHg

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	6.090	0.000	INFINITE	2.069	6.420	6.420	INFINITE
100	6.959	41.746	55.541	1.379	6.420	6.420	9.920
200	6.961	46.570	49.980	0.683	6.420	6.420	7.509
298	6.949	49.351	49.351	0.000	6.420	6.420	6.276
300	6.949	49.394	49.351	0.013	6.420	6.420	6.247
400	7.010	51.403	49.625	0.711	6.064	6.340	5.837
500	7.107	52.977	50.183	1.817	5.146	5.413	5.055
600	7.253	54.285	50.727	2.134	4.227	4.494	4.354
700	7.430	55.419	51.284	2.420	3.297	3.564	3.619
800	7.630	56.419	51.854	2.679	2.297	2.564	2.771
900	7.767	57.324	52.448	2.868	1.285	1.552	1.732
1000	7.920	58.150	52.977	3.011	0.261	0.528	0.600
1100	8.086	58.911	53.463	3.111	-0.761	-0.489	0.500
1200	8.262	59.603	53.911	3.176	-1.743	-1.471	0.400
1300	8.447	60.226	54.325	3.203	-2.716	-2.444	0.300
1400	8.639	60.784	54.706	3.191	-3.683	-3.411	0.200
1500	8.836	61.278	55.057	3.131	-4.640	-4.368	0.100
1600	9.038	61.703	55.381	3.021	-5.589	-5.317	0.000
1700	9.244	62.062	55.679	2.861	-6.524	-6.252	-0.100
1800	9.454	62.357	55.943	2.651	-7.448	-7.176	-0.200
1900	9.668	62.592	56.173	2.391	-8.363	-8.091	-0.300
2000	9.886	62.762	56.367	2.081	-9.269	-9.000	-0.400
2100	10.108	62.867	56.524	1.721	-10.167	-9.900	-0.500
2200	10.334	62.907	56.645	1.311	-11.058	-10.791	-0.600
2300	10.564	62.882	56.721	0.851	-11.943	-11.676	-0.700
2400	10.798	62.794	56.753	0.351	-12.823	-12.556	-0.800
2500	11.036	62.643	56.741	-0.191	-13.698	-13.431	-0.900
2600	11.278	62.429	56.685	-0.711	-14.569	-14.292	-1.000
2700	11.524	62.153	56.587	-1.211	-15.436	-15.159	-1.100
2800	11.774	61.816	56.447	-1.681	-16.299	-16.022	-1.200
2900	12.028	61.419	56.264	-2.121	-17.158	-16.881	-1.300
3000	12.286	60.962	56.038	-2.531	-18.013	-17.736	-1.400
3100	12.548	60.557	55.762	-2.901	-18.864	-18.587	-1.500
3200	12.814	60.103	55.437	-3.241	-19.711	-19.434	-1.600
3300	13.084	59.609	55.062	-3.551	-20.554	-20.277	-1.700
3400	13.358	59.076	54.637	-3.831	-21.393	-21.116	-1.800
3500	13.636	58.503	54.162	-4.081	-22.228	-21.951	-1.900
3600	13.918	57.890	53.637	-4.301	-23.059	-22.782	-2.000
3700	14.204	57.237	53.062	-4.491	-23.886	-23.609	-2.100
3800	14.494	56.544	52.437	-4.651	-24.709	-24.432	-2.200
3900	14.788	55.811	51.762	-4.781	-25.528	-25.251	-2.300
4000	15.086	55.038	51.037	-4.881	-26.343	-26.066	-2.400
4100	15.388	54.225	50.262	-4.951	-27.154	-26.877	-2.500
4200	15.694	53.372	49.437	-5.001	-27.961	-27.684	-2.600
4300	15.999	52.479	48.562	-5.021	-28.764	-28.487	-2.700
4400	16.308	51.546	47.637	-5.011	-29.563	-29.286	-2.800
4500	16.619	50.573	46.662	-4.971	-30.358	-30.081	-2.900
4600	16.932	49.560	45.637	-4.901	-31.149	-30.872	-3.000
4700	17.248	48.507	44.562	-4.801	-31.936	-31.659	-3.100
4800	17.567	47.414	43.437	-4.671	-32.719	-32.442	-3.200
4900	17.889	46.281	42.262	-4.511	-33.500	-33.223	-3.300
5000	18.214	45.107	41.037	-4.321	-34.278	-34.001	-3.400
5100	18.542	43.894	39.762	-4.101	-35.053	-34.776	-3.500
5200	18.874	42.641	38.437	-3.851	-35.825	-35.548	-3.600
5300	19.209	41.348	37.062	-3.571	-36.594	-36.317	-3.700
5400	19.548	40.015	35.637	-3.261	-37.359	-37.082	-3.800
5500	19.890	38.642	34.162	-2.921	-38.121	-37.844	-3.900
5600	20.236	37.229	32.637	-2.551	-38.880	-38.603	-4.000
5700	20.586	35.776	31.062	-2.151	-39.636	-39.359	-4.100
5800	20.940	34.283	29.437	-1.721	-40.389	-40.112	-4.200
5900	21.298	32.750	27.762	-1.261	-41.139	-40.862	-4.300
6000	21.660	31.177	26.037	-0.771	-41.886	-41.609	-4.400
6100	22.026	29.564	24.262	-0.251	-42.630	-42.353	-4.500
6200	22.396	27.911	22.437	0.301	-43.371	-43.094	-4.600
6300	22.770	26.218	20.562	0.831	-44.109	-43.832	-4.700
6400	23.148	24.485	18.637	1.341	-44.844	-44.567	-4.800
6500	23.530	22.712	16.662	1.831	-45.576	-45.299	-4.900
6600	23.916	20.900	14.637	2.291	-46.305	-46.028	-5.000
6700	24.306	19.047	12.562	2.721	-47.031	-46.754	-5.100
6800	24.700	17.154	10.437	3.121	-47.754	-47.477	-5.200
6900	25.098	15.221	8.262	3.491	-48.474	-48.197	-5.300
7000	25.500	13.248	6.037	3.831	-49.191	-48.914	-5.400
7100	25.906	11.235	3.762	4.141	-49.905	-49.628	-5.500
7200	26.316	9.182	1.437	4.421	-50.616	-50.339	-5.600
7300	26.730	7.089	-0.938	4.671	-51.324	-51.047	-5.700
7400	27.148	4.956	-3.263	4.891	-52.029	-51.752	-5.800
7500	27.570	2.783	-5.548	5.081	-52.731	-52.454	-5.900
7600	27.996	0.570	-7.741	5.241	-53.430	-53.153	-6.000
7700	28.426	-1.683	-9.840	5.371	-54.126	-53.849	-6.100
7800	28.860	-3.900	-11.841	5.481	-54.819	-54.542	-6.200
7900	29.298	-6.073	-13.742	5.571	-55.509	-55.232	-6.300
8000	29.740	-8.204	-15.543	5.641	-56.196	-55.919	-6.400

September 30, 1961

HYDROGEN IODIDE (HI)

(IDEAL GAS)

MOL. WT. = 127.918

$$\Delta H_f^\circ = 6.82 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^\circ = 6.82 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta G_f^\circ = 6.82 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\omega_e = 2309.06 \text{ cm}^{-1}$$

$$\omega_e = 39.73 \text{ cm}^{-1}$$

$$B_e = 6.512 \text{ cm}^{-1}$$

$$\alpha_e = 0.1715 \text{ cm}^{-1}$$

Thermodynamic Functions.

Molecular constants are from M. Cowan and W. Gordy [Phys. Rev. 104, 551 (1956)] and D. R. J. Boyd and H. W. Thompson [Spectrochim. Acta 5, 308 (1952)]. The calculated functions are in reasonable agreement with the compilation of K. K. Kelley [U. S. Bur. Mines Bull. 564 (1960)].

Heat of Formation.

Using the calculated functions derived above and functions for $H_2(g)$ and $I_2(g)$ given in the JANAF tables, equilibrium data from the literature were used to calculate ΔH_{298}° for the reaction



$$\Delta H_{298}^\circ, \text{ kcal. mole}^{-1}$$

Taylor and Crist ¹ (667° to 764°K)	-2.375 ± .005
Bodenstein ² (556° to 781°K)	-2.053 ± .135
Bright and Hagerty ³ (696° and 779°K)	-2.219 ± .070
Rittenberg and Urey ⁴ (671° and 741°K)	-2.156 ± .072

The data of Taylor and Crist are the most concordant and are given the most weight. Converting to the solid state of iodine, which has been adopted as a JANAF reference state gives the standard heat of formation of hydrogen iodide.

References

- (1) A. H. Taylor and R. H. Crist, *J. Am. Chem. Soc.* **65**, 1377 (1941).
- (2) M. Bodenstein, *Z. physikal. Chem.* **29**, 295 (1899).
- (3) M. P. H. Bright and R. P. Hagerty, *Trans. Faraday Soc.* **43**, 697 (1947).
- (4) D. Rittenberg and H. C. Urey, *J. Am. Chem. Soc.* **56**, 1885 (1934).

Potassium Hydride (KH)

(Crystal) Mol. Wt. = 40.108

HK

POTASSIUM HYDRIDE (KH)

(CRYSTAL)

MOL. WT. = 40.108

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	(F° - H° ₂₉₈)/T	ΔH° _f	ΔF°	Log K _p
0						
100						
200						
298	9.060	12.000	12.000	0.000	-13.819	-8.136
300						5.964
300	9.106	12.056	12.056	0.017	-13.822	-8.101
400	10.450	12.906	12.379	1.011	-14.469	-6.069
500	11.200	13.378	13.137	2.120	-14.472	-3.964
600	11.810	13.568	13.022	3.123	-14.345	-1.732
700	13.051	14.530	14.963	4.597	-14.136	-0.892
800	13.996	15.433	15.812	6.401	-13.852	-0.007
900	14.596	16.293	16.612	8.529	-13.509	1.023
1000	14.900	16.425	17.700	8.725	-13.223	1.348
1100	14.571	17.401	18.556	10.169	-13.779	1.811
1200	14.400	18.079	19.181	11.639	-13.574	2.233
1300	14.250	18.584	19.684	13.128	-13.408	2.635
1400	14.129	19.037	20.135	14.636	-13.261	3.028
1500	14.030	19.435	20.667	16.152	-13.128	3.437

 $\Delta H_f^0 = \text{Unknown}$ $\Delta H_f^0 298.15 = -13.819 \pm 0.011 \text{ kcal. mole}^{-1}$ $S_{298.15}^0 = [12] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_d = [690]^{\circ}\text{K.}$

Heat of Formation.

The value of $\Delta H_f^0 298.15$ was taken from S. R. Gunn and L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1958). The corresponding value reported by C. E. Measer, L. G. Fasolino and C. E. Thalmeier, J. Am. Chem. Soc. **77**, 4524 (1955) was $-15.16 \pm 0.6 \text{ kcal. mole}^{-1}$. In this paper the results of the previous investigations were also reviewed.

Heat Capacity and Entropy.

C_p and $S_{298.15}^0$ were estimated by comparison with those for NaH(c) and LiH(c).

Temperature of Decomposition.

T_d was assumed to be the temperature at which the value of ΔF_f^0 changes from negative to positive.

March 31, 1963

HK

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0			∞.000	INFINITE	2.102	30.003	30.003	INFINITE
100	6.974	39.575	31.660	1.409	26.902	26.015	26.015	61.223
200	7.418	31.660	27.304	1.000	24.400	23.040	23.040	61.223
298	7.418	27.304	0.000	0.000	20.400	20.557	20.557	70.000
300	7.426	27.330	-0.014	-0.014	20.394	20.527	20.527	17.867
400	7.814	49.551	1.776	1.776	29.396	23.062	23.062	12.600
500	8.134	51.321	1.575	1.575	28.002	21.738	21.738	9.501
600	8.370	52.824	0.825	0.825	27.932	20.470	20.470	7.956
700	8.545	54.130	0.492	0.492	27.731	19.241	19.241	6.007
800	8.678	55.260	0.148	0.148	27.527	18.061	18.061	4.928
900	8.762	56.308	0.0774	0.0774	27.332	16.868	16.868	4.096
1000	8.867	57.236	0.0481	0.0481	27.135	15.715	15.715	3.434
1100	8.937	58.087	0.0247	0.0247	26.934	15.607	15.607	3.101
1200	8.976	58.867	0.0149	0.0149	26.751	15.495	15.495	2.768
1300	9.008	59.589	0.0083	0.0083	26.583	15.379	15.379	2.454
1400	9.035	60.261	0.0046	0.0046	26.430	15.263	15.263	2.157
1500	9.057	60.890	0.0026	0.0026	26.289	15.156	15.156	1.883
1600	9.075	61.481	0.0014	0.0014	26.158	15.051	15.051	1.632
1700	9.091	62.039	0.0008	0.0008	26.036	14.957	14.957	1.400
1800	9.105	62.566	0.0004	0.0004	25.922	14.873	14.873	1.185
1900	9.117	63.067	0.0002	0.0002	25.815	14.798	14.798	1.000
2000	9.128	63.543	0.0001	0.0001	25.714	14.732	14.732	0.842
2100	9.137	63.998	0.0000	0.0000	25.619	14.675	14.675	0.700
2200	9.146	64.433	0.0000	0.0000	25.530	14.626	14.626	0.575
2300	9.154	64.850	0.0000	0.0000	25.446	14.584	14.584	0.465
2400	9.161	65.251	0.0000	0.0000	25.367	14.547	14.547	0.365
2500	9.168	65.636	0.0000	0.0000	25.292	14.514	14.514	0.275
2600	9.174	66.007	0.0000	0.0000	25.221	14.484	14.484	0.195
2700	9.180	66.365	0.0000	0.0000	25.154	14.457	14.457	0.125
2800	9.185	66.711	0.0000	0.0000	25.091	14.432	14.432	0.065
2900	9.190	67.045	0.0000	0.0000	25.031	14.408	14.408	0.015
3000	9.195	67.370	0.0000	0.0000	24.974	14.385	14.385	0.000
3100	9.199	67.684	0.0000	0.0000	24.919	14.363	14.363	0.000
3200	9.203	67.984	0.0000	0.0000	24.866	14.342	14.342	0.000
3300	9.207	68.278	0.0000	0.0000	24.815	14.322	14.322	0.000
3400	9.211	68.564	0.0000	0.0000	24.766	14.303	14.303	0.000
3500	9.215	68.842	0.0000	0.0000	24.718	14.285	14.285	0.000
3600	9.219	69.114	0.0000	0.0000	24.672	14.268	14.268	0.000
3700	9.223	69.381	0.0000	0.0000	24.628	14.252	14.252	0.000
3800	9.227	69.643	0.0000	0.0000	24.585	14.237	14.237	0.000
3900	9.231	69.900	0.0000	0.0000	24.543	14.222	14.222	0.000
4000	9.235	70.152	0.0000	0.0000	24.502	14.208	14.208	0.000
4100	9.239	70.400	0.0000	0.0000	24.462	14.194	14.194	0.000
4200	9.243	70.643	0.0000	0.0000	24.423	14.181	14.181	0.000
4300	9.247	70.881	0.0000	0.0000	24.385	14.168	14.168	0.000
4400	9.251	71.115	0.0000	0.0000	24.347	14.155	14.155	0.000
4500	9.254	71.339	0.0000	0.0000	24.309	14.142	14.142	0.000
4600	9.257	71.558	0.0000	0.0000	24.272	14.130	14.130	0.000
4700	9.260	71.772	0.0000	0.0000	24.235	14.118	14.118	0.000
4800	9.263	71.983	0.0000	0.0000	24.198	14.106	14.106	0.000
4900	9.266	72.192	0.0000	0.0000	24.161	14.094	14.094	0.000
5000	9.269	72.397	0.0000	0.0000	24.124	14.082	14.082	0.000
5100	9.272	72.571	0.0000	0.0000	24.087	14.070	14.070	0.000
5200	9.275	72.767	0.0000	0.0000	24.050	14.058	14.058	0.000
5300	9.278	72.959	0.0000	0.0000	24.013	14.046	14.046	0.000
5400	9.281	73.146	0.0000	0.0000	23.976	14.034	14.034	0.000
5500	9.284	73.330	0.0000	0.0000	23.939	14.022	14.022	0.000
5600	9.287	73.518	0.0000	0.0000	23.902	14.010	14.010	0.000
5700	9.290	73.703	0.0000	0.0000	23.865	14.000	14.000	0.000
5800	9.293	73.876	0.0000	0.0000	23.828	13.989	13.989	0.000
5900	9.296	74.051	0.0000	0.0000	23.791	13.978	13.978	0.000
6000	9.299	74.223	0.0000	0.0000	23.754	13.967	13.967	0.000

March 31, 1963

March 31, 1963

MOL. WT. = 40.108

(IDEAL GAS)

POTASSIUM HYDRIDE (KH)

Ground State Configuration $1 \Sigma^+ + \Delta H_f^0 = 30.0 \pm 3.5 \text{ kcal. mole}^{-1}$

$$\begin{aligned} \omega_e &= 985.0 \text{ cm.}^{-1} & \omega_e x_e &= 14.65 \text{ cm.}^{-1} \\ B_e &= 3.407 \text{ cm.}^{-1} & \alpha_e &= 0.0673 \text{ cm.}^{-1} \end{aligned}$$

Heat of Formation.

$\Delta H_f^{298.15}$ was calculated from $D_0^0 = 1.86 \pm 0.15$ e.v. reported by A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., 1953.

Heat Capacity and Entropy.

All molecular and spectroscopic constants were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., 1950.

Potassium Hydroxide (KOH)

(Crystal)

Mol. wt. = 56.10937

HKO

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	8.164	5.705	31.303	-2.526	-100.694	-100.694	INFINITE
200	12.578	12.857	20.368	-1.502	-97.901	-97.901	213.963
298	15.746	18.949	18.949	∞	-90.220	-90.220	102.959
300	15.769	19.046	18.949	∞	-90.594	-90.594	66.407
400	17.400	23.798	19.586	1.029	-90.526	-90.526	65.948
500	19.020	27.853	20.843	3.505	-83.055	-83.055	36.493
600	18.800	34.209	22.685	6.209	-76.632	-76.632	29.009
700	18.800	38.543	24.543	8.769	-69.131	-69.131	23.836
800	18.800	41.823	26.400	11.120	-61.315	-61.315	19.975
900	18.800	43.804	27.680	12.549	-53.315	-53.315	16.402
1000	18.800	44.804	29.375	14.429	-45.023	-45.023	13.002
1100	18.800	45.596	30.769	16.309	-36.463	-36.463	10.533
1200	18.800	46.132	32.074	18.189	-27.834	-27.834	8.914
1300	18.800	46.732	33.309	20.069	-19.268	-19.268	7.593
1400	18.800	47.130	34.462	21.949	-10.732	-10.732	6.533
1500	18.800	51.427	35.541	23.829	-11.150	-11.150	6.342

Dec. 31, 1961; Mar. 31, 1962; June 30, 1962; Mar. 31, 1966

POTASSIUM HYDROXIDE (KOH)

(CRYSTAL)

MOL. WT. = 56.10937

S_{298.15} = 18.95 cal. deg.⁻¹ mole⁻¹
 T_m = 522°K
 T_m = 673°K.

ΔH°_f 0 = -100.7 ± 0.1 kcal. mole⁻¹
 ΔH°_f 298.15 = -101.5 ± 0.1 kcal. mole⁻¹
 ΔH°_f = 1.515 kcal. mole⁻¹
 ΔH°_f = 2.240 kcal. mole⁻¹
 ΔH°_f 298.15 (to monomer) = [46.1] kcal. mole⁻¹
 ΔH°_f 298.15 (to dimer) = [45.6] kcal. mole⁻¹

Heat of Formation.

The standard enthalpy of formation, ΔH°_f 298 (KOH, c) = -101.5 ± 0.1 kcal. mole⁻¹, was calculated from the heat of solution of KOH(c), the heat of hydrolysis of potassium metal and the appropriate auxiliary data.

N. A. Feshetnikov¹ has measured the heat of solution KOH(c) → KOH(650 H₂O) as -13.665 ± 0.009 kcal. mole⁻¹ at 298.15°K. in the solution calorimeter. Using the auxiliary heat of dilution reported by V. B. Parker², the selected heat of solution of KOH(c) at infinite dilution is -13.770 kcal. mole⁻¹. The heat of solution KOH(c) → KOH(25 H₂O) has also been measured as -13.80 ± 0.10 kcal. mole⁻¹ in the solution calorimeter by W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull³. Both results are in good agreement.

The heat of hydrolysis of potassium metal, ΔH°_f 298, has been measured in the solution calorimeter by the following investigators.

Source	Number of Moles of H ₂ O	ΔH° _f 298 kcal. mole ⁻¹	ΔH° _f 298 (KOH(∞ H ₂ O)) kcal. mole ⁻¹	ΔH° _f 298 (KOH, c) kcal. mole ⁻¹
Gunn et al. ⁴	1000	-46.877 ± 0.01	-115.281	-101.511
Messer et al. ⁵	∞	-47.02 ± 0.15	-115.335	-101.565
Ketchen et al. ⁶	∞	-46.894 ± 0.24	-115.209	-101.439

The values of ΔH°_f 298 (KOH(∞ H₂O)) were calculated from the heats of reaction, ΔH°_r 298, using ΔH°_f 298 (H₂O, l) = -68.315 kcal. mole⁻¹. Combination of the selected heat of solution of KOH(c) at infinite dilution with the heat of formation of KOH(∞ H₂O) gives the heat of formation of KOH(c) in the last column of the table. A weighted average of these three measurements was taken for the selected heat of formation of KOH(c).

The earlier investigations have been reviewed by F. R. Bichowsky and F. D. Rossini⁸ and C. E. Messer et al.⁵, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of KOH(c) from 15° to 340°K. have been measured by W. E. Hatton et al.³ who have also observed a sharp peak in the heat capacity curve in the temperature range from 210° to 230°K. These values of C_p were adopted in the calculation. W. D. Powers and G. C. Blalock⁹ have measured the high temperature enthalpy changes of the solid KOH in the α and β phases by the drop method. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities in the α phase. Therefore, the selected heat capacities between 340° and 522°K. were estimated from a graphical extrapolation of the low temperature heat capacity curve, and the tabulated H°-H°₂₉₈ functions are in agreement with their enthalpy measurements within the experimental uncertainty. The heat capacities of KOH(c) in the β phase were obtained from Powers and Blalock⁹.

The entropy (S°₂₉₈ = 18.95 cal. deg.⁻¹ mole⁻¹) was taken from Hatton et al.³, based on an extrapolation of S°₁₅ = 0.054 cal. deg.⁻¹ mole⁻¹.

Transition and Melting Data.

Hatton et al.³ have found a lambda transition at 227.4°K. in the heat capacity measurement. The adopted heat of α-β transition at 522°K. and heat of melting at 673°K. were obtained from Powers and Blalock⁹. P. S. Seward and K. E. Martin¹⁰ found ΔH°_m = 1.83 kcal. mole⁻¹ at 683°K. In phase diagram studies of the system KOH-K₂CO₃.

Heat of Sublimation.

See KOH(g) table for details.

References:

- 1 N. A. Feshetnikov, Zhur. Neorg. Khim., **6**, 662 (1961).
- 2 V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes", NBS-NBS 2, Apr., 1965.
- 3 W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, unpublished work, Dow Thermal Research Lab., 1959.
- 4 S. R. Gunn and L. G. Green, J. Am. Chem. Soc., **80**, 4782 (1958).
- 5 S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Bomb Solution Calorimeter," UCL-7952, Oct. 1963.
- 6 E. E. Ketchen and G. C. Blalock, J. Am. Chem. Soc., **76**, 4736 (1954).
- 7 D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, NBS Technical Note 270-1, Oct. 1965.
- 8 F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1956.
- 9 W. D. Powers and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Hydroxides at High Temperatures," J. Am. Chem. Soc., **71**, 3564 (1949).
- 10 P. S. Seward and K. E. Martin, J. Am. Chem. Soc., **71**, 3564 (1949).

HKO

Potassium Hydroxide (KOH)

(Liquid) Mol. Wt. = 56.10937

HKO

MOL. WT. = 56.10937

POTASSIUM HYDROXIDE (KOH)

(LIQUID)

T, °K.	C _p	S°	-(H°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	deg. ⁻¹	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0									
100	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
200	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
298	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
300	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
400	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
500	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
600	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
700	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
800	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
900	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1000	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1100	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1200	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1300	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1400	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1500	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1600	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1700	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1800	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
1900	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
2000	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
2100	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
2200	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
2300	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
2400	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150
2500	19.860	23.518	23.518	0.000	-	98.433	-	88.879	65.150

Dec. 31, 1961; Mar. 31, 1962; Sep. 30, 1962; Mar. 31, 1966

$S_{298.15}^o = 23.518$ cal. deg.⁻¹ mole⁻¹
 $T_m = 675^\circ\text{K.}$
 T_b (monomeric gas) = 1600°K.
 ΔH_f^o (to monomer) = 32.0 kcal. mole⁻¹

Heat of Formation.

The heat of formation of KOH(l) at 298°K. was obtained from that of the crystal by adding ΔH_m^o and the difference between H_{675}^o - H_{298}^o for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase, $C_p = 19.86$ cal. deg.⁻¹ mole⁻¹, was obtained from the enthalpy measurements in the drop calorimeter by W. D. Powers and G. C. Bialook, ORNL-1653, Oak Ridge Nat'l. Lab., Jan. 1954. The constant C_p was extrapolated below the melting point and up to 2500°K.

The entropy, $S_{298.15}^o = 23.51$ cal. deg.⁻¹ mole⁻¹, was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See KOH(c) table for details.

Vaporization Data.

The boiling point 1600°K. was calculated as the temperature at which the free energies of formation (ΔF_f^o) for both KOH(l) and KOH(g) are equal. The difference in the heats of formation (ΔH_f^o) of KOH(l) and KOH(g) at the boiling point is the heat of vaporization. If $K_2(OH)_2(g)$ is also considered as a minor component in the vapor mixture (approximately 2% of total vapor pressure at the boiling point) the calculated boiling point is unchanged as 1600°K. (see KOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. **21**, 162 (1921), have studied the vapor pressures of liquid KOH and reported the boiling point as 1597°K.

HKO

Potassium Hydroxide (KOH)

HKO

(Ideal Gas) Mol. Wt. = 56.10937

POTASSIUM HYDROXIDE (KOH)

(IDEAL GAS)

MOL. WT. = 56.10937

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	8.000	0.000	INFINITE	-	2.566	-	54.258	INFINITE
100	8.978	48.790	54.695	59.269	1.911	-	55.014	1.207
200	9.497	54.695	58.392	58.392	0.000	-	55.434	61.107
298	9.550	58.392	58.392	58.392	0.000	-	55.434	61.252
300	9.559	58.421	58.393	58.393	0.018	-	55.442	61.002
400	10.028	61.267	58.773	58.773	0.986	-	56.419	56.807
500	10.420	63.549	59.507	59.507	2.021	-	56.914	56.614
600	10.743	65.478	60.346	60.346	3.079	-	56.152	20.434
700	11.012	67.155	61.201	61.201	4.167	-	57.677	17.462
800	11.247	68.601	62.040	62.040	5.281	-	58.027	15.205
900	11.459	69.978	62.869	62.869	6.416	-	58.367	13.436
1000	11.654	71.195	63.684	63.684	7.572	-	58.705	12.017
1100	11.834	72.315	64.364	64.364	8.746	-	59.040	10.644
1200	12.000	73.352	65.070	65.070	9.938	-	59.374	9.353
1300	12.153	74.318	65.744	65.744	11.146	-	59.705	8.259
1400	12.294	75.224	66.380	66.380	12.368	-	60.030	7.320
1500	12.422	76.072	67.007	67.007	13.604	-	60.349	6.522
1600	12.539	76.882	67.622	67.622	14.852	-	60.663	5.792
1700	12.645	77.646	68.168	68.168	16.112	-	60.968	5.162
1800	12.741	78.371	68.715	68.715	17.381	-	61.263	4.602
1900	12.827	79.062	69.262	69.262	18.559	-	61.548	4.099
2000	12.906	79.722	69.749	69.749	19.746	-	61.823	3.647
2100	12.978	80.354	70.239	70.239	21.240	-	62.088	3.238
2200	13.043	80.959	70.713	70.713	22.542	-	62.341	2.865
2300	13.101	81.540	71.171	71.171	23.949	-	62.580	2.525
2400	13.155	82.099	71.615	71.615	25.462	-	62.806	2.212
2500	13.204	82.637	72.045	72.045	26.880	-	63.015	1.925
2600	13.248	83.156	72.462	72.462	27.802	-	63.208	1.658
2700	13.289	83.656	72.868	72.868	29.129	-	63.387	1.412
2800	13.326	84.140	73.262	73.262	30.460	-	63.553	1.183
2900	13.361	84.609	73.645	73.645	31.794	-	63.706	0.969
3000	13.392	85.062	74.018	74.018	33.152	-	63.848	0.773
3100	13.421	85.502	74.382	74.382	34.532	-	63.979	0.582
3200	13.448	85.928	74.736	74.736	35.816	-	64.100	0.406
3300	13.472	86.342	75.081	75.081	37.162	-	64.212	0.240
3400	13.495	86.745	75.418	75.418	38.511	-	64.317	0.085
3500	13.516	87.137	75.748	75.748	39.864	-	64.417	0.000
3600	13.536	87.518	76.069	76.069	41.214	-	64.512	0.203
3700	13.554	87.889	76.384	76.384	42.568	-	64.603	0.335
3800	13.571	88.250	76.691	76.691	43.925	-	64.689	0.461
3900	13.587	88.603	77.000	77.000	45.283	-	64.770	0.581
4000	13.602	88.947	77.287	77.287	46.642	-	64.847	0.695
4100	13.618	89.283	77.575	77.575	48.003	-	64.920	0.804
4200	13.628	89.612	77.858	77.858	49.365	-	65.000	0.908
4300	13.641	89.932	78.135	78.135	50.729	-	65.077	1.008
4400	13.652	90.246	78.407	78.407	52.093	-	65.152	1.104
4500	13.663	90.553	78.675	78.675	53.459	-	65.228	1.196
4600	13.673	90.853	78.935	78.935	54.826	-	65.300	1.285
4700	13.682	91.148	79.192	79.192	56.193	-	65.368	1.370
4800	13.691	91.436	79.444	79.444	57.562	-	65.433	1.453
4900	13.699	91.718	79.691	79.691	58.932	-	65.495	1.532
5000	13.707	91.995	79.935	79.935	60.302	-	65.554	1.609
5100	13.715	92.266	80.174	80.174	61.673	-	65.611	1.684
5200	13.722	92.533	80.409	80.409	63.045	-	65.665	1.756
5300	13.729	92.794	80.640	80.640	64.417	-	65.716	1.827
5400	13.735	93.051	80.868	80.868	65.791	-	65.765	1.895
5500	13.741	93.303	81.091	81.091	67.164	-	65.811	1.962
5600	13.747	93.551	81.312	81.312	68.539	-	65.854	2.027
5700	13.752	93.794	81.529	81.529	69.914	-	65.894	2.091
5800	13.758	94.033	81.742	81.742	71.289	-	65.931	2.153
5900	13.762	94.269	81.952	81.952	72.665	-	65.965	2.214
6000	13.767	94.500	82.160	82.160	74.042	-	65.995	2.274

Mar. 31, 1962; June 30, 1962; Mar. 31, 1966

ΔH_f⁰ = -54.3 ± 5 kcal. mole⁻¹ΔH_f⁰ 298.15 = -55.4 ± 5 kcal. mole⁻¹S_{298.15} = [58.4] cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$$\frac{\omega_j, \text{cm}^{-1}}{408 (1)}$$

$$[1300](1)$$

$$[3700](1)$$

Bond Distance: K-O = [2.21] Å O-H = [0.96] Å

Bond Angle: K-O-H = [110]°

Product of the Moments of Inertia: I_AI_BI_C = [1.2325] × 10⁻¹¹⁶ g.³ cm.⁶σ⁺ = 1

Heat of Formation.

R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. 62, 234 and 486 (1958), have investigated the potassium hydroxide vapor by the mass-spectrometric method and found that the KOH vaporizes mainly as gaseous dimer in the temperature range from 573° to 723°K. Later, Schoonmaker and Porter, J. Chem. Phys. 31, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container. Using the reported partial pressures of KOH(g) and K₂(OH)₂(g) at 641° and 666°K. and JANAF free energy functions, the third law calculations give ΔH_f⁰ 298 = -45.4 ± 5 kcal. mole⁻¹ for 2KOH(g) → K₂(OH)₂(g), and ΔH_f⁰ 298 = 45.41 ± 3.5 kcal. mole⁻¹ for KOH(g), and ΔH_f⁰ 298 = 45.6 ± 5 kcal. mole⁻¹ for 2KOH(g) → K₂(OH)₂(g). The uncertainties given were derived by assuming K₂ to be good to a factor of 5 as stated by the authors and including an extra factor of 2 as possible error in activity. To this was added an estimate of the uncertainty due to functions used. In order to have good agreement between the calculated total pressures of monomeric and dimeric KOH(g) and the observed vapor pressures measured by H. von Wartenberg and F. Albrecht, Z. Elektrochem. 27, 182 (1921), the heat of sublimation to monomeric gas was adjusted to ΔH_g⁰ 298 (to monomer) = 46.08 kcal. mole⁻¹. (The heat of sublimation to dimeric gas was unchanged as ΔH_g⁰ 298 (to dimer) = 45.64 kcal. mole⁻¹). The calculated boiling point is 1600°K. which is in good agreement with 1597 ± 10°K. reported by Wartenberg and Albrecht. The heats of formation were calculated from the selected heats of sublimation as ΔH_f⁰ 298(KOH,g) = -55.4 and ΔH_f⁰ 298(K₂(OH)₂,g) = -157.4 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond distance K-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance K-F(g) (2.17145 Å) which has been accurately measured by R. K. Ritchie and H. Lew, Can. J. Phys. 42, 43 (1964). The bond distance O-H was estimated from that in H₂O(g). The bent molecular configuration with the bond angle of 110° has been proposed by S. H. Bauer, R. M. Diner and R. F. Porter, J. Chem. Phys. 29, 931 (1958), but a linear model has also been suggested by R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. 31, 830 (1959). The bent model has been adopted in the tabulation. The three principal moments of inertia are: I_A = [0.1256] × 10⁻³⁹, I_B = [9.8070] × 10⁻³⁹ and I_C = [9.9326] × 10⁻³⁹ g. cm.².

The K-O stretching frequency (408 cm.⁻¹) was obtained from L. H. Spinar and J. L. Margrave, Spectrochim. Acta 12, 244 (1957) in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

L. Brewer and D. F. Mastick, J. Am. Chem. Soc. 73, 2045 (1951), have calculated theoretically the bond distances of gaseous alkali oxides (Li-O = 1.52 Å, Na-O = 1.94 Å and K-O = 2.27 Å) which have been quoted by Bauer, Diner and Porter, loc. cit., and many other authors.

HKO

T, K	Cp ^a	$-(G^{\circ}-H^{\circ}_{298})/T$ S ^b	$-(G^{\circ}-H^{\circ}_{298})/T$ kcal/mol	ΔH°	ΔG°	Log Kp
0	-0.00	-0.00	INFINITE	20.446	20.446	INFINITE
100	1.524	9.165	20.903	20.903	16.563	62.755
200	4.486	2.561	21.338	21.338	16.050	19.724
298	6.682	4.769	21.660	21.660	16.362	11.494
300	6.712	4.830	21.665	21.665	16.330	11.696
400	8.316	6.988	21.679	21.679	14.515	7.931
500	9.736	8.968	21.689	21.689	12.863	5.500
600	11.085	10.803	21.695	21.695	11.464	3.842
700	12.399	12.500	21.700	21.700	10.318	2.640
800	13.694	14.161	21.705	21.705	9.317	1.780
900	14.980	15.795	21.710	21.710	8.456	1.109
1000	16.259	17.413	21.715	21.715	7.735	.656
1100	17.534	19.022	21.720	21.720	7.151	.357
1200	18.805	20.622	21.725	21.725	6.699	.202
1300	20.075	22.218	21.730	21.730	6.370	.120
1400	21.343	23.812	21.735	21.735	6.100	.079
1500	22.610	25.402	21.740	21.740	5.882	.055

Sept. 30, 1962; Sept. 30, 1967

$$\Delta H^{\circ}_{298} = -20.45 \pm 0.03 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{298,15} = -21.86 \pm 0.03 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 6.40 \pm 0.10 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{298,15} = 55.27 \text{ kcal/mol}$$

Heat of Formation

The heats of solution of Li(c) and LiH(c) in water have been measured by Guntz (1) and Moers (2) using an open Dewar flask calorimeter and by Messer (3) and Gunn (4) using closed bomb calorimetry. Based on the reported values of the enthalpy changes (ΔH°) for the reaction (A) $\text{Li(c)} + \text{H}_2\text{O(l)} = \text{LiOH(aq)} + 1/2\text{H}_2\text{(g)}$, and (B) $\text{LiH(c)} + \text{H}_2\text{O(l)} = \text{LiOH(aq)} + \text{H}_2\text{(g)}$, the corresponding ΔH°_{298} for LiH(c) are calculated. The results are presented in the table below.

The decomposition pressures of LiH(c) have been determined by Hurd (5), at temperatures 782 - 928°K. By use of the second and third law methods, the enthalpy changes for the decomposition reaction (C) $\text{LiH(c)} = \text{Li(l)} + 1/2\text{H}_2\text{(g)}$ are evaluated as 21.87 ± 0.3 and 22.34 kcal/mol , respectively. Based on the third law ΔH°_{298} and $\Delta H^{\circ}_{298}(\text{Li, l}) = 0.569 \text{ kcal/mol}$, we derive the value $\Delta H^{\circ}_{298}(\text{LiH, c}) = -21.77 \pm 0.2 \text{ kcal/mol}$, which is in good agreement with the values obtained by calorimetric method. Guntz (1) measured the decomposition pressure at 953°K for the same reaction. The third law ΔH°_{298} and $\Delta H^{\circ}_{298}(\text{LiH, c})$ are evaluated as 21.86 and -21.29 kcal/mol , respectively.

Johnson (6) has determined the standard Gibbs energy of formation (ΔG°) for LiH(c) from emf measurements over the temperature range 875 - 885°K. The cell utilized an Amoco Iron flag over which H_2 was passed as the cathode and a molten Li anode. LiCl, LiBr and LiI, each saturated with LiH, were used as electrolytes. Using the reported emf values at different temperatures (47 data points) for reaction (C), we derive a $\Delta H^{\circ}_{298} = -21.81 \text{ kcal/mol}$ for LiH(c). The $\Delta H^{\circ}_{298}(\text{LiH, c})$ value reported by Gunn (4) is adopted.

Investigator	Reaction A	Reaction B	Reaction C	Drift eu	ΔH°_{298} kcal/mol
1. Guntz (1896)	-53.2	-31.6	-	-	-21.6
2. Moers (1920)	-52.74±0.2	-31.15±0.1	21.86	-	-21.29
3. Messer (1955)	-53.10±0.11	-31.76±0.10	-	-	-21.34±0.15
4. Gunn (1958)	-53.14±0.02	-31.48±0.02	-	-	-21.66±0.03
5. Hurd (1935)	-	-	22.34	0.5±0.3	-21.77±0.2
6. Johnson (1966)	-	-	22.38	1.0±0.2	-21.81±0.15

Heat Capacity and Entropy

The low temperature heat capacities are obtained from the data of Kostyukov (7), 3.72 - 285.5°K. The cp data reported by Gunther (8) are consistently lower than the adopted ones in the temperature range 74.0 - 90.5°K but considerably higher at 292.7°K. The high temperature enthalpies have been determined by Fieldhouse (9), 413.2 - 914.3°K, and Vogt (14), 878.15 - 953.15°K. The derived high temperature heat capacities are joined smoothly with the low temperature values and extrapolated smoothly above 953.15°K.

S°_{298} is calculated based on the adopted low temperature heat capacities, using $S^{\circ}_0 = 0.0002 \text{ eu}$.

Melting Data

The value of T_m has been reported as 953 (1), 961 ± 1 (10, 12), 959.6 (11), and 961.8 ± 0.3 (13). The value reported by Messer (13) is adopted. The heat of melting (ΔH_m°) has been determined as 5.095 ± 0.46 (13) and $5.237 \pm 0.040 \text{ kcal/mol}$ (14). The first ΔH_m° value was evaluated cryogenically from the lowering of melting point in the systems LiH-Li₂O and LiH-CaH₂.

The second value was derived from enthalpy data measured with copper block calorimeter. The adopted ΔH_m° value is derived from the enthalpy data of Vogt (14) using the adopted heat capacities for LiH(c) and LiH(l).

Heat of Sublimation

The value of ΔH°_{298} is calculated as the difference between ΔH°_{298} for LiH(g) and LiH(c).

References

1. A. Guntz, Compt. Rend., 123, 694 (1896).
2. K. Moers, Z. Anorg. Chem., 113, 179 (1920).
3. C. E. Messer, L. G. Fasolino and C. E. Thalmayer, J. Am. Chem. Soc., 77, 4524 (1955).
4. S. R. Gunn and L. G. Green, J. Am. Chem. Soc., 80, 4762 (1958); S. R. Gunn, UCRL-7992, Univ. of California, July 29, 1964.
5. C. B. Hurd and G. A. Moore, Jr., J. Am. Chem. Soc., 57, 332 (1935).
6. C. Johnson, R. A. Heifrich, and C. L. Croft, J. Phys. Chem., 70, 292 (1966).
<7. V. K. Kostyukov, Russ. Phys. Chem., 10, 100 (1936); English transl., J. Phys. Chem., 40, 885 (1936).8. P. Gunther, Ann. Physik, 63, 476 (1920).
9. I. B. Fieldhouse, J. C. Hedge and J. I. Lang, Armour Research Foundation, PB 151583, November 1958.
10. C. E. Messer, E. B. Damon, P. C. Haybury, J. Mellor and R. A. Seales, J. Phys. Chem., 62, 220 (1958).
11. C. E. Messer and J. Mellor, J. Phys. Chem., 64, 503 (1960).
12. C. E. Messer, J. Am. Chem. Soc., 80, 5760 (1958).
13. C. E. Messer, J. Am. Chem. Soc., 80, 5760 (1958).
14. J. W. Vogt, Thompson Ramo Wooldridge Inc., Cleveland, Ohio, NASA N63-22167, June 1962.

Lithium Hydride (LiH)

(Liquid)

GFW = 7.94697

T, °K	Cp	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H^\circ_{298})/T}$	$H^\circ - H^\circ_{298}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100	14,500	5,314	5,314	.000	-14,573	9.846
200	14,500	5,406	5,314	.028	-14,563	9.762
300	14,500	5,493	5,406	.151	-14,541	9.625
400	14,500	5,579	5,493	.275	-14,518	9.444
500	14,500	5,663	5,579	.400	-14,491	9.224
600	14,500	5,734	5,663	.525	-14,461	8.964
700	14,500	5,801	5,734	.650	-14,428	8.664
800	14,500	5,863	5,801	.775	-14,391	8.324
900	14,500	5,920	5,863	.900	-14,351	7.944
1000	14,500	5,972	5,920	1.025	-14,308	7.524
1100	14,500	6,020	6,020	1.150	-14,261	7.064
1200	14,500	6,063	6,063	1.275	-14,211	6.564
1300	14,500	6,101	6,101	1.400	-14,158	6.024
1400	14,500	6,134	6,134	1.525	-14,101	5.444
1500	14,500	6,162	6,162	1.650	-14,041	4.824
1600	14,500	6,185	6,185	1.775	-13,978	4.164
1700	14,500	6,203	6,203	1.900	-13,911	3.564
1800	14,500	6,216	6,216	2.025	-13,841	2.924
1900	14,500	6,224	6,224	2.150	-13,768	2.244
2000	14,500	6,227	6,227	2.275	-13,691	1.524

LITHIUM HYDRIDE (LiH)

(LIQUID)

GFW = 7.94697

 $S^\circ_{298.15} = 5.314 \text{ gibbs/mol}$ $\Delta H^\circ_{298.15} = -18.573 \text{ kcal/mol}$ $T_m = 961.8 \pm 0.3^\circ\text{K}$ $\Delta H_m^\circ = 5.40 \pm 0.10 \text{ kcal/mol}$ $T_d = 1223^\circ\text{K}$

Heat of Formation

 $\Delta H^\circ_{298}(\ell)$ is obtained from $\Delta H^\circ_{298}(c)$ by adding ΔH_m° and the difference between $H^\circ_{961.8} - H^\circ_{298}$ for crystal and liquid.

The decomposition pressures of $\text{LiH}(\ell)$ at different temperatures have been investigated by Hill (1), Perlow (2), Johnson, and Gibb (3). Based on their reported equilibrium pressures, the enthalpy changes for the reaction $\text{LiH}(\ell) = \text{Li}(\ell) + 1/2\text{H}_2(\text{g})$ are evaluated by the second and third law methods. The results are presented in the table below. It should be noted that the measured decomposition pressures are highly sensitive to composition and change extremely rapidly between 99 and 100 percent purity. Therefore we give no weight to the equilibrium data.

Investigator	Temperature, °K	No. of Points	ΔH°_{298} , kcal/mol		ΔH°_{298} , **
			Second Law	Third Law	
Hill (1938)	973.2	1	—	16.93	—
Perlow (1941)	1043-1098	2	20.10	17.69	-2.2
Johnson*	1050-1090	—	24.69	18.36	-5.9
Gibb (1951)	1073-1173	2	5.66	15.2	+8.5

*The vapor pressure values are calculated from an equation quoted by Gibb (3), but derived from the vapor pressures measured by W. C. Johnson, University of Chicago.

**Based on the third law ΔH°_{298} .

Heat Capacity and Entropy

The enthalpies of $\text{LiH}(\ell)$ in the temperature range 975.15-1075.15°K have been measured by Vogt (5). Using the reported enthalpy values, the heat capacity of $\text{LiH}(\ell)$ is derived as 14.9 gibbs/mol. This Cp value is adopted and extrapolated above and below the measured range.

The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See $\text{LiH}(c)$ table for details.

Decomposition Temperature

T_d is calculated as the temperature at which $\text{LiH}(\ell)$ decomposes into $\text{Li}(\ell)$ and $\text{H}_2(\text{g})$ where the partial pressure of $\text{H}_2(\text{g})$ equals one atmosphere.

References

1. L. L. Hill, Ph. D. Thesis, University of Chicago, 1938.
2. M. R. J. Perlow, Ph. D. Thesis, University of Chicago, 1941.
3. T. R. P. Gibb, J. Electrochem. Soc. 93, 198 (1946).
4. T. R. P. Gibb, NEPA-1841, Apr. 30, 1951.
5. J. W. Vogt, Thompson Ramo Wooldridge Inc., Cleveland, Ohio, NASA N63-22167, June 1962.

Ground State Configuration $1s^2$

$$\Delta H_f^\circ = 33.65 \pm 0.01 \text{ kcal/mol}$$

$$\Delta H_f^{298.15} = 33.61 \pm 0.01 \text{ kcal/mol}$$

$$S_{298}^\circ = 40.821 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

$$\epsilon_i, \text{ cm}^{-1}$$

$$\frac{g_i}{\epsilon_i}$$

$$0 \quad 1$$

$$26513.7 \quad 1$$

$$34912.0 \quad 2$$

$$\omega_e x_e = 23.24 \text{ cm}^{-1}$$

$$\sigma = 1$$

$$\nu_e = 0.2137 \text{ cm}^{-1}$$

$$r_e = 1.595 \text{ \AA}$$

Heat of Formation

R. Velasco, Can. J. Phys. **35**, 1204 (1957), observed the absorption spectra of LiH(g) in the near ultraviolet with high dispersion and absorbing path lengths up to 16 meters. He found a new band system involving the ground state and a $^1\Pi$ excited state. Rotational and vibrational analyses of this system were carried out and the observed breaking off of the rotational structure of the bands was interpreted as due to predissociation by rotation. With this assumption very accurate dissociation limits of the $B^1\Pi$ state were obtained. From these dissociation limits the dissociation energy (D_0) of the ground state of LiH was found to be $2.4288 \pm 0.0002 \text{ eV}$. Based on this D_0 value, we adopt $\Delta H_f^\circ = 33.61 \text{ kcal/mol}$ for LiH(g).

W. Kemperer, J. Chem. Phys. **23**, 2452 (1955), observed the infrared spectrum of LiH(g) in emission in the frequency region 1500 to 970 cm^{-1} , using a Perkin-Elmer double-pass monochromator with NaCl optics. Estimating the minimum LiH pressure as 10 mm and assuming the maximum possible Li pressure, he reported $K = 0.005 \text{ (atm)}$ at 1400°K for the reaction $2\text{Li(g)} + \text{H}_2\text{(g)} = 2\text{LiH(g)}$. We calculate the corresponding enthalpy change, ΔH_{1400}° , to be -9.63 kcal/mol , employing $\Delta S_{1400}^\circ = -17.407 \text{ eu}$. Incorporating this ΔH_{1400}° value with $\Delta H_f^\circ = 35.601 \text{ kcal/mol}$ for Li(g), we obtain $\Delta H_f^\circ = 33.92 \text{ kcal/mol}$ for LiH(g), which is in good agreement with the adopted value.

A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953, derived the value $D_0(\text{LiH}) = 2.5 \pm 0.2 \text{ eV}$ from earlier spectroscopic data.

Heat Capacity and Entropy

The third electronic level and quantum weight are obtained from Velasco, loc. cit. All the other constants are taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., and corrected to the average isotopic species. The moment of inertia is $3.7193 \times 10^{-40} \text{ g cm}^2$.

T, °K	C_p°	$\frac{\text{gibbs/mol}}{S^\circ - (G^\circ - H_{298}^\circ)/T}$	$H^\circ - H_{298}^\circ$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	2.076	33.651	33.651	INFINITE
100	6.964	33.183	1.387	33.841	33.841	69.757
200	13.928	36.015	0.800	33.799	32.776	28.994
298	17.104	40.821	0.000	33.610	28.105	20.645
300	7.109	40.865	0.013	33.606	28.131	20.493
400	7.364	42.943	1.736	33.361	26.343	14.393
500	7.655	44.617	1.487	32.344	24.694	10.764
600	7.921	46.037	2.046	32.040	23.192	8.488
700	8.165	47.276	2.680	31.813	21.734	6.786
800	8.399	48.376	3.329	31.592	20.309	5.588
900	8.478	49.366	4.105	31.386	18.911	4.592
1000	8.601	50.265	4.969	31.191	17.535	3.832
1100	8.703	51.090	5.823	31.005	16.179	3.215
1200	8.790	51.851	6.664	30.825	14.839	2.703
1300	8.864	52.558	7.491	30.650	13.513	2.222
1400	8.929	53.217	8.310	30.477	12.202	1.905
1500	8.987	53.835	9.117	30.307	10.903	1.589
1600	9.038	54.417	9.905	30.138	9.615	1.313
1700	9.085	54.966	10.676	29.976	8.345	1.046
1800	9.128	55.487	11.432	29.821	7.094	0.799
1900	9.168	55.981	12.175	29.676	5.861	0.566
2000	9.206	56.448	12.905	29.540	4.646	0.341
2100	9.241	56.892	13.625	29.413	3.450	0.126
2200	9.275	57.333	14.337	29.294	2.273	0.023
2300	9.307	57.766	15.041	29.182	1.124	0.000
2400	9.338	58.183	15.736	29.076	0.000	0.000
2500	9.367	58.585	16.421	28.976	0.000	0.000
2600	9.394	58.963	17.097	28.881	0.000	0.000
2700	9.420	59.328	17.764	28.791	0.000	0.000
2800	9.445	59.681	18.421	28.706	0.000	0.000
2900	9.470	59.993	19.069	28.626	0.000	0.000
3000	9.495	60.285	19.708	28.551	0.000	0.000
3100	9.521	60.556	20.338	28.481	0.000	0.000
3200	9.547	60.807	20.959	28.416	0.000	0.000
3300	9.573	61.048	21.571	28.356	0.000	0.000
3400	9.600	61.281	22.174	28.299	0.000	0.000
3500	9.628	61.505	22.769	28.246	0.000	0.000
3600	9.656	61.720	23.356	28.196	0.000	0.000
3700	9.685	61.927	23.936	28.149	0.000	0.000
3800	9.711	62.125	24.509	28.106	0.000	0.000
3900	9.736	62.315	25.074	28.066	0.000	0.000
4000	9.763	62.500	25.631	28.028	0.000	0.000
4100	9.789	62.686	26.181	27.992	0.000	0.000
4200	9.816	62.872	26.724	27.958	0.000	0.000
4300	9.843	63.059	27.261	27.926	0.000	0.000
4400	9.870	63.246	27.791	27.896	0.000	0.000
4500	9.899	63.433	28.314	27.868	0.000	0.000
4600	9.927	63.620	28.831	27.842	0.000	0.000
4700	9.956	63.807	29.341	27.818	0.000	0.000
4800	9.986	64.000	29.844	27.796	0.000	0.000
4900	10.016	64.200	30.341	27.776	0.000	0.000
5000	10.047	64.400	30.831	27.758	0.000	0.000
5100	10.079	64.600	31.314	27.742	0.000	0.000
5200	10.111	64.800	31.791	27.728	0.000	0.000
5300	10.144	65.000	32.261	27.716	0.000	0.000
5400	10.178	65.200	32.724	27.706	0.000	0.000
5500	10.213	65.400	33.181	27.698	0.000	0.000
5600	10.248	65.600	33.631	27.692	0.000	0.000
5700	10.284	65.800	34.074	27.688	0.000	0.000
5800	10.321	66.000	34.511	27.686	0.000	0.000
5900	10.358	66.200	34.941	27.686	0.000	0.000
6000	10.396	66.400	35.364	27.687	0.000	0.000

Dec. 31, 1960; Sept. 30, 1967

Lithium Hydroxide (LiOH)

(Crystal)

Mol. wt. = 23.94637

LITHIUM HYDROXIDE (LiOH)

(CRYSTAL)

MOL. WT. = 23.94637

HL10

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔG _f °	Log K _p
0	0.000	0.000	INFINITE	-	1.770	-114.456	-114.456	INFINITE
100	3.922	2.044	15.111	-	1.617	-115.178	-111.911	244.591
200	8.600	6.124	11.218	-	1.019	-115.641	-108.442	118.400
298	11.650	10.225	10.225	-	0.000	-115.840	-104.858	76.863
300	11.900	10.269	10.225	-	0.022	-115.842	-104.790	76.339
400	15.500	14.020	10.719	-	2.760	-115.862	-101.937	42.544
500	18.250	17.272	11.712	-	2.760	-115.840	-97.537	42.546
600	16.300	20.143	12.882	-	4.357	-116.404	-93.507	34.060
700	17.370	22.737	14.107	-	6.040	-116.161	-89.709	26.008
800	18.165	25.117	15.337	-	7.824	-115.821	-85.953	23.481
900	18.636	27.248	16.486	-	9.608	-115.481	-82.248	21.000
1000	18.936	29.303	17.723	-	11.580	-114.981	-78.576	17.173
1100	19.807	31.168	18.661	-	13.538	-114.484	-74.961	14.693
1200	20.234	32.910	19.660	-	15.540	-113.971	-71.390	13.002
1300	20.630	34.546	21.020	-	17.583	-113.414	-67.865	11.409
1400	21.004	36.068	22.042	-	19.663	-112.816	-64.382	10.050
1500	21.350	37.500	23.027	-	21.763	-112.216	-60.944	8.888
1600	21.704	38.939	23.979	-	23.937	-111.565	-57.546	7.860
1700	22.038	40.265	24.898	-	26.124	-145.939	-52.862	6.796
1800	22.364	41.534	25.787	-	28.344	-145.059	-47.412	5.757
1900	22.680	42.746	26.646	-	30.594	-144.145	-42.144	4.744
2000	23.000	43.923	27.483	-	32.881	-143.225	-36.059	4.006

S₂₉₈⁰ = 10.225 cal. deg.⁻¹ mole⁻¹
 T_m = 744.3°K.

Heat of Formation.

The standard enthalpy of formation, ΔH_f⁰ 298 (LiOH, c) = -115.84 ± 0.1 kcal. mole⁻¹, was calculated from the heat of solution of lithium hydroxide (c), the heat of hydrolysis of lithium metal and the appropriate auxiliary data. N. A. Fessenden⁷ has measured the heat of solution LiOH(c) → LiOH(400 H₂O) as -5.479 ± 0.007 kcal. mole⁻¹ at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker², the selected heat of solution of lithium hydroxide (c) at infinite dilution is -5.632 kcal. mole⁻¹.

The heat of hydrolysis of lithium metal, ΔH_f⁰ 298, has been measured in the solution calorimeter by the following investigators.

Source	Number of moles of H ₂ O	ΔH _f ⁰ 298 kcal. mole ⁻¹	ΔH _f ⁰ 298 (LiOH(c)) kcal. mole ⁻¹	ΔH _f ⁰ 298 (LiOH, c) kcal. mole ⁻¹
Gunn et al. ³	1000	-53.115 ± 0.019	-121.532	-115.900
Messer et al. ⁴	∞	-53.075 ± 0.20	-121.380	-115.758

The values of ΔH_f⁰ 298 (LiOH(c)) were calculated from the heats of reaction ΔH_f⁰ 298, using the ΔH_f⁰ 298 (H₂O, l) = -68.315 kcal. mole⁻¹.⁵ Combination of the selected heat of solution of LiOH(c) at infinite dilution with the heat of formation of LiOH(c) gives the heat of formation of LiOH(c) in the last column of the table. A weighted average of these measurements was taken for the adopted heat of formation of lithium hydroxide (c).

The earlier calorimetric investigations have been reviewed by P. R. Bichowsky and P. D. Rossini⁶, and C. E. Messer et al.⁴, and these data are not adopted in the tabulation.

Heat Capacity and Entropy.

The low temperature heat capacities of lithium hydroxide (c) from 15.91° to 302.85°K. have been measured by T. W. Bauer, H. L. Johnston and E. C. Kerr.⁷ The high temperature heat capacities which were determined from the enthalpy measurements in the temperature range from 418° to 876°K. by the drop method have been reported by C. H. Shomate and A. J. Cohen.⁸ The low temperature and the high temperature heat capacities have been joined smoothly by the Shomate method.⁹ The smooth values of heat capacity of LiOH(c) were adopted in the tabulation.

W. D. Powers and O. C. Blalock¹⁰ have also measured the high temperature enthalpy changes of LiOH(c) by the drop method. Their results are in agreement with the tabulated H_m-H₂₉₈ values within the experimental uncertainty. The entropy (S₂₉₈⁰ = 10.225 cal. deg.⁻¹ mole⁻¹) was obtained from Bauer et al.⁷, based on an extrapolation of S₁₆⁰ = 0.028 cal. deg.⁻¹ mole⁻¹.

Melting Data.

The adopted heat of melting and the melting point were obtained from the enthalpy measurements by Shomate and Cohen.⁸ Powers and Blalock¹⁰ also found the heat of melting ΔH_m⁰ = 5.029 kcal. mole⁻¹ at 746°K. which is in good agreement with the adopted value.

Reference:

- N. A. Fessenden, Zhur. Neorg. Khim., **6**, 682 (1961).
- V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-RS-NBS 2, Apr. 1965.
- S. R. Gunn and L. O. Green, J. Am. Chem. Soc., **80**, 4782 (1958).
- S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking-Boat Solution Calorimeters," J. Am. Chem. Soc., **77**, 4524 (1955).
- C. E. Messer, L. O. Fasolino and C. E. Thalmer, J. Am. Chem. Soc., **77**, 4524 (1955).
- D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, NBS Technical Note 270-1, Oct. 1965.
- P. R. Bichowsky and P. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp. New York, 1955.
- T. W. Bauer, H. L. Johnston and E. C. Kerr, J. Am. Chem. Soc., **72**, 5174 (1950).
- C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc., **77**, 285 (1955).
- C. H. Shomate, J. Phys. Chem., **59**, 568 (1955).
- W. D. Powers and O. C. Blalock, "Enthalpy and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures," ORNL-1655, Oak Ridge Nat'l. Lab., Jan. 1954.

HL10

T, K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0								
100	20.740	11.574	11.574	0.000	-113.263	-102.683		75.269
200	20.740	11.702	11.575	0.038	-113.249	-102.618		74.757
300	20.740	11.769	11.575	0.098	-113.249	-102.618		74.194
400	20.740	11.829	11.575	0.146	-113.249	-102.618		73.725
500	20.740	11.879	11.575	0.186	-113.249	-102.618		73.325
600	20.740	11.924	11.575	0.220	-113.249	-102.618		72.916
700	20.740	11.964	11.575	0.250	-113.249	-102.618		72.506
800	20.740	12.000	11.575	0.276	-113.249	-102.618		72.096
900	20.740	12.034	11.575	0.300	-113.249	-102.618		71.686
1000	20.740	12.067	11.575	0.322	-113.249	-102.618		71.276
1100	20.740	12.099	11.575	0.344	-113.249	-102.618		70.866
1200	20.740	12.130	11.575	0.366	-113.249	-102.618		70.456
1300	20.740	12.160	11.575	0.388	-113.249	-102.618		70.046
1400	20.740	12.189	11.575	0.409	-113.249	-102.618		69.636
1500	20.740	12.218	11.575	0.430	-113.249	-102.618		69.226
1600	20.740	12.246	11.575	0.451	-113.249	-102.618		68.816
1700	20.740	12.274	11.575	0.472	-113.249	-102.618		68.406
1800	20.740	12.301	11.575	0.493	-113.249	-102.618		67.996
1900	20.740	12.328	11.575	0.514	-113.249	-102.618		67.586
2000	20.740	12.355	11.575	0.535	-113.249	-102.618		67.176
2100	20.740	12.382	11.575	0.556	-113.249	-102.618		66.766
2200	20.740	12.408	11.575	0.577	-113.249	-102.618		66.356
2300	20.740	12.435	11.575	0.598	-113.249	-102.618		65.946
2400	20.740	12.461	11.575	0.619	-113.249	-102.618		65.536
2500	20.740	12.487	11.575	0.640	-113.249	-102.618		65.126
2600	20.740	12.513	11.575	0.661	-113.249	-102.618		64.716
2700	20.740	12.539	11.575	0.682	-113.249	-102.618		64.306
2800	20.740	12.565	11.575	0.703	-113.249	-102.618		63.896
2900	20.740	12.591	11.575	0.724	-113.249	-102.618		63.486
3000	20.740	12.617	11.575	0.745	-113.249	-102.618		63.076
3100	20.740	12.643	11.575	0.766	-113.249	-102.618		62.666
3200	20.740	12.669	11.575	0.787	-113.249	-102.618		62.256
3300	20.740	12.695	11.575	0.808	-113.249	-102.618		61.846
3400	20.740	12.721	11.575	0.829	-113.249	-102.618		61.436
3500	20.740	12.747	11.575	0.850	-113.249	-102.618		61.026

Dec. 31, 1960; Mar. 31, 1966

S_{298.15} = 11.574 cal. deg.⁻¹ mole⁻¹
 T_m = 744.3°K.
 T_b(monomeric gas) = 1803°K.
 ΔH_f° 298.15 = -113.263 kcal. mole⁻¹
 ΔH_m° = 5.010 kcal. mole⁻¹
 ΔH_v°(to monomer) = 40.1 kcal. mole⁻¹

Heat of Formation.

The heat of formation of LiOH(l) at 298.15°K. was obtained from that of the crystal by adding ΔH_m° and the difference between H_{744.3}°K. 298.15 for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacity of the liquid phase, C_p = 20.74 cal. deg.⁻¹ mole⁻¹, was obtained from the enthalpy measurements in the drop calorimeter by C. H. Shomate and A. J. Cohen, J. Am. Chem. Soc. **77**, 285 (1955).

W. D. Powers and G. C. Blalock, ORNL-1653, Oak Ridge Nat'l. Lab., have also determined the heat capacity of lithium hydroxide (l), C_p = 22.03 cal. deg.⁻¹ mole⁻¹, from the enthalpy measurements by the drop method.

The entropy (S_{298.15} = 11.574 cal. deg.⁻¹ mole⁻¹) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiOH(c) table for details.

Vaporization Data.

The boiling point was calculated as the temperature at which the free energies of formation (ΔF_f°) for both LiOH(l) and LiOH(g) are equal. The difference in the heats of formation (ΔH_f°) of LiOH(l) and LiOH(g) at the boiling point is the heat of vaporization (ΔH_v°).

Lithium Hydroxide (LiOH)

(Ideal Gas) Mol. Wt. = 23.94637

LITHIUM HYDROXIDE (LiOH)

(IDEAL GAS)

MOL. WT. = 23.94637

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	2.400	58.089	58.089	INFINITE
100	7.949	43.240	59.292	1.605	58.149	128.947
200	8.041	48.764	52.803	1.808	58.433	65.305
298	8.474	52.044	0.000	58.843	60.329	44.222
300	8.485	52.097	0.016	58.851	60.339	43.957
400	9.107	52.822	5.384	59.296	60.767	33.202
500	9.686	56.718	1.835	60.488	61.008	26.666
600	10.163	58.228	53.813	2.829	60.935	22.244
700	10.551	60.124	54.603	3.865	61.339	19.063
800	10.852	61.253	55.183	4.863	61.563	16.563
900	11.093	62.459	60.030	61.033	61.882	14.342
1000	11.400	64.041	56.874	7.146	62.398	13.273
1100	11.620	65.138	57.576	8.318	62.717	12.030
1200	11.818	66.157	58.249	9.490	63.024	10.989
1300	12.000	67.195	58.912	10.662	63.326	10.088
1400	12.157	68.200	59.515	11.888	63.606	9.342
1500	12.302	68.849	60.108	13.111	63.885	8.679
1600	12.432	69.647	60.680	14.348	64.156	8.096
1700	12.550	70.405	61.230	15.597	64.469	7.409
1800	12.657	71.112	61.750	16.858	64.762	6.658
1900	12.755	71.772	62.250	18.128	65.045	5.858
2000	12.837	72.468	62.764	19.408	65.318	5.088
2100	12.915	73.096	63.241	20.695	65.577	4.369
2200	12.985	73.699	63.703	21.960	65.824	3.696
2300	13.050	74.276	64.140	23.200	66.060	3.076
2400	13.106	74.831	64.560	24.460	66.280	2.506
2500	13.159	75.370	65.005	25.913	66.492	2.006
2600	13.207	75.887	65.413	27.231	66.696	1.566
2700	13.251	76.386	65.811	28.594	66.892	1.186
2800	13.291	76.866	66.197	29.921	67.079	0.866
2900	13.327	77.329	66.571	31.221	67.257	0.596
3000	13.361	77.788	66.939	32.547	67.427	0.366
3100	13.392	78.227	67.297	33.884	67.589	0.176
3200	13.420	78.655	67.645	35.225	67.743	0.026
3300	13.446	79.066	67.985	36.568	67.889	-0.174
3400	13.470	79.461	68.319	37.914	68.028	-0.374
3500	13.493	79.859	68.641	39.242	68.161	-0.574
3600	13.514	80.239	68.958	40.613	68.289	-0.774
3700	13.533	80.610	69.268	41.965	68.412	-0.974
3800	13.552	80.971	69.571	43.319	68.530	-1.174
3900	13.569	81.321	69.868	44.666	68.644	-1.374
4000	13.584	81.667	70.158	46.033	68.753	-1.574
4100	13.599	82.002	70.443	47.392	68.857	-1.774
4200	13.612	82.330	70.722	48.753	68.956	-1.974
4300	13.627	82.651	71.006	50.118	69.051	-2.174
4400	13.639	82.967	71.285	51.487	69.142	-2.374
4500	13.650	83.271	71.558	52.842	69.229	-2.574
4600	13.659	83.571	71.866	54.207	69.312	-2.774
4700	13.669	83.864	72.040	55.574	69.391	-2.974
4800	13.678	84.152	72.290	56.947	69.466	-3.174
4900	13.688	84.432	72.530	58.310	69.537	-3.374
5000	13.696	84.711	72.775	59.679	69.604	-3.574
5100	13.704	84.982	73.012	61.049	69.667	-3.774
5200	13.711	85.249	73.245	62.420	69.726	-3.974
5300	13.718	85.511	73.474	63.791	69.781	-4.174
5400	13.725	85.769	73.699	65.162	69.832	-4.374
5500	13.732	86.018	73.921	66.536	69.879	-4.574
5600	13.738	86.266	74.139	67.910	69.922	-4.774
5700	13.744	86.509	74.354	69.284	69.961	-4.974
5800	13.750	86.746	74.566	70.658	69.996	-5.174
5900	13.756	86.988	74.766	72.032	70.027	-5.374
6000	13.759	87.214	74.979	73.409	70.054	-5.574

Dec. 31, 1960; Mar. 31, 1966

Point Group C_s
 $S_{298.15}^\circ = [52.0] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = 1

$\Delta H_f^\circ 0 = -58.1 \pm 4 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -58.8 \pm 4 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

$\omega_e, \text{ cm.}^{-1}$
 $\frac{[1000](1)}{[1300](1)}$
 $\frac{[1000](1)}{[3700](1)}$

Bond Distances: Li-O = $[1.60] \text{ \AA}$ O-H = $[0.96] \text{ \AA}$
 Bond Angle: Li-O-H = $[110]^\circ$
 Product of the Moments of Inertia: $I_{AB}I_C = [0.6156 \times 10^{-117}] \text{ g.}^3 \text{ cm.}^6$

$\sigma = 1$

Heat of Formation

J. Berkowitz, D. J. Menchi and M. A. Chupka, J. Chem. Phys. 33, 535 (1960), have studied the equilibrium of $\text{Li}_2\text{O}(c) + \text{H}_2\text{O}(g)$ system by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K , the heat of reaction $\text{Li}_2\text{O}(c) + \text{H}_2\text{O}(g) \rightarrow 2\text{LiOH}(g)$ at 298.15°K has been calculated by both the second and the third law methods as 86.1 and $83.2 \text{ kcal. mole}^{-1}$, respectively. (The third law drift is $-2.2 \pm 2.6 \text{ e.u.}$) The third law value was taken for the calculation of the heat of formation of $\text{LiOH}(g)$ at 298.15°K .

Heat Capacity and Entropy

Since the bond distance Li-F(g) ($r_e = 1.56389 \text{ \AA}$) was accurately measured from the microwave studies by L. Wharton, W. Klempner, L. P. Gold, R. Strauch, J. J. Gallagher and V. E. Derr, J. Chem. Phys. 39, 1203 (1963), the bond distance Li-O in $\text{LiOH}(g)$ was estimated by adding the bond length difference (0.04 \AA) between H-OH(g) and H-F(g) to the bond distance Li-F(g). Also the bond distance Li-O(g) was estimated as 1.62 \AA from the matrix-isolated infrared spectrum by D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963). These two are in good agreement. The bond distance O-H was estimated from that in $\text{H}_2\text{O}(g)$. The adopted bent molecular configuration with bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. F. Porter, J. Chem. Phys. 29, 991 (1958). The three principal moments of inertia are $I_A = [0.1237] \times 10^{-39}$, $I_B = [2.1699] \times 10^{-39}$ and $I_C = [2.2956] \times 10^{-39} \text{ g. cm.}^2$.

The Li-O stretching frequency was estimated to be the same as that in $\text{Li}_2\text{O}(g)$ ($\nu = 987 \text{ cm.}^{-1}$, see $\text{Li}_2\text{O}(g)$ table). The bending and the O-H stretching frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rapid convergence to a constant as a heavier atom is attached.

MAGNESIUM MONOHYDRIDE (MgH) (IDEAL GAS) GFW = 25.31997

T, °K	C _p ^a	S ^b	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔH ^c	ΔG ^c	Log K _p
0	∞.000	∞.000	INFINITE	- 2.075	40.533	40.533	INFINITE
100	6.991	38.524	52.471	- 1.385	40.690	36.284	- 83.670
200	6.973	43.132	46.792	- .688	40.523	35.611	- 39.132
298	7.070	46.150	46.150	∞.000	40.400	35.022	- 24.646
300	7.074	46.150	∞.013	40.396	33.580	24.463	
400	7.288	48.257	46.430	∞.731	40.152	31.344	- 17.126
500	7.572	49.915	46.966	1.474	39.904	29.172	- 12.751
600	7.834	51.319	47.577	2.265	39.654	27.047	- 9.852
700	8.060	52.544	48.201	3.040	39.407	24.967	- 7.795
800	8.248	53.633	48.813	3.856	39.145	22.921	- 6.262
900	8.403	54.614	49.404	4.688	38.860	20.910	- 5.078
1000	8.531	55.506	49.971	5.535	38.429	19.113	- 4.177
1100	8.638	56.324	50.511	6.394	38.123	17.395	- 3.456
1200	8.728	57.080	51.028	7.262	37.797	15.708	- 2.861
1300	8.806	57.781	51.521	8.139	37.449	14.047	- 2.362
1400	8.873	58.436	51.991	9.033	4.712	12.894	- 2.013
1500	8.933	59.051	52.442	9.914	4.723	13.478	- 1.964
1600	8.986	59.629	52.873	10.810	4.733	14.040	- 1.920
1700	9.034	60.175	53.287	11.711	4.743	14.645	- 1.883
1800	9.078	60.693	53.684	12.616	4.753	15.226	- 1.849
1900	9.119	61.185	54.066	13.526	4.764	15.807	- 1.818
2000	9.157	61.656	54.434	14.440	4.773	16.387	- 1.791
2100	9.193	62.101	54.788	15.358	4.782	16.968	- 1.765
2200	9.227	62.530	55.130	16.279	4.790	17.549	- 1.743
2300	9.260	62.941	55.461	17.203	4.798	18.129	- 1.723
2400	9.293	63.335	55.781	18.131	4.805	18.710	- 1.704
2500	9.324	63.715	56.091	19.061	4.810	19.287	- 1.686
2600	9.355	64.082	56.391	19.995	4.816	19.867	- 1.670
2700	9.387	64.435	56.683	20.933	4.821	20.446	- 1.659
2800	9.418	64.777	56.966	21.873	4.826	21.022	- 1.641
2900	9.450	65.108	57.241	22.816	4.830	21.604	- 1.628
3000	9.483	65.429	57.508	23.763	4.833	22.180	- 1.616
3100	9.517	65.741	57.769	24.713	4.836	22.757	- 1.604
3200	9.551	66.043	58.023	25.666	4.837	23.336	- 1.594
3300	9.586	66.338	58.270	26.623	4.838	23.913	- 1.584
3400	9.623	66.625	58.512	27.584	4.837	24.492	- 1.574
3500	9.661	66.904	58.748	28.548	4.833	25.070	- 1.565
3600	9.700	67.177	58.978	29.516	4.828	25.648	- 1.557
3700	9.741	67.443	59.203	30.488	4.819	26.229	- 1.549
3800	9.783	67.704	59.424	31.464	4.810	26.806	- 1.542
3900	9.826	67.958	59.639	32.445	4.796	27.385	- 1.535
4000	9.871	68.208	59.850	33.429	4.779	27.963	- 1.528
4100	9.917	68.452	60.057	34.419	4.757	28.543	- 1.522
4200	9.965	68.691	60.260	35.413	4.732	29.126	- 1.516
4300	10.013	68.926	60.459	36.412	4.701	29.706	- 1.510
4400	10.063	69.157	60.654	37.416	4.667	30.288	- 1.504
4500	10.114	69.384	60.845	38.425	4.626	30.870	- 1.499
4600	10.167	69.607	61.033	39.439	4.570	31.455	- 1.494
4700	10.220	69.826	61.218	40.458	4.520	32.045	- 1.490
4800	10.274	70.042	61.400	41.483	4.467	32.626	- 1.485
4900	10.330	70.254	61.578	42.513	4.400	33.215	- 1.481
5000	10.386	70.461	61.754	43.549	4.327	33.804	- 1.478
5100	10.443	70.670	61.927	44.590	4.245	34.388	- 1.474
5200	10.501	70.873	62.097	45.637	4.155	34.983	- 1.470
5300	10.559	71.074	62.264	46.690	4.057	35.578	- 1.467
5400	10.618	71.272	62.429	47.749	3.950	36.169	- 1.464
5500	10.678	71.467	62.592	48.814	3.833	36.770	- 1.461
5600	10.739	71.660	62.752	49.885	3.706	37.368	- 1.458
5700	10.799	71.850	62.910	50.962	3.570	37.978	- 1.456
5800	10.861	72.039	63.066	52.045	3.423	38.574	- 1.454
5900	10.922	72.225	63.219	53.134	3.265	39.187	- 1.452
6000	10.984	72.409	63.371	54.229	3.096	39.792	- 1.449

Dec. 31, 1980; Dec. 31, 1956

Ground State Configuration $2\Sigma^+$

$S_{298.15}^\circ = 46.15$ gibbs/mol

$\Delta H_f^\circ = 40.5 \pm 11.5$ kcal/mol

$\Delta H_{298.15}^\circ = 40.4 \pm 11.5$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	ϵ_1	$\epsilon_1, \text{cm}^{-1}$	ϵ_1	$\epsilon_1, \text{cm}^{-1}$	ϵ_1
0	2	35400	2	42070	2
19221.2	2	[36730]	2	48000	4
19224.7	2	41120	4		

$\omega_e = 1495.7 \text{ cm}^{-1}$

$\omega_e x_e = 31.5 \text{ cm}^{-1}$

$\sigma = 1$

$\alpha_e = 0.1668 \text{ cm}^{-1}$

$x_e = 1.73 \text{ \AA}$

Heat of Formation.

The heat of formation is calculated using $D_0^\circ = 2.0 \pm 0.5$ e.v. derived from a graphical extrapolation of the $V(0-3)$ energy levels of the $X^2\Sigma^+$ state reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Edition, Chapman and Hall Ltd., London, 1953. G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Co., Inc., New York, 1950, reported $D_0^\circ \leq 2.49$ e.v. assuming predissociation of the $c^4\Pi$ state of MgH into $\text{Mg}(^3P)$ and $\text{H}(^2S)$.

Heat Capacity and Entropy.

The molecular constants and electronic levels are obtained from Herzberg, loc. cit., except for the electronic levels 35400 and 48000 obtained from M. A. Khan, Proc. Phys. Soc. (London) **80**, 209 - 21 (1962).

Magnesium Monohydroxide (MgOH)
(Ideal Gas) $\text{GFW} = 41.31937$

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^b	ΔG ^c	Log K _p
0	6.958	0.000	INFINITE	2.169	50.923	50.923	INFINITE
100	6.958	44.924	53.640	1.474	51.109	52.085	113.831
200	7.320	49.812	53.644	1.767	51.613	52.995	57.910
298	8.360	52.916	52.916	0.000	52.000	53.499	39.209
300	8.362	52.968	52.916	0.015	52.009	53.499	39.674
400	9.485	55.535	53.259	1.810	52.430	53.931	29.467
500	10.342	57.748	53.940	1.804	52.793	54.262	23.718
600	10.970	59.692	54.740	2.071	53.123	54.526	19.861
700	11.413	61.344	55.543	2.309	53.426	54.747	16.814
800	11.717	62.674	56.243	2.527	53.747	54.929	14.098
900	12.128	64.384	57.213	2.654	54.074	55.023	11.361
1000	12.394	65.676	57.995	2.681	54.539	54.929	12.005
1100	12.528	66.899	58.749	2.681	54.872	54.754	10.879
1200	12.628	68.011	59.466	2.655	55.167	54.504	9.910
1300	12.699	69.011	60.146	2.605	55.426	54.204	9.130
1400	12.743	69.902	60.833	2.538	55.653	53.862	8.362
1500	12.763	70.697	61.474	2.465	55.849	53.491	7.642
1600	12.761	71.401	62.080	2.383	56.016	53.004	6.969
1700	12.736	72.019	62.646	2.295	56.156	52.496	6.339
1800	12.688	72.557	63.183	2.203	56.268	51.974	5.759
1900	12.617	73.013	63.687	2.108	56.354	51.443	5.220
2000	12.524	73.394	64.163	2.012	56.416	50.900	4.728
2100	12.411	73.690	64.614	1.916	56.456	50.348	4.276
2200	12.278	73.905	65.043	1.821	56.476	49.788	3.869
2300	12.128	74.033	65.453	1.727	56.476	49.218	3.501
2400	11.963	74.075	65.835	1.635	56.456	48.640	3.168
2500	11.784	74.033	66.197	1.545	56.416	48.056	2.872
2600	11.597	73.905	66.536	1.458	56.354	47.468	2.614
2700	11.405	73.690	66.846	1.374	56.268	46.876	2.389
2800	11.207	73.394	67.128	1.293	56.156	46.280	2.196
2900	11.004	73.013	67.387	1.215	56.016	45.680	2.032
3000	10.797	72.557	67.619	1.141	55.849	45.076	1.896
3100	10.586	72.019	67.820	1.071	55.653	44.468	1.784
3200	10.371	71.401	67.995	1.005	55.426	43.856	1.692
3300	10.152	70.697	68.133	0.943	55.167	43.240	1.624
3400	9.929	69.902	68.233	0.885	54.872	42.620	1.576
3500	9.702	69.011	68.297	0.831	54.539	42.000	1.548
3600	9.471	68.011	68.326	0.781	54.167	41.376	1.536
3700	9.236	66.899	68.318	0.734	53.747	40.748	1.536
3800	8.997	65.676	68.274	0.691	53.268	40.116	1.548
3900	8.754	64.384	68.197	0.651	52.729	39.480	1.572
4000	8.507	63.011	68.080	0.613	52.132	38.836	1.608
4100	8.256	61.543	67.923	0.578	51.476	38.184	1.656
4200	8.001	60.080	67.728	0.546	50.764	37.524	1.716
4300	7.743	58.628	67.495	0.517	50.000	36.856	1.788
4400	7.482	57.183	67.228	0.491	49.192	36.180	1.872
4500	7.217	55.748	66.928	0.467	48.340	35.496	1.968
4600	6.958	54.326	66.592	0.445	47.448	34.804	2.076
4700	6.705	52.916	66.213	0.425	46.516	34.104	2.196
4800	6.457	51.513	65.792	0.407	45.544	33.400	2.328
4900	6.214	50.119	65.333	0.391	44.532	32.692	2.472
5000	5.976	48.743	64.837	0.376	43.480	31.980	2.628
5100	5.743	47.384	64.305	0.362	42.396	31.264	2.796
5200	5.515	46.043	63.738	0.349	41.276	30.544	2.976
5300	5.292	44.716	63.137	0.337	40.120	29.816	3.168
5400	5.074	43.401	62.503	0.326	38.936	29.080	3.372
5500	4.861	42.101	61.837	0.315	37.724	28.336	3.588
5600	4.653	40.816	61.140	0.305	36.484	27.584	3.816
5700	4.450	39.546	60.413	0.295	35.216	26.824	4.056
5800	4.252	38.291	59.657	0.286	33.928	26.056	4.308
5900	4.059	37.051	58.874	0.277	32.616	25.280	4.572
6000	3.871	35.826	58.063	0.269	31.280	24.496	4.848

Dec. 31, 1960 June 30, 1967

MAGNESIUM MONOHYDROXIDE (MgOH) (IDEAL GAS) $\text{GFW} = 41.31937$

Point Group [C_{∞v}]

$\Delta H_f^\circ = [-51 \pm 20] \text{ kcal/mol}$

$\Delta H_f^\circ = [-52.9] \text{ gibbs/mol}$

$S_{298.15}^\circ = [52.9] \text{ gibbs/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$

g_i

[27000]

[10000]

[8000]

Vibrational Frequencies and Degeneracies

ω_i, cm^{-1}

[36000]

[10000]

[8000]

Bond Distances: O-Mg = [1.80] Å

Bond Angle: Mg-O-H = [180°]

Rotational Constant: B_e = 0.47595 cm⁻¹

Heat of Formation

The heat of formation is based on the following estimates. The relation D₀⁰(M-X)/D₀⁰(X-H-X) = 0.46 ± 0.03 for several alkaline earth dihalides has been reported by R. A. Kent, J. D. McDonald and J. L. Margrave, J. Phys. Chem. 70, 874 (1966). Assuming that this relation applies to hydroxides, we may estimate D₀⁰(Mg-OH) = 87 ± 12 kcal/mol. A value of D₀⁰(Mg-OH) = 105 ± 12 kcal/mol is obtained by comparison with D₀⁰(Be-OH) = 111 ± 10, D₀⁰(Ca-OH) = 100 ± 10 and D₀⁰(Sr-OH) = 95 ± 10 kcal/mol. The value for BeOH is from the JANAF tables, while those for CaOH and SrOH are from flame studies of L. V. Gurvich, private communication, High Temperature Institute, Moscow, 1966. The average value of D₀⁰(Mg-OH) = 96 kcal/mol is used to calculate the heat of formation.

A value of D₀⁰(Mg-OH) = 56 ± 5 kcal/mol was derived from intensity measurements on the flame spectrum of magnesium by E. M. Bulewicz and T. M. Sugden, Trans. Faraday Soc. 55, 770 (1959). This appears to be too small.

Heat Capacity and Entropy

The ground state is assumed to be ²Σ by analogy with isoelectronic MgF. Ultraviolet emission spectra near 3800 Å were observed for MgOH and MgOD by D. Pesic and A. G. Gaydon, Proc. Phys. Soc. (London) 73, 244 (1959), and L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962). Vibrational and rotational analyses were not performed. Assuming that the observed spectra correspond to the transition A²Π + X²Σ, we estimate the first excited state at 27000 cm⁻¹. The vibrational frequencies ν₁ and ν₃ are estimated from those of H₂O(g) and MgO(g). The ν₂ is tentatively estimated at 1000 cm⁻¹.

A linear structure is assumed by use of the prediction of A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953), for "HAB" molecules with less than 11 valence electrons (MgOH has 9 valence electrons). Confirmation of this prediction is scanty for molecules having "A" as the most electronegative element; however, recent microwave evidence [R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. 44, 3131 (1966)] for the linearity of KOH and CaOH confirms the prediction for these molecules having 8 valence electrons. The O-H bond distance is assumed to be the same as that of H₂O(g) and the Mg-O bond distance is estimated from that of MgO(g).

HMGO

Magnesium Monohydroxide Unipositive Ion (MgOH⁺)

(Ideal Gas) GFW = 41.31882

T, °K	C _p ^o	gkcal/mol S ^o - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
100						
200						
298	8.687	51.871	0.00	143.000	140.335	-102.868
300	9.610	51.871	.017	143.002	140.318	-102.222
400	10.945	52.236	.975	143.140	139.404	-76.167
500	10.861	52.066	2.025	143.330	138.450	-60.516
600	11.398	50.046	3.139	143.595	137.452	-50.067
700	11.797	46.834	4.300	143.769	136.420	-42.592
800	12.115	42.431	5.496	143.985	135.354	-36.977
900	12.384	36.874	6.605	144.163	134.264	-32.604
1000	12.618	30.191	7.792	144.239	133.333	-29.140
1100	12.826	22.403	9.244	142.424	132.433	-26.312
1200	13.012	14.527	10.536	142.595	131.517	-23.953
1300	13.178	6.576	11.846	142.747	130.587	-21.954
1400	13.328	6.558	13.171	112.517	130.156	-20.314
1500	13.462	6.068	14.511	113.038	131.366	-19.140
1600	13.582	71.355	15.863	113.563	132.569	-18.108
1700	13.690	72.181	17.227	114.092	133.763	-17.194
1800	13.787	72.667	18.601	114.622	134.862	-16.377
1900	13.874	73.115	19.994	115.155	135.995	-15.643
2000	13.952	74.228	21.375	115.689	137.077	-14.970
2100	14.022	75.111	22.774	116.224	138.132	-14.376
2200	14.085	75.764	24.179	116.757	139.164	-13.825
2300	14.143	76.392	25.591	117.290	140.170	-13.319
2400	14.195	76.995	27.008	117.822	141.154	-12.854
2500	14.242	77.575	28.430	118.352	142.112	-12.429
2600	14.284	78.135	29.856	118.881	143.055	-12.025
2700	14.323	78.675	31.286	119.407	143.976	-11.654
2800	14.359	79.196	32.721	119.931	144.873	-11.308
2900	14.392	79.701	34.158	120.452	145.758	-10.985
3000	14.421	80.189	35.599	120.969	146.619	-10.681
3100	14.449	80.662	37.042	121.484	147.466	-10.396
3200	14.474	81.121	38.489	121.994	148.297	-10.128
3300	14.497	81.567	39.937	122.500	149.111	-9.875
3400	14.519	82.000	41.388	123.000	149.912	-9.636
3500	14.539	82.421	42.841	123.495	150.694	-9.410
3600	14.557	82.931	44.296	123.985	151.466	-9.195
3700	14.574	83.430	45.752	124.467	152.221	-8.991
3800	14.590	83.919	47.210	124.943	152.968	-8.798
3900	14.605	84.398	48.670	125.412	153.695	-8.613
4000	14.619	84.866	50.131	125.871	154.414	-8.437
4100	14.632	85.329	51.594	126.322	155.121	-8.269
4200	14.644	85.782	53.058	126.765	155.820	-8.108
4300	14.655	86.227	54.523	127.198	156.507	-7.955
4400	14.665	86.664	55.989	127.621	157.185	-7.807
4500	14.675	87.094	57.456	128.031	157.850	-7.666
4600	14.685	86.516	58.924	128.432	158.513	-7.531
4700	14.693	86.732	60.392	128.821	159.161	-7.401
4800	14.702	87.042	61.862	129.198	159.802	-7.276
4900	14.710	87.345	63.333	129.562	160.436	-7.156
5000	14.717	87.642	64.804	129.913	161.062	-7.040
5100	14.724	87.934	66.276	130.250	161.678	-6.928
5200	14.730	88.220	67.749	130.573	162.293	-6.821
5300	14.737	88.500	69.222	130.893	162.905	-6.718
5400	14.743	88.776	70.696	131.178	163.498	-6.617
5500	14.748	89.046	72.171	131.457	164.098	-6.521
5600	14.753	89.312	73.646	131.719	164.683	-6.427
5700	14.759	89.573	75.121	131.966	165.279	-6.337
5800	14.763	89.830	76.598	132.197	165.855	-6.250
5900	14.768	90.082	78.074	132.410	166.436	-6.165
6000	14.772	90.331	79.551	132.607	167.010	-6.083

June 30, 1968

MAGNESIUM MONOHYDROXIDE UNIPOSITIVE ION (MgOH⁺)

GFW = 41.31882

(IDEAL GAS)

Point Group [C_{∞v}]
 $S_{298.15}^o = [51.9 \pm 2] \text{ gkcal/mol}$
 $\Delta H_{298.15}^o = [144 \pm 40] \text{ kcal/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e, cm^{-1}

[800] (1)

[900] (2)

[3500] (1)

O-H = [0.96] Å

$\sigma = 1$

Bond Distance: Mg-O = [1.8] Å

Bond Angle: Mg-O-H = [180°]

Rotational Constant: $B_0 = [0.4765] \text{ cm}^{-1}$

Heat of Formation

The gaseous molecules NaOH, MgOH and AlOH have 8, 9 and 10 valence electrons, respectively. Due to the similarity in molecular structure, we assume that the ionization potential (IP) of MgOH is approximately the average of IP(NaOH) and IP(AlOH). Adopting IP = 9 and 7.5 eV for NaOH (2) and AlOH (2), respectively, we obtain IP(MgOH) = 8.5 eV. Based on this value and $\Delta H_{298.15}^o(\text{MgOH}, g) = -52 \pm 20 \text{ kcal/mol}$ we derive $\Delta H_{298.15}^o(\text{MgOH}^+, g) = 143 \pm 40 \text{ kcal/mol}$ which is tentatively adopted. The estimated value IP(MgOH) is close to IP(MgF) = $7.8 \pm 0.3 \text{ eV}$ (1), where MF and MgOH are isoelectronic molecules, and thus confirms the value within its uncertainty.

Heat Capacity and Entropy

Walsh (3) predicted that ABH molecules (H = hydrogen atom) containing 10 or less valence electrons will be linear in their ground state. Since MgOH⁺ molecule has 8 valence electrons, we assume it to be linear. The vibrational frequencies are estimated by comparison with those for NaOH(g) and MgOH(g). The O-H bond distance is assumed to be the same as that in H₂O(g). The Mg-O bond distance is estimated (4). The moment of inertia is $5.874 \times 10^{-39} \text{ g cm}^2$. The ground state quantum weight is assumed to be the same as that of NaOH(g). The enthalpy at 0°K is -2.24 kcal/mol .

References

1. C. W. Beckett and E. C. Cassidy, Natl. Bur. Std. Rept. 8628, 1 January 1965.
2. See JANAF AlOH⁺(g) table (Dec. 31, 1967) for details.
3. A. D. Walsh, J. Chem. Soc. 1953, 2288 (1953).
4. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

HMgO⁺

HMgO⁺

(Ideal Gas) Mol. Wt. = 15.01467

IMIDOZEN (NH)

(IDEAL GAS)

MOL. WT. = 15.01467

Ground State Configuration $3\bar{\Sigma}^-$
 $S_{298.15}^\circ = 43.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 298.15 = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$

Electronic Level and Quantum Weight

$$\frac{E_1 + \text{cm.}^{-1}}{0} \frac{g_1}{3}$$

$\omega_e x_e = 94.7 \text{ cm.}^{-1}$
 $\omega_e = 16.6684 \text{ cm.}^{-1}$
 $\sigma = 1$
 $r_e = 1.038 \text{ \AA}$

Heat of Formation.

The value, $\Delta H_f^\circ 298 (\text{NH}, g) = 81.0 \pm 2.5 \text{ kcal. mole}^{-1}$, was calculated from the selected dissociation energy, $D_0 = 83 \pm 2 \text{ kcal. mole}^{-1}$, based on the following investigations. J. L. Franklin, V. H. Disher, R. M. Reese and M. Krause, *J. Am. Chem. Soc.* 80, 298 (1958) and R. I. Reed and V. Sneeden, *J. Chem. Soc.* 4132 (1959) have determined the dissociation energy of $\text{NH}(g)$ by electron impact as $83 \pm 2 \text{ kcal. mole}^{-1}$ and $85.3 \pm 6 \text{ kcal. mole}^{-1}$, respectively. A. L. Compagnon and P. O. Ellison, *J. Chem. Phys.* 32, 1132 (1960), and P. C. H. Jordan and H. C. Lonquet-Higgins, *Mol. Phys.* 5, 121 (1962) have calculated theoretically the dissociation energy by a semi-empirical method and obtained $83.3 \text{ kcal. mole}^{-1}$ and $81.2 \text{ kcal. mole}^{-1}$, respectively. These results are in good agreement. G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, 1950, has estimated the dissociation energy $D_0(\text{NH}, g) = 3.8 \text{ e.v.}$ ($87.6 \text{ kcal. mole}^{-1}$) based on the average of two earlier theoretical calculations by R. S. Mulliken, ($D_0 = 4.2 \text{ e.v.}$), *Rev. Mod. Phys.* 4, 1 (1932) and O. King ($D_0 = 3.4 \text{ e.v.}$), *J. Chem. Phys.* 5, 378 (1938). A. G. Gaydon, "Dissociation Energies", 2nd Ed. Chapman & Hall Ltd, London, 1953, favored G. Glockler's estimation $D_0 = 86.3 \text{ kcal. mole}^{-1}$ which was based upon the comparison of force constants and D values of related hydrides (i.e. CH, OH and PH).

Heat Capacity & Entropy.

The rotational constants B_e and α_e were obtained from R. N. Dixon, *Can. J. Phys.* 37, 1171 (1959). The vibrational constants ω_e and $\omega_e x_e$ were calculated from Dixon's data: $B_e = 16.6684 \text{ cm.}^{-1}$, $D_e = 16.85 \times 10^{-4} \text{ cm.}^{-1}$ and $\omega_e = 3125.6 \text{ cm.}^{-1}$ by the relation $D_e = 4 B_e^2 / \omega_e^2$ and $\omega_e = \omega_e - 2 \omega_e x_e$.

D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* 41, 2838 (1964) have observed from the spectrum of NH the vibrational fundamental $\omega = 3135 \pm 2 \text{ cm.}^{-1}$ in Ar and N_2 matrices. K. Rosengren and O. C. Flament, *J. Chem. Phys.* 43, 507 (1965) also reported $\omega = 3122.2 \pm 0.6 \text{ cm.}^{-1}$ in N_2 matrix and $\omega = 3131.6 \pm 0.4 \text{ cm.}^{-1}$ in Ar matrix.

Nitroxyl Hydride (HNO)

(Ideal Gas) Mol. Wt. = 31.016

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	∞.000	∞.000	∞.000	24.498	24.498	∞.000
100	43.877	59.902	2.387	24.498	24.498	24.498	∞.000
200	43.877	59.902	1.592	24.415	24.415	24.415	∞.000
298	8.279	52.729	0.000	23.800	23.800	23.800	∞.000
300	8.287	52.730	.015	23.796	23.796	23.796	∞.000
400	8.788	53.060	.868	23.598	23.598	23.598	∞.000
500	9.342	53.702	1.775	23.438	23.438	23.438	∞.000
600	9.869	54.001	2.735	23.315	23.315	23.315	∞.000
700	10.345	54.559	3.747	23.222	23.222	23.222	∞.000
800	10.766	55.065	4.803	23.155	23.155	23.155	∞.000
900	11.134	55.528	5.898	23.107	23.107	23.107	∞.000
1000	11.454	55.948	7.028	23.078	23.078	23.078	∞.000
1100	11.731	56.323	8.187	23.061	23.061	23.061	∞.000
1200	11.970	56.584	9.373	23.055	23.055	23.055	∞.000
1300	12.177	56.751	10.580	23.056	23.056	23.056	∞.000
1400	12.356	56.840	11.807	23.064	23.064	23.064	∞.000
1500	12.511	56.858	13.051	23.074	23.074	23.074	∞.000
1600	12.646	56.800	14.309	23.087	23.087	23.087	∞.000
1700	12.764	56.690	15.579	23.101	23.101	23.101	∞.000
1800	12.867	56.536	16.861	23.116	23.116	23.116	∞.000
1900	12.958	56.343	18.152	23.130	23.130	23.130	∞.000
2000	13.038	56.113	19.452	23.143	23.143	23.143	∞.000
2100	13.108	55.850	20.760	23.155	23.155	23.155	∞.000
2200	13.171	55.558	22.074	23.164	23.164	23.164	∞.000
2300	13.227	55.240	23.394	23.172	23.172	23.172	∞.000
2400	13.277	54.900	24.719	23.177	23.177	23.177	∞.000
2500	13.322	54.543	26.049	23.178	23.178	23.178	∞.000
2600	13.363	54.166	27.383	23.178	23.178	23.178	∞.000
2700	13.399	53.773	28.721	23.174	23.174	23.174	∞.000
2800	13.432	53.366	30.063	23.167	23.167	23.167	∞.000
2900	13.463	52.946	31.408	23.158	23.158	23.158	∞.000
3000	13.490	52.515	32.755	23.145	23.145	23.145	∞.000
3100	13.515	52.076	34.106	23.130	23.130	23.130	∞.000
3200	13.538	51.628	35.458	23.110	23.110	23.110	∞.000
3300	13.559	51.173	36.813	23.088	23.088	23.088	∞.000
3400	13.578	50.704	38.170	23.063	23.063	23.063	∞.000
3500	13.596	50.223	39.529	23.034	23.034	23.034	∞.000
3600	13.612	49.733	40.889	23.002	23.002	23.002	∞.000
3700	13.628	49.233	42.251	22.966	22.966	22.966	∞.000
3800	13.642	48.716	43.615	22.928	22.928	22.928	∞.000
3900	13.655	48.184	44.980	22.887	22.887	22.887	∞.000
4000	13.667	47.639	46.346	22.842	22.842	22.842	∞.000
4100	13.678	47.084	47.713	22.794	22.794	22.794	∞.000
4200	13.689	46.519	49.081	22.744	22.744	22.744	∞.000
4300	13.699	45.946	50.451	22.691	22.691	22.691	∞.000
4400	13.708	45.359	51.821	22.634	22.634	22.634	∞.000
4500	13.717	44.760	53.192	22.574	22.574	22.574	∞.000
4600	13.725	44.150	54.564	22.513	22.513	22.513	∞.000
4700	13.732	43.529	55.937	22.448	22.448	22.448	∞.000
4800	13.739	42.898	57.311	22.380	22.380	22.380	∞.000
4900	13.746	42.259	58.685	22.310	22.310	22.310	∞.000
5000	13.752	41.613	60.060	22.238	22.238	22.238	∞.000
5100	13.758	40.960	61.435	22.162	22.162	22.162	∞.000
5200	13.764	40.299	62.812	22.086	22.086	22.086	∞.000
5300	13.770	39.629	64.188	22.006	22.006	22.006	∞.000
5400	13.775	38.950	65.563	21.923	21.923	21.923	∞.000
5500	13.779	38.264	66.934	21.839	21.839	21.839	∞.000
5600	13.784	37.573	68.301	21.752	21.752	21.752	∞.000
5700	13.788	36.878	69.670	21.663	21.663	21.663	∞.000
5800	13.792	36.179	71.039	21.571	21.571	21.571	∞.000
5900	13.796	35.476	72.408	21.478	21.478	21.478	∞.000
6000	13.800	34.769	73.778	21.382	21.382	21.382	∞.000

March 31, 1963

NITROXYL HYDRIDE (HNO)

(IDEAL GAS)

Point Group C_sS°_{298.15} = 52.729 cal. deg.⁻¹ mole⁻¹

Ground State Multiplicity = [1]

ΔH_f⁰ = 24.5 kcal. mole⁻¹ΔH_f⁰ = 23.6 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

λ, cm.⁻¹

2854.17 (1)

1570 (1)

1110 (1)

Bond Distance: H-N = 1.020 ± 0.02 Å N=O = 1.239 ± 0.005 Å

Bond Angle: H-N-O = 114° 25' ± 2°

Product of the Moments of Inertia: I_AI_BI_C = 5.939 X 10⁻¹¹⁸ g.³ cm.⁶

Heat of Formation

ΔH_f⁰ = 23.15 for HNO(g) was calculated from D(H-NO) = 48.6 kcal. mole⁻¹ at 0°K. reported by M. J. Y. Clement and D. A. Ramsay, Can. J. Phys. 39, 205 (1961).

Heat Capacity and Entropy

Vibrational frequencies were assigned by J. L. Bancroft, J. M. Hollas and D. A. Ramsay, Can. J. Phys. 40, 322 (1962) and H. Brown and G. Pinetel, J. Chem. Phys. 29, 883 (1958). Bond distances and bond angles were taken from J. L. Bancroft, J. M. Hollas, and D. A. Ramsay, loc. cit. The molecular constants given by P. W. Dalby, Can. J. Phys. 36, 1336 (1958) were: r(N=O) = 1.2116 Å, r(N-H) = 1.0628 Å, and \angle HNO = 108.6°. The three principal moments of inertia are: 1.262 X 10⁻⁴⁰, 2.1067 X 10⁻⁵⁹, and 2.2330 X 10⁻⁵⁹ g. cm.²

HNO

MOL. WT. = 31.016

HNO

(Ideal Gas) Mol. Wt. = 47.016

NITROUS ACID, CIS-(HNO₂) (IDEAL GAS)

MOL. WT. = 47.016

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	keal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	2.635	-	16.852	-	16.852	INFINITE
100	8.027	49.729	68.125	1.840	17.492	-	15.187	33.190
200	9.238	55.595	60.527	-0.96	17.971	-	12.693	13.870
298	10.840	59.586	60.913	-	18.340	-	10.020	7.344
300	10.869	59.653	60.913	-	18.346	-	9.968	7.261
400	12.275	62.979	60.030	1.180	18.593	-	7.135	3.898
500	13.412	65.845	60.913	2.466	18.738	-	4.252	1.858
600	14.318	68.374	61.950	3.854	-	-	1.247	-0.490
700	15.044	70.637	63.032	5.254	-	-	-	-
800	15.637	72.686	64.113	6.659	-	-	-	-
900	16.131	74.557	65.171	8.048	-	-	-	-
1000	16.548	76.279	66.197	10.082	-	-	-	-
1100	16.905	77.873	67.187	11.755	-	-	-	-
1200	17.213	79.358	68.122	13.172	-	-	-	-
1300	17.480	80.746	69.057	15.197	-	-	-	-
1400	17.712	82.050	69.939	16.956	-	-	-	-
1500	17.915	83.279	70.787	18.738	-	-	-	-
1600	18.093	84.442	71.605	20.539	-	-	-	-
1700	18.253	85.554	72.395	22.364	-	-	-	-
1800	18.389	86.590	73.153	24.188	-	-	-	-
1900	18.511	87.568	73.886	26.033	-	-	-	-
2000	18.620	88.540	74.595	27.890	-	-	-	-
2100	18.717	89.511	75.281	29.757	-	-	-	-
2200	18.802	90.476	75.949	31.632	-	-	-	-
2300	18.882	91.437	76.599	33.517	-	-	-	-
2400	18.952	92.397	77.233	35.409	-	-	-	-
2500	19.015	93.354	77.819	37.308	-	-	-	-
2600	19.073	94.309	78.407	39.212	-	-	-	-
2700	19.127	95.262	78.997	41.122	-	-	-	-
2800	19.177	96.213	79.585	43.037	-	-	-	-
2900	19.225	97.162	80.171	44.956	-	-	-	-
3000	19.254	98.110	80.755	46.880	-	-	-	-
3100	19.290	99.053	81.319	48.807	-	-	-	-
3200	19.323	100.000	81.871	50.737	-	-	-	-
3300	19.353	100.946	82.416	52.671	-	-	-	-
3400	19.381	101.881	82.958	54.608	-	-	-	-
3500	19.407	102.812	83.505	56.547	-	-	-	-
3600	19.431	103.739	84.051	58.489	-	-	-	-
3700	19.453	104.662	84.598	60.434	-	-	-	-
3800	19.473	105.588	85.146	62.382	-	-	-	-
3900	19.493	106.510	85.694	64.332	-	-	-	-
4000	19.510	107.428	86.241	66.278	-	-	-	-
4100	19.527	108.342	86.787	68.229	-	-	-	-
4200	19.543	109.253	87.334	70.184	-	-	-	-
4300	19.557	110.160	87.881	72.142	-	-	-	-
4400	19.570	111.064	88.428	74.099	-	-	-	-
4500	19.583	111.965	88.974	76.053	-	-	-	-
4600	19.595	112.863	89.520	78.012	-	-	-	-
4700	19.607	113.758	90.067	80.000	-	-	-	-
4800	19.617	114.650	90.614	82.000	-	-	-	-
4900	19.627	115.539	91.161	84.000	-	-	-	-
5000	19.636	116.425	91.707	86.000	-	-	-	-
5100	19.645	117.308	92.253	88.000	-	-	-	-
5200	19.653	118.186	92.800	90.000	-	-	-	-
5300	19.660	119.061	93.346	92.000	-	-	-	-
5400	19.667	120.000	93.891	94.000	-	-	-	-
5500	19.676	120.939	94.436	96.000	-	-	-	-
5600	19.683	121.878	94.981	98.000	-	-	-	-
5700	19.690	122.817	95.526	100.000	-	-	-	-
5800	19.697	123.756	96.071	102.000	-	-	-	-
5900	19.701	124.695	96.616	104.000	-	-	-	-
6000	19.707	125.634	97.161	106.000	-	-	-	-

June 30, 1963

Point Group C_{2v} $\Delta H_f^0 = -16.85 \pm 0.32$ kcal. mole⁻¹ $\Delta H_f^0 = -16.85 \pm 0.32$ kcal. mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

 ω, cm^{-1} ω, cm^{-1}

Bond Distances: O-N = 1.20 Å N-O = 1.46 Å O-H = 0.98 Å

Bond Angle: O-N-O = 114° N-O-H = 103°

Product of the Moments of Inertia: $I_{AB}^2 = 5.5074 \times 10^{-116} \text{ g}^3 \text{ cm}^6$

Heat of Formation.

P. G. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961) reported ΔH_f^0 298.15 = -9.06 ± 0.32 kcal. mole⁻¹ for the reaction: $\text{NO(g)} + \text{NO}_2(\text{g}) + \text{H}_2\text{O(g)} \rightleftharpoons 2\text{HNO}_2(\text{g})$, yielding ΔH_f^0 298.15 = -18.57 ± 0.20 kcal. mole⁻¹ for $\text{HNO}_2(\text{g})$. L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys., 19, 1599 (1951) estimated the difference in energy of cis- and trans- $\text{HNO}_2(\text{g})$ to be 506 ± 250 cal. mole⁻¹. Hence the value of ΔH_f^0 298.15 for cis- $\text{HNO}_2(\text{g})$ was calculated.

The heat of reaction and the equilibrium constants for the formation of $\text{HNO}_2(\text{g})$ have been calculated by M. M. Karavayev and G. A. Skvortsov, Russ. J. Phys. Chem. 36, 566 (1962). The value of ΔH_f^0 298.15 reported is -18.9 kcal. mole⁻¹. However, based on the heat of formation of liquid HNO_2 , F. G. Ashmore and B. P. Levitt, Trans. Faraday Soc., 53, 945 (1957) give ΔH_f^0 = -13.7 kcal. mole⁻¹. The corresponding value reported by W. A. Rosser and H. Wise, J. Chem. Phys., 28, 571 (1957) is -20.0 kcal. mole⁻¹, based on the experimental data of L. G. Wayne and D. M. Vost, J. Chem. Phys., 19, 41 (1951), and the entropy of the equilibrium mixture of the trans- and cis- $\text{HNO}_2(\text{g})$ calculated by L. H. Jones, R. M. Badger and G. E. Moore, loc. cit.

Heat Capacity and Entropy.

Vibrational frequencies, bond distances, and bond angles were obtained from L. Dor and P. Tarte, Bull. Soc. Roy. Sci., LG. 478 (1951) and L. H. Jones, R. M. Badger and G. E. Moore, loc. cit. The three principal moments of inertia are: 1.0277 × 10⁻³⁹, 6.8242 × 10⁻³⁹, and 7.8520 × 10⁻³⁹ g. cm².

T, °K.	C _p ^o	cal. mole ⁻¹ deg ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	INFINITE	-	2.451	-17.349	INFINITE	
100	8.027	49.616	1.896	-18.008	-15.202	1.420	
200	9.328	55.504	60.500	-0.999	-18.408	13.118	
298	11.000	59.546	59.546	0.000	-18.840	10.508	7.702
300	11.029	59.614	59.566	0.020	-18.846	10.456	7.617
400	12.543	65.886	60.991	1.312	-18.852	7.652	6.164
500	14.614	70.712	63.034	5.374	-18.858	4.794	5.072
600	16.885	74.959	67.218	11.615	-18.865	2.515	
700	18.773	78.442	68.176	13.519	-18.866	1.066	0.71
800	19.877	80.829	68.096	15.252	-18.867	0.393	1.085
900	20.357	81.883	68.008	16.788	-18.868	0.253	1.085
1000	20.550	82.223	68.023	18.161	-18.869	0.213	1.085
1100	16.895	77.959	67.218	11.615	-18.865	12.659	2.515
1200	17.193	76.442	68.176	13.519	-18.866	15.542	2.830
1300	17.454	74.959	68.096	15.252	-18.867	18.416	3.096
1400	17.682	73.202	67.500	16.788	-18.868	21.282	3.322
1500	17.882	71.657	70.652	18.161	-18.869	24.144	3.517
1600	18.059	69.517	71.652	20.585	-18.869	26.992	3.687
1700	18.215	67.617	72.441	22.399	-18.870	29.837	3.836
1800	18.374	65.867	73.202	24.227	-18.870	32.673	3.967
1900	18.508	64.288	73.934	26.069	-18.871	35.508	4.084
2000	18.587	62.868	74.647	27.922	-18.871	38.350	4.188
2100	18.685	61.518	75.334	29.786	-17.986	41.167	4.282
2200	18.773	60.389	75.998	31.659	-17.874	43.960	4.367
2300	18.852	59.425	76.642	33.540	-17.762	46.767	4.444
2400	18.925	58.623	77.267	35.429	-17.655	49.573	4.514
2500	18.987	57.983	77.873	37.324	-17.552	52.369	4.578
2600	19.046	57.499	78.462	39.226	-17.451	55.166	4.637
2700	19.099	57.068	79.034	41.133	-17.355	57.957	4.691
2800	19.147	56.684	79.590	43.046	-17.262	60.743	4.741
2900	19.191	56.347	80.132	44.963	-17.173	63.531	4.788
3000	19.231	56.058	80.660	46.884	-17.089	66.311	4.831
3100	19.268	55.819	81.174	48.809	-17.009	69.089	4.871
3200	19.302	55.621	81.676	50.738	-16.933	71.864	4.908
3300	19.334	55.464	82.165	52.669	-16.862	74.638	4.943
3400	19.364	55.343	82.643	54.604	-16.794	77.410	4.976
3500	19.389	55.263	83.110	56.542	-16.731	80.178	5.006
3600	19.414	55.212	83.567	58.482	-16.673	82.948	5.035
3700	19.436	55.184	84.013	60.424	-16.619	85.715	5.063
3800	19.458	55.170	84.450	62.369	-16.568	88.481	5.089
3900	19.478	55.165	84.877	64.316	-16.521	91.243	5.113
4000	19.496	55.162	85.295	66.265	-16.474	94.005	5.136
4100	19.513	55.162	85.705	68.215	-16.422	96.767	5.158
4200	19.529	55.162	86.107	70.167	-16.407	99.528	5.179
4300	19.544	55.162	86.501	72.121	-16.376	102.280	5.199
4400	19.558	55.162	86.887	74.076	-16.346	105.046	5.217
4500	19.571	55.162	87.266	76.032	-16.316	107.805	5.235
4600	19.584	55.162	87.638	77.990	-16.305	110.569	5.253
4700	19.595	55.162	88.004	79.949	-16.289	113.325	5.269
4800	19.606	55.162	88.362	81.909	-16.276	116.084	5.285
4900	19.616	55.162	88.715	83.870	-16.265	118.835	5.300
5000	19.626	55.162	89.061	85.832	-16.258	121.582	5.315
5100	19.636	55.162	89.401	87.795	-16.255	124.332	5.329
5200	19.644	55.162	89.736	89.759	-16.253	127.086	5.342
5300	19.652	55.162	90.065	91.724	-16.254	129.848	5.355
5400	19.659	55.162	90.389	93.690	-16.258	132.619	5.367
5500	19.668	55.162	90.708	95.656	-16.264	135.382	5.379
5600	19.675	55.162	91.022	97.623	-16.275	138.134	5.391
5700	19.681	55.162	91.331	99.591	-16.286	140.883	5.402
5800	19.688	55.162	91.635	101.560	-16.301	143.634	5.413
5900	19.694	55.162	91.934	103.530	-16.319	146.389	5.423
6000	19.700	55.162	92.230	105.500	-16.337	149.148	5.433

June 30, 1963

Point Group C₈

S_{298.15} = 59.548 cal. deg⁻¹ mole⁻¹

Ground State Multiplicity = [1]

ΔH_f^o = -17.37 ± 0.32 kcal. mole⁻¹

ΔH_f^o = -18.84 ± 0.32 kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω_e, cm⁻¹

ω_x, cm⁻¹

ω_y, cm⁻¹

ω_z, cm⁻¹

ω₄, cm⁻¹

ω₅, cm⁻¹

ω₆, cm⁻¹

ω₇, cm⁻¹

ω₈, cm⁻¹

ω₉, cm⁻¹

ω₁₀, cm⁻¹

ω₁₁, cm⁻¹

ω₁₂, cm⁻¹

ω₁₃, cm⁻¹

ω₁₄, cm⁻¹

ω₁₅, cm⁻¹

ω₁₆, cm⁻¹

ω₁₇, cm⁻¹

ω₁₈, cm⁻¹

ω₁₉, cm⁻¹

ω₂₀, cm⁻¹

ω₂₁, cm⁻¹

ω₂₂, cm⁻¹

ω₂₃, cm⁻¹

ω₂₄, cm⁻¹

ω₂₅, cm⁻¹

ω₂₆, cm⁻¹

ω₂₇, cm⁻¹

ω₂₈, cm⁻¹

ω₂₉, cm⁻¹

ω₃₀, cm⁻¹

ω₃₁, cm⁻¹

ω₃₂, cm⁻¹

ω₃₃, cm⁻¹

ω₃₄, cm⁻¹

ω₃₅, cm⁻¹

ω₃₆, cm⁻¹

ω₃₇, cm⁻¹

ω₃₈, cm⁻¹

ω₃₉, cm⁻¹

ω₄₀, cm⁻¹

ω₄₁, cm⁻¹

ω₄₂, cm⁻¹

ω₄₃, cm⁻¹

ω₄₄, cm⁻¹

ω₄₅, cm⁻¹

ω₄₆, cm⁻¹

ω₄₇, cm⁻¹

ω₄₈, cm⁻¹

ω₄₉, cm⁻¹

ω₅₀, cm⁻¹

ω₅₁, cm⁻¹

ω₅₂, cm⁻¹

ω₅₃, cm⁻¹

ω₅₄, cm⁻¹

ω₅₅, cm⁻¹

ω₅₆, cm⁻¹

ω₅₇, cm⁻¹

ω₅₈, cm⁻¹

ω₅₉, cm⁻¹

ω₆₀, cm⁻¹

ω₆₁, cm⁻¹

ω₆₂, cm⁻¹

ω₆₃, cm⁻¹

ω₆₄, cm⁻¹

ω₆₅, cm⁻¹

ω₆₆, cm⁻¹

ω₆₇, cm⁻¹

ω₆₈, cm⁻¹

ω₆₉, cm⁻¹

ω₇₀, cm⁻¹

ω₇₁, cm⁻¹

ω₇₂, cm⁻¹

ω₇₃, cm⁻¹

ω₇₄, cm⁻¹

ω₇₅, cm⁻¹

ω₇₆, cm⁻¹

ω₇₇, cm⁻¹

ω₇₈, cm⁻¹

ω₇₉, cm⁻¹

ω₈₀, cm⁻¹

ω₈₁, cm⁻¹

ω₈₂, cm⁻¹

ω₈₃, cm⁻¹

ω₈₄, cm⁻¹

ω₈₅, cm⁻¹

ω₈₆, cm⁻¹

ω₈₇, cm⁻¹

ω₈₈, cm⁻¹

ω₈₉, cm⁻¹

ω₉₀, cm⁻¹

ω₉₁, cm⁻¹

ω₉₂, cm⁻¹

ω₉₃, cm⁻¹

ω₉₄, cm⁻¹

ω₉₅, cm⁻¹

ω₉₆, cm⁻¹

ω₉₇, cm⁻¹

ω₉₈, cm⁻¹

ω₉₉, cm⁻¹

ω₁₀₀, cm⁻¹

ω₁₀₁, cm⁻¹

ω₁₀₂, cm⁻¹

ω₁₀₃, cm⁻¹

ω₁₀₄, cm⁻¹

ω₁₀₅, cm⁻¹

ω₁₀₆, cm⁻¹

ω₁₀₇, cm⁻¹

ω₁₀₈, cm⁻¹

ω₁₀₉, cm⁻¹

ω₁₁₀, cm⁻¹

ω₁₁₁, cm⁻¹

Nitric Acid (HNO₃)

(Ideal Gas) Mol. Wt. = 63.016

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.107	53.003	INFINITE	-2.815	-29.755	INFINITE
200	10.110	58.129	64.745	-2.018	-29.755	58.342
298	12.748	63.663	63.663	-1.123	-31.527	24.403
300	12.795	63.742	63.663	-1.024	-31.527	12.966
400	15.103	67.750	64.194	-1.423	-32.472	12.821
500	16.930	71.325	65.269	-3.028	-32.664	3.382
600	18.348	74.543	66.551	-4.795	-32.736	∞
700	19.457	77.465	68.007	-6.745	-32.736	∞
800	20.325	80.114	69.267	-8.878	-32.736	∞
900	21.031	82.550	70.610	-10.747	-32.544	2.970
1000	21.613	84.797	71.917	-12.880	-32.397	17.198
1100	22.098	86.880	73.184	-15.066	-32.227	4.400
1200	22.508	88.831	74.407	-17.297	-32.035	4.932
1300	22.858	90.571	75.497	-19.578	-31.822	5.761
1400	23.159	92.142	76.473	-21.897	-31.612	6.761
1500	23.419	93.594	77.319	-24.196	-31.386	6.089
1600	23.646	94.968	78.075	-26.550	-31.155	6.373
1700	23.847	96.278	78.754	-28.964	-30.919	6.623
1800	24.017	97.527	79.371	-31.432	-30.678	6.842
1900	24.170	98.728	80.000	-33.957	-30.444	7.038
2000	24.306	100.000	82.746	-36.537	-30.207	7.212
2100	24.426	102.010	83.635	-38.588	-29.971	7.369
2200	24.530	104.242	84.582	-40.906	-29.730	7.510
2300	24.630	106.292	85.332	-43.106	-29.510	7.637
2400	24.716	108.292	85.961	-45.091	-29.284	7.755
2500	24.793	109.303	86.928	-46.847	-29.066	7.861
2600	24.863	107.274	87.692	-48.499	-28.849	7.958
2700	24.924	108.126	88.435	-50.029	-28.640	8.048
2800	24.984	108.854	89.057	-51.435	-28.440	8.127
2900	25.037	110.001	90.661	-52.726	-28.236	8.207
3000	25.085	110.851	90.947	-54.012	-28.044	8.277
3100	25.129	111.674	91.215	-55.298	-27.856	8.343
3200	25.170	112.480	91.468	-56.586	-27.675	8.404
3300	25.206	113.268	91.705	-57.875	-27.500	8.461
3400	25.240	114.001	91.924	-59.164	-27.331	8.515
3500	25.271	114.733	93.731	-60.452	-27.167	8.564
3600	25.300	115.445	94.325	-61.740	-27.009	8.612
3700	25.327	116.139	94.905	-63.028	-26.857	8.658
3800	25.352	116.819	95.478	-64.316	-26.707	8.703
3900	25.375	117.473	96.028	-65.604	-26.567	8.747
4000	25.397	118.116	96.573	-66.892	-26.431	8.794
4100	25.417	118.743	97.106	-68.180	-26.301	8.809
4200	25.435	119.356	97.628	-69.468	-26.174	8.842
4300	25.451	119.956	98.140	-70.756	-26.054	8.874
4400	25.469	120.540	98.643	-72.044	-25.936	8.904
4500	25.485	121.113	99.136	-73.332	-25.824	8.932
4600	25.499	121.673	99.620	-74.620	-25.716	8.960
4700	25.512	122.226	100.095	-75.908	-25.613	8.986
4800	25.526	122.773	100.562	-77.196	-25.517	9.011
4900	25.538	123.285	101.020	-78.484	-25.421	9.036
5000	25.549	123.801	101.470	-79.772	-25.325	9.056
5100	25.560	124.307	101.913	-81.060	-25.238	9.078
5200	25.570	124.799	102.349	-82.348	-25.152	9.099
5300	25.580	125.291	102.781	-83.636	-25.067	9.119
5400	25.589	125.769	103.198	-84.924	-24.982	9.138
5500	25.597	126.239	103.613	-86.212	-24.916	9.157
5600	25.605	126.700	104.021	-87.500	-24.845	9.174
5700	25.613	127.159	104.423	-88.788	-24.776	9.191
5800	25.621	127.618	104.825	-90.076	-24.706	9.208
5900	25.628	128.037	105.209	-91.364	-24.636	9.226
6000	25.634	128.467	105.593	-92.652	-24.566	9.238

June 30, 1963

NITRIC ACID (HNO₃)

(IDEAL GAS)

MOL. WT. = 63.016

Point Group C_{3v}ΔH°_f 0 = -29.76 ± 0.10 kcal. mole⁻¹S°_{298.15} = 63.663 cal. deg.⁻¹ mole⁻¹ΔH°_f 298.15 = -32.10 ± 0.10 kcal. mole⁻¹

Ground State Multiplicity = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	ω, cm. ⁻¹
1320 (1)	765 (1)
886 (1)	3580 (1)
680 (1)	1335 (1)
1710 (1)	465 (1)
583 (1)	

Bond Distance: O-N = 1.206 ± 0.005 Å N-O = 1.405 ± 0.005 Å O-H = [0.96] Å

Bond Angle: O-N-O = 130° ± 20° N-O-H = 102° ± 30°

Product of the Moments of Inertia: I_AI_BI_C = 6.08612 X 10⁻¹¹⁵ g.³ cm.⁶

Heat of Formation.

ΔH°_f 298.15 was taken from National Bureau of Standards Report 7437, January 1, 1962. Equilibria involving HNO₃ were measured by E. J. Jones, J. Am. Chem. Soc. 85, 2274 (1943), G. Peck, J. Am. Chem. Soc. 76, 5858 (1954) and H. E. Abel, H. Schmid and M. Stein-Wien, Z. Elektrochem. 55, 692 (1950), yielding ΔH°_f = -32.06, -32.02, and -32.09 kcal. mole⁻¹, respectively. G. Becker and W. A. Roth, Z. Elektrochem. 40, 835 (1934) and J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882-1886, measured the heat of neutralization of HNO₃(aq.) with NH₃, combining these values with the data for NH₃NO₃ yields ΔH°_f = -32.27 and -32.07 kcal. M. Berthelot, "Sur la Force des Matieres Explosives," 3rd. ed., Paris, 1883, measured the heat of reaction of N₂O₄(g) and Cl₂(g), obtaining ΔH°_f = -32.10 kcal. mole⁻¹. The value of ΔH°_f 298.15 reported by M. R. Forsythe and W. P. Giauque, J. Am. Chem. Soc. 64, 48 (1942) was -31.994 kcal. mole⁻¹. The value adopted is the weighted average of these six values.

Heat Capacity and Entropy.

Vibrational frequencies were obtained from A. Palm and M. Kilpatrick, J. Chem. Phys. 23, 1562 (1955). Bond distances and bond angles were taken from D. J. Millen and J. R. Morton, J. Chem. Soc., 1523 (1960). The basic parameters of HNO₃(g) reported by P. A. Aikman, L. V. Vilkey and V. Y. Rosolovskii, Zhur. Strukt. Khim. 1, 1 (1960) were: r(N-O) = 1.22 ± 0.01 Å; r(N-O) = 1.40 ± 0.01 Å and ∠ O-N-O = 135° ± 2.5°. Forsythe and Giauque, loc. cit. have calculated the absolute entropy of pure nitric acid (g) from calorimetric data. The value obtained was S°_{298.15} = 63.62 cal. deg.⁻¹ mole⁻¹. The entropy of nitric acid vapor at 298.1°K. has also been computed by H. Cohn, C. K. Ingold, and H. G. Poole, J. Chem. Soc. 4272 (1952) to be 63.70 cal. deg.⁻¹ mole⁻¹. The three principal moments of inertia are: 6.4299 X 10⁻³⁹, 7.0314 X 10⁻³⁹, and 1.3461 X 10⁻³⁸ g. cm.²

HNO₃

Sodium Hydride (NaH)

(Crystal) Mol. Wt. = 23.999

SODIUM HYDRIDE (NaH)

(CRYSTAL)

MOL. WT. = 23.999

HfNa

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞
100	4.182	2.763	15.913	-1.406	-12.433	INFINITE
200	6.763	4.182	15.913	-1.315	-11.439	25.000
298	8.698	5.294	15.913	-1.260	-10.485	10.485
300	8.732	5.294	15.913	-1.250	-10.423	9.480
400	10.150	6.618	15.913	-1.160	-9.485	5.819
500	11.270	7.732	15.913	-1.070	-8.541	3.325
600	12.120	8.698	15.913	-1.000	-7.597	1.768
700	12.780	9.485	15.913	-0.940	-6.653	0.001
800	13.240	10.000	15.913	-0.890	-5.709	-0.530
900	13.550	10.375	15.913	-0.850	-4.765	-0.950
1000	13.750	10.625	15.913	-0.820	-3.821	-1.271
1100	13.880	10.790	15.913	-0.790	-2.877	-1.526
1200	13.960	10.880	15.913	-0.760	-1.933	-1.815
1300	14.000	10.920	15.913	-0.730	-0.989	-2.308
1400	14.020	10.940	15.913	-0.700	-0.045	-2.723
1500	14.030	10.950	15.913	-0.670	0.901	-3.076

Heat of Formation.

ΔH_f^o 298.15 was obtained from S. R. Gunn and L. G. Green, *J. Am. Chem. Soc.* **80**, 4782 (1958). The value of ΔH_f^o 298.15 reported by C. E. Messer, L. G. Fessolino and C. E. Thalmayer, *J. Am. Chem. Soc.* **77**, 4524 (1955) was -13.60 ± 0.27 kcal. mole⁻¹ which is in excellent agreement with the value given by S. R. Gunn and L. G. Green, loc. cit. The results of the previous investigations were also reviewed by C. E. Messer, et al., loc. cit.

Heat Capacity and Entropy.

C_p below 350°K were measured by E. F. Westrum, et al., University of Michigan, Ann Arbor, Michigan, private communication, May 18, 1960. C_p above 350°K were estimated by comparison with those for LiH(c). C_p 59.94 ~ 91.84°K., were also measured by E. V. Sayre and J. J. Beaver, *J. Chem. Phys.* **18**, 584 (1950). S° at 100°, 200°, and 298.15° were taken from E. F. Westrum, et al., loc. cit., using S°₁₀(extrap.) = 0.008 cal. deg.⁻¹ mole⁻¹.

Temperature of Decomposition.

T_d was estimated from the value of ΔF° in the table. The value of T_d given by D. M. Banus, J. J. McSharry and E. A. Sullivan, *J. Am. Chem. Soc.* **77**, 2007 (1955) was 940°K. It was assumed that NaH would behave similarly to LiH and that decomposition pressures would be purity dependent, and this would produce apparently high T_d's.

March 31, 1963

HfNa

Sodium Hydride (NaH)

(Ideal Gas) Mol. Wt. = 23.999

MOL. WT. = 23.999

(IDEAL GAS)

SODIUM HYDRIDE (NaH)

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞.000	INFINITE	2.086	30.166	30.166	INFINITE
100	6.811	37.330	1.396	30.136	28.213	6.8057
200	7.241	44.000	0.685	29.700	24.602	6.8057
300	7.246	45.000	0.013	29.695	24.571	6.8057
400	7.246	45.280	0.755	28.745	22.959	6.8057
500	7.241	45.805	1.530	28.430	21.550	6.8057
600	8.172	50.372	2.335	28.166	20.199	7.357
700	8.377	51.647	3.163	27.935	18.890	7.897
800	8.537	52.777	4.009	27.733	17.612	8.401
900	8.664	53.790	4.869	27.547	16.359	8.872
1000	8.767	54.708	5.741	27.370	15.125	9.305
1100	8.853	55.540	6.622	27.192	13.907	9.703
1200	8.926	56.321	7.511	27.016	12.706	10.069
1300	8.989	57.052	8.407	26.843	11.521	10.405
1400	9.044	57.737	9.309	26.674	10.352	10.703
1500	9.094	58.372	10.215	26.510	9.200	10.969
1600	9.139	58.961	11.127	26.351	8.066	11.203
1700	9.181	59.507	12.043	26.196	6.949	11.403
1800	9.220	60.012	12.963	26.045	5.849	11.577
1900	9.257	60.478	13.887	25.898	4.766	11.726
2000	9.292	60.907	14.815	25.755	3.699	11.851
2100	9.325	61.331	15.746	25.616	2.648	11.955
2200	9.357	61.752	16.680	25.481	1.613	12.041
2300	9.388	62.169	17.617	25.350	0.594	12.110
2400	9.418	62.583	18.557	25.224	-0.409	12.164
2500	9.447	62.994	19.500	25.103	-1.428	12.204
2600	9.475	63.439	20.446	24.986	-2.461	12.231
2700	9.503	63.877	21.395	24.873	-3.508	12.247
2800	9.531	64.313	22.347	24.764	-4.569	12.253
2900	9.558	64.748	23.301	24.660	-5.644	12.250
3000	9.584	65.182	24.259	24.560	-6.733	12.238
3100	9.610	65.617	25.210	24.464	-7.836	12.217
3200	9.636	66.053	26.161	24.372	-8.953	12.187
3300	9.662	66.489	27.114	24.284	-10.084	12.149
3400	9.688	66.926	28.070	24.199	-11.229	12.104
3500	9.713	67.363	29.029	24.118	-12.388	12.053
3600	9.738	67.799	30.000	24.041	-13.561	11.997
3700	9.763	68.235	30.973	23.968	-14.748	11.936
3800	9.788	68.671	31.949	23.899	-15.949	11.870
3900	9.813	69.107	32.927	23.834	-17.164	11.799
4000	9.837	69.543	33.907	23.772	-18.394	11.723
4100	9.862	69.979	34.889	23.713	-19.638	11.643
4200	9.886	70.415	35.873	23.657	-20.896	11.559
4300	9.910	70.851	36.859	23.604	-22.168	11.471
4400	9.935	71.287	37.847	23.553	-23.454	11.379
4500	9.959	71.723	38.837	23.504	-24.754	11.283
4600	9.983	72.159	39.829	23.457	-26.068	11.184
4700	10.007	72.595	40.823	23.412	-27.396	11.081
4800	10.031	73.031	41.819	23.369	-28.738	10.975
4900	10.055	73.467	42.817	23.327	-30.094	10.866
5000	10.078	73.903	43.817	23.287	-31.464	10.754
5100	10.102	74.339	44.819	23.248	-32.848	10.639
5200	10.126	74.775	45.823	23.210	-34.246	10.521
5300	10.150	75.211	46.829	23.174	-35.658	10.400
5400	10.173	75.647	47.837	23.139	-37.084	10.276
5500	10.197	76.083	48.847	23.105	-38.524	10.150
5600	10.221	76.519	49.859	23.072	-40.000	10.021
5700	10.244	76.955	50.873	23.040	-41.491	9.889
5800	10.268	77.391	51.889	23.009	-43.000	9.753
5900	10.291	77.827	52.907	22.979	-44.524	9.614
6000	10.315	78.263	53.927	22.950	-46.064	9.471

Ground State Configuration $1s^2 +$
 $S_{298.15}^o = 45.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = 30.2 \pm 4.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = 298.15 = 29.7 \pm 4.6 \text{ kcal. mole}^{-1}$
 $\omega_e x_e = 19.72 \text{ cm.}^{-1}$
 $\omega_e = 4.9012 \text{ cm.}^{-1}$
 $B_e = 0.1353 \text{ cm.}^{-1}$
 $\sigma = 1$

Heat of Formation

ΔH_f^o 298.15 was calculated from $D_0^o = 2.05 \pm 0.2 \text{ e.v.}$ reported by A. G. Daydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall Ltd., 1953.

Heat Capacity and Entropy

All molecular and spectroscopic constants were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, Inc., 1950.

SODIUM HYDROXIDE (NaOH)

(CRYSTAL)

MOL. WT. = 39.99717

Mol. Wt. = 39.99717

Sodium Hydroxide (NaOH)

(Crystal)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _f
0	∞	∞	∞	∞	∞	∞
100	6.631	3.713	2.506	-100.815	-98.127	214.456
200	11.850	10.176	2.254	-101.020	-98.401	103.266
298	14.228	13.440	1.602	-101.866	-99.607	68.607
300	14.260	15.488	1.518	-101.899	-99.798	66.147
400	15.520	19.772	1.026	-102.453	-87.060	47.567
500	17.963	23.461	0.716	-102.252	-83.230	36.360
600	20.560	26.710	0.418	-100.221	-79.559	28.970
700	20.560	32.879	0.243	-99.611	-76.164	23.760
800	20.560	35.624	0.166	-99.002	-72.856	19.003
900	20.560	38.046	0.098	-98.399	-69.624	16.007
1000	20.560	40.212	0.053	-97.803	-66.458	14.524
1100	20.560	42.172	0.032	-97.228	-63.354	12.587
1200	20.560	43.961	0.019	-96.675	-60.303	10.890
1300	20.560	45.606	0.011	-96.044	-57.303	9.224
1400	20.560	47.130	0.006	-95.374	-54.356	7.798
1500	20.560	48.549	0.003	-94.664	-51.464	6.569
1600	20.560	49.875	0.001	-93.914	-48.624	5.501
1700	20.560	51.122	0.000	-93.124	-45.834	4.594
1800	20.560	52.287	0.000	-92.294	-43.094	3.737
1900	20.560	53.369	0.000	-91.424	-40.404	2.930
2000	20.560	54.363	0.000	-90.514	-37.764	2.163

Heat of Formation.

The standard enthalpy of formation, ΔH_f° 298 (NaOH, c) = -101.90 ± 0.1 kcal. mole⁻¹, was calculated from the heat of solution of sodium hydroxide (c) and the heat of sodium metal hydrolysis and the appropriate auxiliary data.

N. A. Peshtetnikov¹ has measured the heat of solution NaOH(c) → NaOH(aq) as -10.445 ± 0.015 kcal. mole⁻¹ at 298.15°K. by solution calorimetry. Using the auxiliary heat of dilution reported by V. B. Parker², the selected heat of solution of sodium hydroxide (c) at infinite dilution is -10.555 kcal. mole⁻¹. Also L. E. Murch and W. F. Glaque¹¹ measured calorimetrically the heat of solution of solid samples of NaOH·nH₂O in the range from n = 0.1 to 1.0. When extrapolated to n = 0 and infinite dilution², this result yields the heat of solution of NaOH(c) at infinite dilution, ΔH_s° 298 = -10.636 kcal. mole⁻¹, which is in good agreement with the value selected.

The heat of sodium metal hydrolysis, ΔH_f° 298, has been measured in the solution calorimeter by the following investigators. Na(c) + H₂O(l) → NaOH(aq) + 1/2 H₂(g) ΔH_f° 298

Source	Number of Moles of H ₂ O	ΔH_f° 298 kcal. mole ⁻¹	ΔH_f° 298 (NaOH(aq), c) kcal. mole ⁻¹	ΔH_f° 298 (NaOH, c) kcal. mole ⁻¹
Gunn et al. ³	1000	-44.047 ± 0.008	-112.446	-101.899
Messer et al. ⁴	CO	-44.215 ± 0.20	-112.530	-101.975
Ketchen et al. ⁵	CO	-44.054 ± 0.20	-112.369	-101.814

The values of ΔH_f° 298 (NaOH(aq), c) were calculated from the heats of reaction ΔH_f° 298 using the ΔH_f° 298 (H₂O, l) = -68.315 kcal. mole⁻¹.⁶ Combination of the selected heat of solution of NaOH(c) at infinite dilution with the heat of formation of NaOH(aq) gives the heat of formation of NaOH(c) in the last column of the table. A weighted average of these three measurements has been taken for the selected heat of formation of sodium hydroxide (c).

The earlier investigations have been reviewed by F. R. Bichowsky and F. D. Rossini⁹, and C. E. Messer et al.⁴, and these earlier reported data are not adopted in the tabulation.

Heat Capacity and Entropy.

L. E. Murch and W. F. Glaque¹¹ have measured low temperature heat capacities of NaOH·0.04014 H₂O and NaOH·0.97776 H₂O from 15° to 320°K. and calculated the values of C_p for the pure phase of NaOH(c). T. B. Douglas and J. L. Dever⁹ have measured the enthalpy changes from 273° to 973°K. in the drop calorimeter and derived the heat capacities. The low temperature and the high temperature heat capacities were joined smoothly by Murch and Glaque, and the smooth values were adopted in the tabulation. Low temperature heat capacities from 60° to 300°K. have also been measured by J. C. R. Kelly and P. E. Snyder⁷, whose data are in good agreement with those reported by Murch and Glaque. M. M. Popov and D. M. Ginzburg¹⁰ have determined the heat capacities of NaOH(c) in the temperature range from 298° to 577°K. from the enthalpy measurements by drop calorimetry. The reported $H_{500}^\circ - H_{298}^\circ$ = 3.112 kcal. mole⁻¹ is in good agreement with the tabulated value.

Transition and Melting Data.

The adopted heat of transition and the transition temperature, and the adopted heat of melting and the melting point were obtained from Douglas and Dever,⁹ Popov and Ginzburg,¹⁰ reported the heat of transition ΔH_{tr}° = 1.930 kcal. mole⁻¹ at 576.8°K. and the heat of melting ΔH_m° = 1.629 kcal. mole⁻¹ at 595.16°K.

Heat of Sublimation.

See NaOH(g) table for details.

Reference:

- 1 N. A. Peshtetnikov, Zhur. Neorg. Khim. 6, 682 (1961).
- 2 V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NBS-NBS 2, April, 1965.
- 3 S. R. Gunn and L. G. Green, J. Am. Chem. Soc. 80, 4782 (1958).
- 4 S. R. Gunn, "Note Concerning an Electrical Resistor in the Rocking-Bomb Solution Calorimeters," UCL-7992, Oct. 1964.
- 5 E. E. Ketchen and W. F. Glaque, J. Am. Chem. Soc. 77, 4524 (1955).
- 6 D. C. Wagner, M. H. Evans, I. Helwig, V. B. Parker, S. M. Bailey and R. H. Schumm, NBS Tech. Note 270-1, Oct. 1965.
- 7 J. C. R. Kelly and P. E. Snyder, J. Am. Chem. Soc. 73, 4114 (1951), ibid, 73, 5933 (1951).
- 8 T. B. Douglas and J. L. Dever, J. Res. Nat'l. Bur. Std. 55, 81 (1954).
- 9 F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1955.
- 10 M. M. Popov and G. M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956). G. M. Ginzburg, ibid, 26, 968 (1956).
- 11 L. E. Murch and W. F. Glaque, J. Phys. Chem. 66, 2052 (1962).

Sodium Hydroxide (NaOH)

HNaO

(Liquid)

Mol. Wt. = 39.99717

SODIUM HYDROXIDE (NaOH)

(LIQUID)

MOL. WT. = 39.99717

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0								
100								
200								
298	20.590	17.727	17.727	0.000	-99.698	-89.659	-89.659	65.722
300	20.588	17.857	17.727	0.039	-99.984	-89.595	-89.595	65.270
400	20.546	23.615	18.549	2.036	-96.377	-85.700	-85.700	60.000
500	20.504	28.675	19.300	4.206	-93.377	-83.820	-83.820	56.000
600	20.570	32.275	21.621	6.272	-90.702	-79.579	-79.579	28.987
700	20.430	35.435	23.547	8.332	-88.098	-76.441	-76.441	28.866
800	20.290	38.154	25.207	10.358	-85.509	-73.387	-73.387	29.049
900	20.150	40.236	26.780	12.380	-83.067	-70.467	-70.467	17.087
1000	20.010	42.051	28.264	14.388	-80.395	-67.487	-67.487	14.149
1100	19.870	44.552	29.659	16.382	-77.382	-64.623	-64.623	12.839
1200	19.730	46.775	30.973	18.362	-74.362	-61.346	-61.346	11.473
1300	19.590	48.849	32.212	20.328	-71.362	-58.000	-58.000	9.515
1400	19.450	50.835	33.381	22.280	-68.380	-54.593	-54.593	8.102
1500	19.310	52.652	35.487	24.228	-65.438	-51.125	-51.125	6.805
1600	19.170	54.874	35.536	26.142	-62.514	-47.603	-47.603	5.825
1700	19.030	56.832	36.531	28.052	-59.614	-44.094	-44.094	4.894
1800	18.910	58.116	37.478	29.949	-56.749	-40.531	-40.531	4.071
1900	18.795	59.609	38.381	31.836	-53.919	-36.921	-36.921	3.286
2000	18.690	60.997	39.243	33.708	-51.128	-33.254	-33.254	2.582
2100	18.595	57.007	40.067	35.572	-48.398	-29.547	-29.547	2.090
2200	18.515	57.870	40.857	37.428	-45.724	-25.784	-25.784	1.555
2300	18.447	58.691	41.615	39.276	-43.108	-22.064	-22.064	1.088
2400	18.393	59.475	42.343	41.118	-40.545	-18.481	-18.481	0.674
2500	18.346	60.223	43.043	42.955	-38.035	-14.935	-14.935	0.217
2600	18.310	60.944	43.718	44.787	-35.584	-11.412	-11.412	0.157
2700	18.287	61.634	44.369	46.617	-33.191	-8.009	-8.009	0.503
2800	18.265	62.299	44.997	48.445	-30.856	-4.727	-4.727	1.822
2900	18.250	62.940	45.600	50.270	-28.581	-1.568	-1.568	1.416
3000	18.238	63.558	46.193	52.095	-26.365	1.490	1.490	1.394

$$S_{298.15}^{\circ} = 17.727 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{\circ} 298.15 = -89.988 \text{ kcal. mole}^{-1}$$

$$T_m = 592.25^{\circ}\text{K.}$$

$$\Delta H_m^{\circ} = 1.519 \text{ kcal. mole}^{-1}$$

$$T_b(\text{monomeric gas}) = 1682.7^{\circ}\text{K.}$$

$$\Delta H_v^{\circ}(\text{to monomer}) = 37.9 \text{ kcal. mole}^{-1}$$

Heat of Formation.

The heat of formation of NaOH(l) at 298°K. was obtained from that of the crystal by adding ΔH_m° and the difference between $H_{592.25}^{\circ}$ - $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The selected heat capacities in the temperature range from 592.3° to 1000°K. were obtained from the enthalpy measurements of sodium hydroxide (l) in the drop calorimeter by T. B. Douglas and J. L. Dever¹. The heat capacities below the melting point and above 1000°K. were extrapolated from the selected heat capacity curve.

Douglas and Dever¹ have also compared their heat capacity values with those from W. D. Fowles and G. C. Blalock² who have applied the same drop method to determine the heat capacities of NaOH(l). Both results are in reasonable agreement. M. M. Popov and G. M. Ginzburg³ applying the same technique obtained different values of heat capacity. The smoothed enthalpy data reported by Ginzburg⁴ are 200 to 500 cal. mole⁻¹ smaller than the tabulated values at the temperature range from 700° to 1000°K.

The entropy ($S_{298}^{\circ} = 17.65 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$) was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See NaOH(c) table for details.

Vaporization Data.

The boiling point 1682.7°K. was calculated as the temperature at which the free energies of formation (ΔF_f°) for both NaOH(l) and NaOH(g) are equal. The difference in the heats of formation (ΔH_f°) of NaOH(l) and NaOH(g) at the boiling point is the heat of vaporization. If $\text{Na}_2(\text{OH})_2(\text{g})$ is also considered as a minor component in the vapor mixture (approximately 6% of total vapor pressure at the boiling point) the calculated boiling point is 1653°K. (see NaOH(g) table for details).

H. von Wartenberg and P. Albrecht, Z. Elektrochem. 27, 162 (1921), have studied the vapor pressures of liquid NaOH and reported the boiling point as 1661°K.

Reference:

- 1 T. B. Douglas and J. L. Dever, J. Res. Nat'l. Bur. Std. 53, 81 (1954).
- 2 W. D. Fowles and G. C. Blalock, "Enthalpies and Specific Heats of Alkali and Alkaline Earth Hydroxides at High Temperatures", ORNL-1653, Oak Ridge Nat'l. Lab. Jan. 1954.
- 3 M. M. Popov and G. M. Ginzburg, Zhur. Obshchei Khim. 26, 971 (1956).
- 4 G. M. Ginzburg, Ibid. 26, 968 (1956).

HNaO

Sodium Hydroxide (NaOH)

(Ideal Gas) Mol. Wt. = 39.99717

SODIUM HYDROXIDE (NaOH)

(IDEAL GAS)

MOL. WT. = 39.99717

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f kcal. mole ⁻¹	ΔF° _f kcal. mole ⁻¹	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	8.095	46.936	-2.550	-49.359	-49.359	INFINITE
200	8.889	52.760	-1.752	-48.618	-48.618	110.232
298	9.486	56.456	∞.000	-48.997	-51.135	55.878
300	9.496	56.515	∞.018	-50.407	-51.615	37.602
400	9.986	59.316	56.835	∞.992	-51.479	28.359
500	10.391	61.589	57.565	2.012	-51.916	22.711
600	10.722	63.516	58.600	3.058	-52.308	18.915
700	10.996	65.188	59.253	4.154	-52.668	16.184
800	11.235	66.672	60.089	5.300	-53.003	14.123
900	11.449	68.008	60.896	6.400	-53.322	12.509
1000	11.646	69.224	61.669	7.555	-53.629	11.210
1100	11.827	70.363	62.407	8.729	-53.924	10.142
1200	11.995	71.376	63.112	9.920	-54.204	9.163
1300	12.149	72.345	63.786	11.128	-54.474	8.077
1400	12.290	73.251	64.430	12.350	-54.774	7.146
1500	12.418	74.103	65.047	13.585	-55.074	6.337
1600	12.535	74.909	65.638	14.833	-55.370	5.639
1700	12.642	75.672	66.206	16.092	-55.659	5.003
1800	12.738	76.397	66.752	17.361	-55.947	4.447
1900	12.825	77.088	67.278	18.639	-56.235	3.948
2000	12.904	77.748	67.785	19.926	-56.527	3.500
2100	12.976	78.380	68.275	21.220	-56.825	3.093
2200	13.041	78.989	68.748	22.521	-57.126	2.724
2300	13.100	79.566	69.206	23.828	-57.430	2.386
2400	13.154	80.124	69.649	25.140	-57.736	2.075
2500	13.203	80.662	70.079	26.458	-58.043	1.790
2600	13.247	81.181	70.496	27.781	-58.353	1.526
2700	13.288	81.682	70.901	29.108	-58.665	1.282
2800	13.325	82.166	71.295	30.438	-58.978	1.049
2900	13.360	82.634	71.678	31.773	-59.293	.844
3000	13.391	83.087	72.051	33.110	-59.610	.664
3100	13.420	83.527	72.416	34.451	-59.931	.509
3200	13.447	83.953	72.768	35.794	-60.257	.372
3300	13.472	84.368	73.113	37.140	-60.587	.251
3400	13.494	84.770	73.450	38.488	-60.920	.143
3500	13.516	85.152	73.779	39.839	-61.255	.050
3600	13.535	85.543	74.101	41.191	-61.593	.000
3700	13.554	85.914	74.415	42.546	-61.934	.000
3800	13.571	86.275	74.722	43.902	-62.279	.000
3900	13.586	86.628	75.023	45.260	-62.626	.000
4000	13.601	86.972	75.317	46.619	-62.975	.000
4100	13.615	87.308	75.606	47.980	-63.327	.000
4200	13.628	87.637	75.888	49.342	-63.682	.000
4300	13.640	87.957	76.165	50.706	-64.039	.000
4400	13.651	88.271	76.437	52.070	-64.400	.000
4500	13.662	88.578	76.703	53.436	-64.764	.000
4600	13.672	88.878	76.965	54.803	-65.131	.000
4700	13.682	89.173	77.221	56.170	-65.500	.000
4800	13.691	89.461	77.473	57.539	-65.871	.000
4900	13.699	89.743	77.721	58.908	-66.244	.000
5000	13.707	90.020	77.964	60.279	-66.619	.000
5100	13.715	90.291	78.203	61.652	-66.996	.000
5200	13.722	90.558	78.436	63.022	-67.375	.000
5300	13.728	90.819	78.669	64.394	-67.756	.000
5400	13.735	91.076	78.897	65.767	-68.138	.000
5500	13.741	91.328	79.120	67.141	-68.522	.000
5600	13.747	91.576	79.341	68.515	-68.907	.000
5700	13.752	91.819	79.557	69.890	-69.293	.000
5800	13.757	92.058	79.771	71.266	-69.680	.000
5900	13.762	92.293	79.981	72.642	-70.068	.000
6000	13.767	92.525	80.186	74.018	-70.457	.000

Dec. 31, 1960; Mar. 31, 1966

Point Group C_{2v}
 $S_{298.15} = [56.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = -49.4 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = -50.4 \pm 5 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

$\omega_e \text{ cm.}^{-1}$
 437 (1)
 (1300)(1)
 (3700)(1)

Bond Distance: Na-O = [1.97] Å O-H = [0.96] Å

Bond Angle: Na-O-H = [110°]

Product of the Moments of Inertia: $I_A I_B I_C = [6.3062] \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

σ = 1

Heat of Formation.

R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. **28**, 454 (1958), have found in their mass-spectrometric studies that the NaOH(l) vaporizes mainly as gaseous dimer in the temperature range from 575° to 723°K. They have also calculated by the slope method the heat of dimerization, $\Delta H_d^\circ = -54 \pm 5 \text{ kcal. mole}^{-1}$, for $2\text{NaOH(g)} = \text{Na}_2\text{(OH)}_2\text{(g)}$ and the heat of sublimation, $\Delta H_s^\circ = 46.3 \pm 3 \text{ kcal. mole}^{-1}$, for $\text{NaOH(c)} = \text{NaOH(g)}$. The second law values were determined using ion intensity ratios, however, a third law calculation using a single data point converted by the authors to absolute pressure (J. Phys. Chem. **62**, 486 (1958)) yields $\Delta H_d^\circ = -51.6 \text{ kcal. mole}^{-1}$, $\Delta H_s^\circ = 49.5 \text{ kcal. mole}^{-1}$ and $\Delta H_f^\circ = 49.5 \text{ kcal. mole}^{-1}$ (to dimer) = 41.1 kcal. mole⁻¹, which are in agreement within the limit of uncertainty. Later, Porter and Schoonmaker, J. Chem. Phys. **31**, 830 (1959), found the activity of molten alkali hydroxide had been reduced in the presence of MgO in their sample container, and the uncertainty in the heat of sublimation might be $\pm 5 \text{ kcal. mole}^{-1}$, but the heat of dimerization should not be seriously affected because it was calculated from slopes of both species. In order to have good agreement between the calculated total pressures of monomer and dimer of sodium hydroxide (g) and the observed vapor pressures by H. von Wartenberg and P. Albrecht, Z. Elektrochem. **27**, 162 (1921), the heat of dimerization and the heat of sublimation have been so chosen as $\Delta H_d^\circ = -54 \text{ kcal. mole}^{-1}$ and $\Delta H_s^\circ = 49.5 \text{ kcal. mole}^{-1}$ (to monomer) = 51.5 kcal. mole⁻¹, respectively, which are still within the limit of Porter and Schoonmaker's data. The calculated boiling point is 1653°K. which is in good agreement with 1661 ± 20°K. reported by Wartenberg and Albrecht, loc. cit. The heats of formation were calculated from the selected heat of dimerization and heat of sublimation as $\Delta H_f^\circ = -50.4 \text{ kcal. mole}^{-1}$ and $\Delta H_f^\circ = -154.8 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The bent molecular configuration with the bond angle of 110° was proposed by S. H. Bauer, R. M. Diner and P. P. Porter, J. Chem. Phys. **29**, 931 (1958). The bond distance Na-O was estimated from that in H₂O(g). The bond distance Na-O was estimated by adding the bond length difference (0.04 Å) between H-OH(g) and H-F(g) to the bond distance Na-F(g) (1.9259 Å) which has been accurately measured by R. K. Bauer and H. Lew, Can. J. Phys. **41**, 1461 (1963). The Na-O stretching frequency was obtained from L. H. Spinar and J. L. Margrave, Spectrochim. Acta **12**, 244 (1956), in the infrared spectroscopic studies. The O-H stretching and the bending frequencies were estimated by comparison with H-OH, D-OH and T-OH which indicate rigid convergence to a constant as a heavier atom is attached. The three principal moments of inertia are $I_A = [0.1252] \times 10^{-59}$, $I_B = [6.449] \times 10^{-59}$ and $I_C = [6.5742] \times 10^{-59} \text{ g. cm.}^2$.

Hydroxyl (OH)
(Ideal Gas)

MOL. WT. = 17.0074

(IDEAL GAS)

HYDROXYL (OH)

Ground State Configuration 2π
 $S_{298.15}^{\circ} = 43.680 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} = 9.290 \pm 0.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = 9.432 \pm 0.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_i, \text{ cm.}^{-1}$	$\frac{g_i}{2}$
0	2
139.7	2

$\sigma = 1$
 $r_e = 0.9706 \text{ \AA}$

$\omega_e x_e = 82.81 \text{ cm.}^{-1}$
 $\alpha_e = 0.714 \text{ cm.}^{-1}$

$\omega_e = 3755.21 \text{ cm.}^{-1}$
 $B_e = 18.871 \text{ cm.}^{-1}$

Heat of Formation.

P. Oray, Trans. Farad. Soc. 55, 408 (1959) has summarized the determinations of the heat of formation of OH and concludes that the short extrapolation by Barrow, Arkiv. Fysik, 11, 281 (1956) of the $B(\sum^+)$ $\rightarrow A(\sum^+)$ system gives the most reliable result. The value of $D_0 = 101.33 \text{ kcal. mole}^{-1}$ was adopted and leads to a heat of formation of $9.432 \text{ kcal. mole}^{-1}$. A recent determination of the dissociation energy from measurements of the concentration of the radicals in water oxygen mixtures by A. P. Furmal and A. V. Prost, Vestn. Mosk. Univ., Ser. II Khim. 16, 25 (1961) gives $\Delta H_f^{\circ}(\text{OH}) = 102.8 \pm 0.8 \text{ kcal. mole}^{-1}$ in good agreement with the adopted value. Also V. A. Medvedev, V. V. Korobov and V. F. Baibuz, Zhur. Fiz. Khim. 33, 58 (1959) reported a heat of dissociation of $102.2 \pm 1 \text{ kcal. mole}^{-1}$ from dissociation of water in a spherical bomb.

Heat Capacity and Entropy.

The molecular constants were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. This calculation gives values in excellent agreement with L. Hear, A. S. Friedman and C. W. Beckett, National Bureau of Standards Monograph No. 20, May 1961. The agreement with the higher order correction calculations of H. L. Johnston, J. Belzer and L. Savodnik, TR 316-5, Ohio State University, available as ATI 139 987, is good between 298 and 4000°K. This earlier work uses different constants and also a different value of the ground state splitting constant, but at 6000°K. the entropy difference is still less than 0.25%.

Mol. Wt. = 17.0074

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	-2.162	9.289	INFINITE	INFINITE
100	7.798	35.726	50.308	-1.467	9.001	-19.472	-19.472
200	7.356	40.985	44.541	-1.111	9.393	-8.671	-9.475
298	7.167	43.680	43.680	0.000	9.432	8.307	-6.089
300	7.165	43.925	43.881	0.013	9.269	-6.046	-6.046
400	7.087	45.971	42.725	0.725	7.930	-1.321	-1.321
500	7.055	47.551	44.687	1.432	6.434	7.540	-3.296
600	7.057	48.837	45.275	2.137	5.163	7.163	-2.609
700	7.090	49.927	45.663	2.845	4.379	6.791	-2.120
800	7.130	50.851	45.972	3.553	3.852	6.428	-1.715
900	7.173	51.721	46.235	4.258	3.472	6.162	-1.375
1000	7.232	52.491	47.468	5.003	3.250	5.706	-1.247
1100	7.439	53.195	47.975	5.742	3.353	5.353	-1.064
1200	7.549	53.847	48.437	6.491	3.164	5.005	-0.912
1300	7.656	54.455	48.852	7.246	4.561	4.561	-0.794
1400	7.768	55.027	49.221	8.006	4.067	4.067	-0.706
1500	7.867	55.566	49.556	8.805	3.580	3.580	-0.580
1600	7.963	56.077	50.079	9.596	3.642	3.642	-0.497
1700	8.053	56.563	50.447	10.397	3.307	3.307	-0.425
1800	8.117	57.025	50.789	11.207	3.847	2.895	-0.361
1900	8.177	57.465	51.106	12.024	4.581	2.395	-0.301
2000	8.286	57.891	51.466	12.849	8.881	2.313	-0.253
2100	8.253	58.296	51.782	13.681	8.849	1.988	-0.207
2200	8.415	58.686	52.087	14.520	8.815	1.662	-0.165
2300	8.526	59.062	52.366	15.366	8.786	1.336	-0.127
2400	8.576	59.422	52.624	16.214	8.756	1.014	-0.092
2500	8.576	59.773	52.945	17.069	8.711	0.690	-0.060
2600	8.622	60.110	53.214	17.929	8.675	0.372	-0.031
2700	8.685	60.436	53.476	18.794	8.637	0.054	-0.004
2800	8.746	60.756	53.736	19.664	8.597	-0.278	0.021
2900	8.780	61.058	54.070	20.535	8.557	-0.598	0.054
3000	8.780	61.355	54.218	21.411	8.515	-0.893	0.065
3100	8.814	61.644	54.453	22.291	8.472	-1.208	0.085
3200	8.846	61.924	54.682	23.176	8.427	-1.519	0.104
3300	8.876	62.196	54.906	24.064	8.381	-1.826	0.131
3400	8.905	62.462	55.126	24.959	8.333	-2.137	0.157
3500	8.933	62.721	55.338	25.841	8.283	-2.446	0.153
3600	8.959	62.973	55.546	26.735	8.232	-2.751	0.167
3700	8.984	63.218	55.750	27.632	8.179	-3.052	0.180
3800	9.008	63.458	55.948	28.531	8.126	-3.350	0.193
3900	9.031	63.693	56.145	29.434	8.069	-3.640	0.205
4000	9.053	63.922	56.337	30.338	8.011	-3.961	0.216
4100	9.074	64.145	56.525	31.245	7.952	-4.256	0.227
4200	9.095	64.364	56.709	32.153	7.892	-4.553	0.237
4300	9.115	64.578	56.889	33.064	7.830	-4.851	0.247
4400	9.134	64.788	57.064	33.976	7.768	-5.150	0.257
4500	9.153	64.994	57.240	34.890	7.701	-5.450	0.264
4600	9.171	65.195	57.411	35.807	7.635	-5.726	0.272
4700	9.189	65.393	57.579	36.725	7.567	-6.018	0.280
4800	9.206	65.588	57.744	37.644	7.498	-6.314	0.287
4900	9.223	65.776	57.906	38.566	7.429	-6.592	0.294
5000	9.239	65.963	58.065	39.489	7.358	-6.882	0.301
5100	9.255	66.146	58.222	40.414	7.286	-7.162	0.307
5200	9.271	66.326	58.376	41.340	7.213	-7.448	0.313
5300	9.286	66.502	58.527	42.267	7.139	-7.730	0.318
5400	9.301	66.676	58.677	43.197	7.065	-8.007	0.324
5500	9.316	66.847	58.824	44.128	6.989	-8.284	0.329
5600	9.330	67.015	58.968	45.060	6.912	-8.563	0.334
5700	9.344	67.180	59.111	45.994	6.835	-8.837	0.339
5800	9.358	67.342	59.252	46.929	6.757	-9.107	0.344
5900	9.372	67.503	59.390	47.866	6.678	-9.385	0.348
6000	9.386	67.661	59.527	48.803	6.598	-9.659	0.352

Dec. 31, 1960; Mar. 31, 1966

Hydroxyl Unipositive Ion (OH⁺)

(Ideal Gas) Mol. Wt. = 17.0068

HO⁺

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _f
0							
100	6.969	43.657	43.657	-0.000	314.800	312.254	-229.888
200	6.969	43.700	43.657	-0.13	314.809	312.238	-227.465
300	6.982	45.707	43.631	1.710	315.301	311.306	-170.090
400	7.020	47.268	44.448	1.410	315.783	310.252	-135.611
500	7.095	48.554	45.028	2.115	309.101	309.101	-112.590
600	7.204	49.655	45.612	2.830	316.728	307.871	-96.122
700	7.337	50.626	46.179	3.557	317.200	306.573	-83.752
800	7.480	51.498	46.723	4.298	317.675	305.217	-74.117
900	7.625	52.294	47.241	5.053	318.155	303.807	-66.397
1000	7.765	53.027	47.734	5.823	318.639	302.349	-60.071
1200	7.897	53.709	48.204	6.606	319.128	300.847	-54.792
1300	8.019	54.345	48.652	7.402	319.619	299.304	-50.317
1400	8.131	54.944	49.080	8.209	320.115	297.722	-46.476
1500	8.233	55.508	49.490	9.028	320.612	296.106	-43.143
1600	8.326	56.043	49.883	9.856	321.109	294.454	-40.321
1700	8.410	56.550	50.260	10.692	321.608	292.775	-37.639
1800	8.487	57.033	50.623	11.537	322.106	291.063	-35.340
1900	8.557	57.494	50.973	12.390	322.605	289.326	-33.280
2000	8.621	57.934	51.310	13.249	323.104	287.562	-31.423
2100	8.680	58.356	51.636	14.114	323.601	285.772	-29.741
2200	8.734	58.761	51.950	14.984	324.097	283.959	-28.209
2300	8.785	59.151	52.255	15.860	324.591	282.121	-26.808
2400	8.831	59.526	52.550	16.741	325.085	280.266	-25.527
2500	8.875	59.887	52.837	17.626	325.575	278.387	-24.337
2600	8.915	60.236	53.114	18.516	326.066	276.491	-23.241
2700	8.954	60.573	53.384	19.409	326.554	274.576	-22.225
2800	8.990	60.899	53.647	20.307	327.040	272.642	-21.281
2900	9.024	61.216	53.903	21.207	327.524	270.680	-20.400
3000	9.056	61.522	54.152	22.111	328.006	268.720	-19.576
3100	9.087	61.819	54.394	23.019	328.488	266.738	-18.805
3200	9.116	62.108	54.631	23.929	328.967	264.740	-18.081
3300	9.144	62.389	54.862	24.842	329.445	262.725	-17.400
3400	9.171	62.663	55.087	25.758	329.920	260.694	-16.757
3500	9.197	62.929	55.307	26.676	330.394	258.652	-16.151
3600	9.223	63.188	55.523	27.597	330.866	256.598	-15.578
3700	9.247	63.441	55.733	28.521	331.336	254.526	-15.034
3800	9.270	63.688	55.939	29.446	331.805	252.446	-14.519
3900	9.293	63.929	56.141	30.375	332.273	250.351	-14.029
4000	9.315	64.165	56.339	31.305	332.737	248.241	-13.563
4100	9.337	64.395	56.532	32.238	333.201	246.123	-13.120
4200	9.358	64.621	56.722	33.172	333.664	243.994	-12.696
4300	9.379	64.841	56.909	34.109	334.125	241.856	-12.292
4400	9.399	65.057	57.091	35.048	334.585	239.703	-11.906
4500	9.419	65.268	57.271	35.989	335.042	237.541	-11.537
4600	9.438	65.476	57.447	36.932	335.500	235.370	-11.183
4700	9.457	65.679	57.620	37.877	335.956	233.188	-10.843
4800	9.476	65.878	57.790	38.823	336.412	230.997	-10.518
4900	9.494	66.074	57.957	39.772	336.866	228.794	-10.205
5000	9.513	66.266	58.121	40.722	337.319	226.584	-9.904
5100	9.530	66.454	58.283	41.674	337.771	224.367	-9.615
5200	9.548	66.639	58.442	42.628	338.223	222.140	-9.336
5300	9.566	66.821	58.598	43.584	338.674	219.906	-9.068
5400	9.583	67.000	58.752	44.541	339.124	217.656	-8.809
5500	9.600	67.176	58.904	45.500	339.574	215.406	-8.559
5600	9.617	67.350	59.053	46.461	340.021	213.134	-8.318
5700	9.634	67.520	59.200	47.424	340.470	210.872	-8.085
5800	9.650	67.688	59.345	48.388	340.918	208.591	-7.860
5900	9.667	67.853	59.488	49.354	341.365	206.305	-7.642
6000	9.683	68.015	59.628	50.321	341.812	204.019	-7.431

Mar. 31, 1966

HO⁺

HYDROXYL UNIPOSITIVE ION (OH⁺) (IDEAL GAS) MOL. WT. = 17.0068

Ground State Configuration $3 \sum^-$
 $\Delta H_f^o = 313.3 \pm 2.5 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = 43.657 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o 298.15 = 314.8 \pm 2.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_i, \text{ cm.}^{-1}$ g_i
 0 3
 $\omega_e x_e = [74]$ $\sigma^+ = 1$
 $B_e = 16.795 \text{ cm.}^{-1}$ $\alpha_e = 0.732 \text{ cm.}^{-1}$ $r_e = 1.0289 \text{ \AA}$

Heat of Formation.

The ionization potential of hydroxyl has been determined by M. M. Mann, A. Rustulid and J. T. Tate, Phys. Rev. 58, 340 (1940) from electron impact data on water vapor, as 13.6 e.v. S. N. Poner and R. L. Hudson, J. Chem. Phys. 25, 602 (1956) have measured the appearance potential of OH⁺ from OH as $13.18 \pm 0.1 \text{ e.v.}$ (303.98 kcal.). This value was the one adopted to obtain the heat of formation of OH⁺(g) from that of OH(g) at 0°K.

Heat Capacity and Entropy.

The molecular constants, with the exception of $\omega_e x_e$, were all given by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. New York, 1950. The value of $\omega_e x_e$ was estimated by analogy with OH(g) and other diatomic hydrides.
 The value of $H_{298}^o - H_{298}^o$ at 0°K. is -2.06 kcal. mole⁻¹.

Hydroxyl Uninegative Ion (OH⁻)

(Ideal Gas) Mol. Wt. = 17.0079

T, °K.	C _v ^o	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
100							
200							
298	6.965	41.229	41.229	-0.000	-34.400	-33.248	24.371
300	6.965	41.272	41.229	+0.13	-34.409	-33.240	24.216
400	6.969	43.276	41.512	+1.710	-34.912	-32.776	17.908
500	6.978	44.832	42.018	+1.407	-35.427	-32.182	14.067
600	7.002	46.106	42.596	2.106	-35.952	-31.484	11.468
700	7.047	47.188	43.177	2.808	-36.486	-30.696	9.584
800	7.116	48.133	43.739	3.516	-37.027	-29.833	8.150
900	7.204	48.977	44.275	4.232	-37.571	-28.902	7.018
1000	7.306	49.741	44.784	4.957	-38.115	-27.908	6.099
1100	7.415	50.442	45.267	5.693	-38.659	-26.862	5.337
1200	7.527	51.092	45.725	6.440	-39.200	-25.766	4.693
1300	7.638	51.699	46.162	7.199	-39.738	-24.623	4.140
1400	7.746	52.269	46.578	7.968	-40.275	-23.441	3.659
1500	7.848	52.807	46.975	8.748	-40.810	-22.219	3.237
1600	7.944	53.317	47.356	9.537	-41.345	-20.964	2.864
1700	8.034	53.801	47.721	10.336	-41.878	-19.672	2.520
1800	8.118	54.263	48.072	11.144	-42.409	-18.351	2.228
1900	8.196	54.704	48.409	11.960	-42.941	-17.001	1.956
2000	8.267	55.126	48.734	12.783	-43.472	-15.622	1.707
2100	8.334	55.531	49.049	13.613	-44.004	-14.215	1.479
2200	8.396	55.920	49.352	14.449	-44.536	-12.785	1.270
2300	8.453	56.294	49.646	15.292	-45.067	-11.327	1.076
2400	8.505	56.655	49.930	16.140	-45.601	-9.849	0.897
2500	8.556	57.004	50.206	16.993	-46.136	-8.352	0.730
2600	8.602	57.340	50.474	17.851	-46.671	-6.827	0.574
2700	8.645	57.666	50.735	18.713	-47.208	-5.288	0.428
2800	8.685	57.981	50.988	19.580	-47.747	-3.725	0.291
2900	8.723	58.286	51.234	20.450	-48.285	-2.141	0.161
3000	8.758	58.582	51.474	21.324	-48.827	-0.539	0.039
3100	8.792	58.870	51.708	22.202	-49.369	1.079	0.076
3200	8.823	59.150	51.936	23.082	-49.913	2.711	0.185
3300	8.853	59.422	52.159	23.966	-50.459	4.364	0.289
3400	8.881	59.686	52.377	24.853	-51.005	6.035	0.388
3500	8.908	59.944	52.589	25.742	-51.554	7.720	0.482
3600	8.934	60.196	52.797	26.635	-52.104	9.420	0.572
3700	8.958	60.441	53.000	27.529	-52.657	11.140	0.658
3800	8.982	60.680	53.199	28.426	-53.211	12.871	0.740
3900	9.004	60.913	53.394	29.326	-53.766	14.618	0.819
4000	9.026	61.142	53.585	30.227	-54.323	16.377	0.895
4100	9.047	61.365	53.772	31.131	-54.882	18.154	0.968
4200	9.067	61.583	53.955	32.036	-55.442	19.959	1.038
4300	9.086	61.797	54.135	32.944	-56.004	21.740	1.105
4400	9.105	62.006	54.312	33.854	-56.567	23.552	1.170
4500	9.123	62.211	54.485	34.765	-57.132	25.380	1.233
4600	9.141	62.411	54.655	35.678	-57.697	27.226	1.294
4700	9.158	62.608	54.822	36.593	-58.265	29.077	1.352
4800	9.174	62.801	54.987	37.510	-58.834	30.943	1.409
4900	9.190	62.990	55.148	38.428	-59.404	32.817	1.464
5000	9.206	63.176	55.307	39.348	-59.974	34.701	1.517
5100	9.222	63.359	55.463	40.269	-60.546	36.603	1.569
5200	9.237	63.538	55.616	41.192	-61.120	38.510	1.619
5300	9.251	63.714	55.767	42.116	-61.694	40.437	1.667
5400	9.266	63.887	55.916	43.042	-62.269	42.367	1.715
5500	9.280	64.057	56.063	43.970	-62.845	44.312	1.761
5600	9.294	64.224	56.207	44.898	-63.422	46.268	1.806
5700	9.307	64.389	56.349	45.828	-64.000	48.225	1.840
5800	9.321	64.551	56.489	46.760	-64.579	50.203	1.882
5900	9.334	64.711	56.627	47.692	-65.159	52.184	1.933
6000	9.347	64.868	56.763	48.626	-65.739	54.174	1.973

Mar. 31, 1966

HYDROXYL UNINEGATIVE ION (OH⁻)

MOL. WT. = 17.0079

Ground State Configuration $1\sum^+$
 $S_{298.15}^o = 41.229 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^o = -32.9 \pm 1.0 \text{ kcal. mole}^{-1}$
 $\Delta F_f^o = -34.4 \pm 1.0 \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_1, \text{ cm.}^{-1}$ $\frac{\epsilon_1}{\epsilon_2}$

0 1

$\omega_e x_e = [74.7] \text{ cm.}^{-1}$

$\sigma^+ = 1$

$\omega_e = 3735 \pm 560 \text{ cm.}^{-1}$

$r_e = 1.834 \text{ \AA}$

$B_e = 18.87 \text{ cm.}^{-1}$

$\alpha_e = [0.65] \text{ cm.}^{-1}$

Heat of Formation

L. M. Branscomb, Joint Institute for Laboratory Astrophysics Report No. 62, Feb. 1st, 1966 has deduced an electron affinity of OH of $1.83 \pm 0.04 \text{ e.v.}$ ($42.2 \pm 0.9 \text{ kcal.}$) from the photodetachment spectrum of OH⁻(g). The vibrational state was deduced to be the ground state since no other absorption sequences could be detected by a thorough search. F. M. Page, Faraday Soc. Discussions 19, 87 (1955) has reviewed the methods and results of earlier determinations of the electron affinity of OH(g) and concludes that it is $65 \pm 1 \text{ kcal.}$ However he does state that it is not generally known whether the flame systems chiefly investigated are in thermodynamic equilibrium. In a later paper F. M. Page and T. M. Sugden, Trans. Faraday Soc. 53, 1092 (1957) conclude that much higher concentrations of radicals are obtained in flames than predicted thermodynamically. However for certain systems at lower temperatures they estimate only a factor of 3 increase in concentration and thus calculate the electron affinity as $61 \text{ kcal. mole}^{-1}$. The value reported by Branscomb, loc. cit. is adopted here.

Heat Capacity and Entropy

Branscomb loc. cit. has used his photodetachment spectra to obtain values of ω_e , B_e and r_e for OH⁻(g) which are remarkably similar to those for OH(g). The values of $\omega_e x_e$ and α_e were estimated by comparison with OH(g) and other hydrides. The ground state configuration was assumed to be that of HP(g) with which it is isoelectronic.

The value of H_{298}^o at 0°K. is $-2.057 \text{ kcal. mole}^{-1}$.

HO⁻

Hydroperoxy (HO₂)

(Ideal Gas) Mol. Wt. = 33.008

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	-0.000	∞	INFINITE	-2.390	5.497	INFINITE
100	7.840	46.618	1.574	1.596	5.499	-13.566
200	8.003	51.135	5.5132	.799	5.214	-7.792
298	8.338	54.383	.000	.000	5.000	-7.049
300	8.347	54.534	.015	.015	4.986	-7.057
400	8.507	58.911	1.757	1.757	4.859	-7.022
500	8.670	58.960	5.466	1.757	4.859	-7.022
600	9.080	60.734	2.771	4.508	4.134	-3.901
700	10.405	62.305	3.791	4.399	12.501	-3.903
800	10.089	63.009	5.657	4.307	13.663	-3.732
900	10.089	63.009	5.657	4.307	13.663	-3.732
1000	11.365	66.189	59.123	7.066	16.021	-3.501
1100	11.612	67.284	59.816	8.215	17.209	-3.419
1200	11.831	68.304	60.481	9.387	18.401	-3.351
1300	12.027	69.258	61.120	10.570	19.597	-3.294
1400	12.197	70.150	61.725	11.765	20.797	-3.246
1500	12.350	71.003	62.323	13.019	21.996	-3.205
1600	12.485	71.804	62.891	14.261	23.197	-3.168
1700	12.606	72.565	63.438	15.515	24.401	-3.137
1800	12.714	73.288	63.965	16.782	25.605	-3.109
1900	12.811	73.974	64.474	18.061	26.817	-3.084
2000	12.895	74.638	64.966	19.353	28.041	-3.061
2100	12.972	75.269	65.442	20.657	29.226	-3.041
2200	13.041	75.874	65.902	21.937	30.435	-3.023
2300	13.106	76.455	66.349	23.245	31.665	-3.007
2400	13.167	77.010	66.777	24.577	32.922	-2.992
2500	13.210	77.552	67.202	25.876	34.209	-2.978
2600	13.256	78.071	67.610	27.200	35.286	-2.964
2700	13.298	78.572	68.007	28.528	36.502	-2.954
2800	13.337	79.058	68.393	29.858	37.719	-2.944
2900	13.375	79.525	68.765	31.190	38.938	-2.934
3000	13.403	79.979	69.135	32.534	40.142	-2.928
3100	13.432	80.419	69.492	33.875	41.386	-2.918
3200	13.459	80.846	69.840	35.220	42.610	-2.910
3300	13.487	81.261	70.179	36.567	43.839	-2.903
3400	13.507	81.663	70.507	37.917	45.069	-2.897
3500	13.528	82.055	70.836	39.268	46.299	-2.891
3600	13.547	82.437	71.153	40.622	47.534	-2.886
3700	13.565	82.808	71.463	41.978	48.771	-2.881
3800	13.582	83.170	71.766	43.332	50.011	-2.876
3900	13.598	83.523	72.066	44.689	51.254	-2.872
4000	13.612	83.867	72.354	46.055	52.493	-2.868
4100	13.626	84.204	72.639	47.417	53.741	-2.864
4200	13.638	84.532	72.918	48.780	54.989	-2.861
4300	13.650	84.857	73.192	50.144	56.252	-2.858
4400	13.662	85.177	73.461	51.503	57.519	-2.855
4500	13.672	85.474	73.724	52.876	58.789	-2.853
4600	13.682	85.775	73.983	54.244	60.013	-2.851
4700	13.691	86.069	74.237	55.613	61.274	-2.849
4800	13.699	86.358	74.486	56.982	62.539	-2.847
4900	13.708	86.640	74.736	58.352	63.809	-2.845
5000	13.716	86.917	74.972	59.724	65.069	-2.844
5100	13.723	87.189	75.209	61.096	66.346	-2.843
5200	13.730	87.455	75.442	62.468	67.616	-2.842
5300	13.736	87.715	75.670	63.840	68.886	-2.841
5400	13.743	87.974	75.897	65.216	70.159	-2.840
5500	13.748	88.226	76.119	66.590	71.460	-2.839
5600	13.754	88.474	76.337	67.965	72.742	-2.839
5700	13.759	88.717	76.552	69.341	74.029	-2.838
5800	13.764	88.957	76.767	70.717	75.315	-2.838
5900	13.769	89.192	76.973	72.094	76.601	-2.838
6000	13.774	89.423	77.178	73.471	77.911	-2.838

Mar. 31, 1964

HYDROPEROXYL (HO₂)

(IDEAL GAS)

Point Group C₁
ΔH°_f 0 = 6 ± 2 kcal. mole⁻¹
ΔH°_f 298.15 = 54.393 cal. deg.⁻¹ mole⁻¹
ΔH°_f 298.15 = 5 ± 2 kcal. mole⁻¹
Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	g _i
1389.4	(1)
1101	(1)
5414	(1)

Bond length: H-O = [0.958] Å
Bond angle: HOO = [120°]
Product of the Moments of Inertia: I_AI_BI_C = [0.6424] X 10⁻¹¹⁷ g.³ cm.³
σ = 1

Heat of Formation.

S. N. Foner and R. L. Hudson, J. Chem. Phys. 36, 2681 (1962) have determined the ionization potential of HO₂ and the appearance potential of HO₂⁺ from H₂O₂. Using the ΔH°_f of H₂O₂(g) determined by P. A. Giguere and I. D. Liu, J. Am. Chem. Soc. 77, 6477 (1955), they calculate ΔH°_f 0 HO₂ = 5.7 ± 2 kcal. mole⁻¹.

Heat Capacity and Entropy.

The point group must be C₁ as the two oxygen atoms have been shown to be non-equivalent, from the increased number of infra-red bands obtained when using O₂¹⁸ enriched with 28% of O₂¹⁸, by D. E. Milligan and M. E. Jacox, J. Chem. Phys. 39, 2027 (1963). They also reported the three frequencies given above in the infra-red spectrum of the matrix isolated HO₂ radical. The bond lengths were taken equal to those estimated by M. E. Boyd, J. Chem. Phys. 37, 1317 (1962), the angle was that recommended by Milligan and Jacox, loc. cit. Boyd's conclusion that the lowest energy configuration should be an isosceles triangle could not be accepted in view of the nonequivalence of the oxygen atoms. The electronic ground state was taken as 2A'' as predicted by A. D. Walsh, J. Chem. Soc. London, 2288 (1953).

Phosphorus Monohydride (PH)
(Ideal Gas) GFW = 31.98177

T, K	C _p ^a	h _{298.15} ^b /mol	S ^c	(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^d	ΔG ^e	Log K ^f
0	0.000	0.000	INFINITE	2.047	60.407	60.407	60.407	INFINITE
100	6.959	39.295	53.092	1.380	60.424	60.424	60.424	126.697
200	6.962	44.120	47.538	0.984	60.432	60.432	60.432	36.772
298	6.970	46.900	46.900	0.000	60.432	60.432	60.432	0.000
300	6.970	46.944	46.901	-0.013	60.432	60.432	60.432	0.000
400	7.008	46.953	47.174	0.711	60.416	60.416	60.416	27.476
500	7.100	50.525	47.693	1.414	60.200	60.200	60.200	20.845
600	7.242	51.832	48.277	2.133	59.985	59.985	59.985	16.507
700	7.411	52.661	48.867	2.866	59.709	59.709	59.709	13.393
800	7.596	53.061	49.461	3.596	59.384	59.384	59.384	10.912
900	7.796	53.956	49.996	4.333	59.004	59.004	59.004	8.432
1000	7.914	55.691	50.524	5.156	58.589	58.589	58.589	6.485
1100	8.037	56.452	51.029	5.965	58.134	58.134	58.134	4.869
1200	8.166	57.159	51.511	6.777	57.646	57.646	57.646	3.475
1300	8.307	57.839	52.011	7.591	57.124	57.124	57.124	2.302
1400	8.459	58.523	52.432	8.285	56.574	56.574	56.574	1.373
1500	8.615	59.276	52.837	10.152	55.999	55.999	55.999	0.694
1600	8.705	60.101	53.225	11.008	55.399	55.399	55.399	0.206
1700	8.805	60.996	53.599	11.844	54.774	54.774	54.774	0.000
1800	8.914	61.874	54.000	12.654	54.124	54.124	54.124	0.000
1900	9.030	61.724	54.427	14.557	53.454	53.454	53.454	0.000
2000	9.104	62.396	54.897	15.454	52.764	52.764	52.764	0.000
2100	9.243	63.192	55.396	17.299	52.054	52.054	52.054	0.000
2200	9.308	63.939	55.970	18.226	51.324	51.324	51.324	0.000
2300	9.432	64.694	56.649	20.101	50.574	50.574	50.574	0.000
2400	9.547	65.461	57.381	21.999	49.804	49.804	49.804	0.000
2500	9.647	66.247	58.161	23.914	49.014	49.014	49.014	0.000
2600	9.740	67.047	58.984	25.844	48.204	48.204	48.204	0.000
2700	9.830	67.864	59.844	27.784	47.374	47.374	47.374	0.000
2800	9.917	68.694	60.734	29.734	46.524	46.524	46.524	0.000
2900	10.002	69.534	61.654	31.694	45.654	45.654	45.654	0.000
3000	10.087	70.384	62.604	33.664	44.764	44.764	44.764	0.000
3100	10.172	71.244	63.584	35.644	43.854	43.854	43.854	0.000
3200	10.257	72.114	64.584	37.634	42.924	42.924	42.924	0.000
3300	10.342	72.994	65.604	39.634	41.974	41.974	41.974	0.000
3400	10.427	73.884	66.644	41.644	41.004	41.004	41.004	0.000
3500	10.512	74.784	67.704	43.674	40.014	40.014	40.014	0.000
3600	10.597	75.694	68.784	45.724	39.004	39.004	39.004	0.000
3700	10.682	76.614	69.884	47.784	38.004	38.004	38.004	0.000
3800	10.767	77.544	70.994	49.854	37.004	37.004	37.004	0.000
3900	10.852	78.484	72.114	51.934	36.004	36.004	36.004	0.000
4000	10.937	79.434	73.244	54.024	35.004	35.004	35.004	0.000
4100	11.022	80.394	74.384	56.124	34.004	34.004	34.004	0.000
4200	11.107	81.364	75.534	58.234	33.004	33.004	33.004	0.000
4300	11.192	82.344	76.694	60.354	32.004	32.004	32.004	0.000
4400	11.277	83.334	77.864	62.484	31.004	31.004	31.004	0.000
4500	11.362	84.334	79.044	64.624	30.004	30.004	30.004	0.000
4600	11.447	85.344	80.234	66.774	29.004	29.004	29.004	0.000
4700	11.532	86.364	81.434	68.934	28.004	28.004	28.004	0.000
4800	11.617	87.394	82.644	71.104	27.004	27.004	27.004	0.000
4900	11.702	88.434	83.864	73.284	26.004	26.004	26.004	0.000
5000	11.787	89.484	85.094	75.474	25.004	25.004	25.004	0.000
5100	11.872	90.544	86.334	77.674	24.004	24.004	24.004	0.000
5200	11.957	91.614	87.584	79.884	23.004	23.004	23.004	0.000
5300	12.042	92.694	88.844	82.104	22.004	22.004	22.004	0.000
5400	12.127	93.784	90.114	84.334	21.004	21.004	21.004	0.000
5500	12.212	94.884	91.394	86.574	20.004	20.004	20.004	0.000
5600	12.297	95.994	92.684	88.824	19.004	19.004	19.004	0.000
5700	12.382	97.114	93.984	91.084	18.004	18.004	18.004	0.000
5800	12.467	98.244	95.294	93.354	17.004	17.004	17.004	0.000
5900	12.552	99.384	96.614	95.634	16.004	16.004	16.004	0.000
6000	12.637	100.534	97.944	97.924	15.004	15.004	15.004	0.000

Dec. 31, 1960; Sept. 30, 1962; June 30, 1967

PHOSPHORUS MONOHYDRIDE (PH) (IDEAL GAS) GFW = 31.98177

Ground State Configuration 3s²

S_{298.15} = 46.9 gibbs/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i	E _i , cm ⁻¹	g _i
0	3	29560	6
[7650]	2	[38110]	2
[15150]	1	[57490]	1

ω_e = 2380 cm⁻¹ ω_eX_e = [55] cm⁻¹ σ = 1

B_e = 8.412 cm⁻¹

r_e = 1.43 Å

Heat of Formation

Jordan (1) estimated the dissociation energy (D₀) of PH(g) as 70.44 kcal/mol using a semiempirical theoretical method. The corresponding value for the heat of formation (ΔH_{298.15}^o) is 60.6 ± 8 kcal/mol.

Heat Capacity and Entropy

Jordan (1) predicted five electronic levels (X²Σ, A²Δ, B²Π, D²Π, E²Σ) based on the reported value (2) of 29560 cm⁻¹ for the C²Π level (this level is designated A²Π by Herzberg (2)). Several qualitative spectroscopic investigations of PH(g) have been reported and are in general accord with the predictions of Jordan (1). Isaha and Pearce (3) reported the values of the rotational constant B_e and the fundamental vibrational frequency ω_e. The value of ω_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The value of the anharmonic vibrational term ω_eX_e is estimated from the relation ω_eX_e = ω_e²/(4D₀ + 2ω_e).

References

1. P. C. Jordan, J. Chem. Phys. **41**, 1442 (1964).
2. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
3. M. Isaha and R. W. B. Pearce, Proc. Roy. Soc. (London) **A173**, 265 (1939), and R. W. B. Pearce, *ibid.*, **A123**, 328 (1930).

HP

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	4.000	INFINITE	INFINITE	2.074	57.032	57.032	INFINITE
100	46.117	84.849	1.3893	56.940	54.508	-119.122	-
200	6.970	52.737	0.000	56.940	54.508	-119.122	-
298	7.045	52.737	0.000	56.940	54.508	-119.122	-
300	7.048	52.737	0.013	56.445	49.955	-36.646	-
400	7.244	54.833	0.015	56.135	47.835	-26.135	-
500	7.501	56.476	0.016	55.874	45.786	-23.012	-
600	7.755	57.867	0.017	55.597	43.796	-15.052	-
700	7.980	59.079	0.018	55.304	41.861	-13.125	-
800	8.170	60.158	0.019	55.000	39.987	-11.016	-
900	8.328	61.129	0.020	54.687	38.067	-9.384	-
1000	8.461	62.014	0.021	54.367	36.102	-8.084	-
1100	8.574	62.826	0.022	54.043	34.196	-7.025	-
1200	8.672	63.576	0.023	53.715	32.344	-6.165	-
1300	8.761	64.274	0.024	53.384	30.540	-5.404	-
1400	8.843	64.926	0.025	53.050	28.782	-4.740	-
1500	8.921	65.539	0.026	52.715	27.069	-4.172	-
1600	8.997	66.117	0.027	52.380	25.402	-3.699	-
1700	9.072	66.665	0.028	52.045	23.780	-3.327	-
1800	9.146	67.185	0.029	51.710	22.202	-2.955	-
1900	9.220	67.682	0.030	51.375	20.668	-2.582	-
2000	9.294	68.157	0.031	51.040	19.178	-2.209	-
2100	9.368	68.612	0.032	50.705	17.732	-1.836	-
2200	9.441	69.049	0.033	50.370	16.330	-1.463	-
2300	9.513	69.471	0.034	50.035	14.972	-1.090	-
2400	9.585	69.877	0.035	49.700	13.658	-0.717	-
2500	9.657	70.270	0.036	49.365	12.389	-0.344	-
2600	9.729	70.650	0.037	49.030	11.164	0.030	-
2700	9.785	71.018	0.038	48.695	9.984	0.403	-
2800	9.848	71.375	0.039	48.360	8.858	0.776	-
2900	9.908	71.721	0.040	48.025	7.782	1.149	-
3000	9.966	72.058	0.041	47.690	6.750	1.522	-
3100	10.021	72.386	0.042	47.355	5.760	1.895	-
3200	10.074	72.705	0.043	47.020	4.812	2.268	-
3300	10.124	73.016	0.044	46.685	3.906	2.641	-
3400	10.171	73.319	0.045	46.350	3.042	3.014	-
3500	10.215	73.614	0.046	46.015	2.219	3.387	-
3600	10.257	73.902	0.047	45.680	1.436	3.760	-
3700	10.296	74.184	0.048	45.345	0.694	4.133	-
3800	10.333	74.459	0.049	45.010	0.000	4.506	-
3900	10.368	74.728	0.050	44.675	-0.742	4.879	-
4000	10.400	74.991	0.051	44.340	-1.524	5.252	-
4100	10.430	75.248	0.052	44.005	-2.346	5.625	-
4200	10.459	75.500	0.053	43.670	-3.209	5.998	-
4300	10.485	75.746	0.054	43.335	-4.113	6.371	-
4400	10.510	75.987	0.055	43.000	-5.058	6.744	-
4500	10.533	76.224	0.056	42.665	-6.044	7.117	-
4600	10.555	76.456	0.057	42.330	-7.070	7.490	-
4700	10.575	76.683	0.058	42.000	-8.130	7.863	-
4800	10.594	76.906	0.059	41.665	-9.226	8.236	-
4900	10.612	77.124	0.060	41.330	-10.358	8.609	-
5000	10.629	77.339	0.061	41.000	-11.526	8.982	-
5100	10.644	77.549	0.062	40.665	-12.730	9.355	-
5200	10.659	77.756	0.063	40.330	-13.970	9.728	-
5300	10.673	77.959	0.064	40.000	-15.246	10.101	-
5400	10.687	78.159	0.065	39.665	-16.558	10.474	-
5500	10.699	78.355	0.066	39.330	-17.906	10.847	-
5600	10.711	78.548	0.067	39.000	-19.290	11.220	-
5700	10.723	78.738	0.068	38.665	-20.710	11.593	-
5800	10.734	78.924	0.069	38.330	-22.166	11.966	-
5900	10.744	79.108	0.070	38.000	-23.658	12.339	-
6000	10.754	79.289	0.071	37.665	-25.186	12.712	-

June 30, 1962

Lead Monohydride (PbH) (Ideal Gas)

Mol. Wt. = 208.22

 $\Delta H_f^\circ 298.15 = 56.5 \pm 4.6$ kcal. mole⁻¹ $S^\circ 298.15 = 52.737$ cal. deg.⁻¹ mole⁻¹Ground State Configuration $2\pi_{1/2}^2$

Electronic Levels and Multiplicities

 $\epsilon, \text{ cm.}^{-1}$ g_i

0 2

[8000]

2

 $\omega_e = 1564.1 \text{ cm.}^{-1}$ $\omega_e x_e = 29.75 \text{ cm.}^{-1}$ $B_e = 4.971 \text{ cm.}^{-1}$ $\alpha_e = 0.144 \text{ cm.}^{-1}$ $\sigma = 1$

Heat of Formation. $\Delta H_f^\circ 298.15$ was calculated from the dissociation energy of PbH(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration and spectroscopic data were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950). Electronic levels and multiplicity were estimated by comparison with those for PbF(g).

Sulfur Monohydride (SH)

(Ideal Gas) GFW = 33.07197

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o) ₂₉₈ /T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	0.000	INFINITE	- 2.216	34.489	INFINITE	
100	7.515	38.378	5.625	34.586	- 70.535	
200	7.515	43.610	4.767	34.660	- 29.915	
298	7.755	46.729	0.000	34.600	- 27.595	- 20.228
300	7.752	46.777	- 0.014	34.598	- 27.552	- 20.072
400	7.579	44.963	4.781	33.918	- 25.244	- 13.793
500	7.479	50.682	4.356	33.363	- 23.137	- 10.113
600	7.468	57.023	48.224	32.922	- 21.133	- 7.698
700	7.524	53.178	48.851	32.521	- 19.224	- 6.002
800	7.620	54.188	49.457	32.168	- 17.089	- 4.393
900	7.735	55.092	50.033	31.853	- 15.707	- 3.814
1000	7.855	55.914	50.591	31.533	- 14.053	- 3.351
1100	7.973	56.668	51.100	31.208	- 12.973	- 2.973
1200	8.084	57.366	51.594	30.877	- 12.038	- 2.658
1300	8.187	58.017	52.063	30.541	- 11.224	- 2.391
1400	8.280	58.628	52.511	30.200	- 10.494	- 2.163
1500	8.366	59.202	52.938	29.854	- 9.773	- 1.965
1600	8.443	59.744	53.346	29.507	- 9.039	- 1.791
1700	8.512	60.258	53.738	29.156	- 8.292	- 1.639
1800	8.576	60.747	54.114	28.800	- 7.530	- 1.502
1900	8.634	61.212	54.475	28.439	- 6.761	- 1.381
2000	8.686	61.656	54.823	28.074	- 5.989	- 1.271
2100	8.734	62.081	55.159	27.704	- 5.215	- 1.172
2200	8.779	62.488	55.483	27.329	- 4.440	- 1.082
2300	8.820	62.880	55.796	26.950	- 3.664	- 0.999
2400	8.858	63.256	56.099	26.566	- 2.888	- 0.924
2500	8.893	63.618	56.393	26.178	- 2.112	- 0.854
2600	8.926	63.968	56.677	25.785	- 1.336	- 0.790
2700	8.957	64.305	56.954	25.388	- 0.560	- 0.731
2800	8.986	64.631	57.222	24.986	0.214	- 0.675
2900	9.014	64.947	57.483	24.579	0.989	- 0.624
3000	9.040	65.253	57.737	24.166	1.763	- 0.576
3100	9.065	65.550	57.984	23.748	2.536	- 0.531
3200	9.089	65.838	58.225	23.325	3.308	- 0.489
3300	9.112	66.118	58.460	22.898	4.079	- 0.449
3400	9.134	66.390	58.689	22.466	4.849	- 0.412
3500	9.155	66.656	58.913	22.029	5.618	- 0.376
3600	9.175	66.914	59.132	21.587	6.386	- 0.343
3700	9.195	67.165	59.346	21.140	7.153	- 0.312
3800	9.214	67.411	59.555	20.688	7.919	- 0.282
3900	9.233	67.650	59.759	20.231	8.684	- 0.254
4000	9.251	67.884	59.959	19.769	9.448	- 0.227
4100	9.269	68.113	60.155	19.302	10.212	- 0.202
4200	9.287	68.337	60.344	18.830	10.975	- 0.177
4300	9.304	68.555	60.526	18.353	11.738	- 0.154
4400	9.322	68.770	60.701	17.871	12.499	- 0.132
4500	9.338	68.979	60.862	17.384	13.259	- 0.111
4600	9.355	69.185	61.000	16.892	14.018	- 0.091
4700	9.372	69.386	61.254	16.395	14.775	- 0.072
4800	9.388	69.583	61.426	15.898	15.531	- 0.053
4900	9.404	69.777	61.594	15.398	16.286	- 0.035
5000	9.421	69.967	61.760	14.894	17.040	- 0.018
5100	9.437	70.154	61.923	14.387	17.793	- 0.002
5200	9.453	70.338	62.083	13.878	18.545	0.014
5300	9.469	70.518	62.240	13.365	19.297	0.029
5400	9.485	70.695	62.395	12.848	20.048	0.044
5500	9.502	70.869	62.547	12.327	20.798	0.058
5600	9.518	71.040	62.698	11.802	21.547	0.071
5700	9.534	71.209	62.845	11.272	22.295	0.084
5800	9.550	71.375	62.991	10.739	23.042	0.097
5900	9.567	71.538	63.135	10.202	23.789	0.109
6000	9.583	71.699	63.276	9.660	24.535	0.120

Dec. 31, 1960; June 30, 1967

SULFUR MONOHYDRIDE (SH)

(IDEAL GAS)

GFW = 33.07197

Ground State Configuration 2π

$$\Delta H_{\text{O}}^{\circ} = 34.4 \pm 4 \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = 46.73 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = 34.6 \pm 4 \text{ kcal/mol}$$

Electronic Levels and Quantum Weights

$\frac{E_i, \text{cm}^{-1}}{0}$	$\frac{g_i}{2}$	$\frac{E_i, \text{cm}^{-1}}{59836}$	$\frac{g_i}{2}$
376.9	2	[63850]	4
30682.4	2	75000	18
$\omega_e = 2702 \text{ cm}^{-1}$	$\omega_e x_e = 60 \text{ cm}^{-1}$	$\sigma = 1$	
$B_e = 9.611 \text{ cm}^{-1}$	$\alpha_e = [0.3] \text{ cm}^{-1}$	$r_e = 1.3397 \text{ \AA}$	

Heat of Formation

Mackie (1) estimated ΔH_{298}° of SH(g) as $34.5 \pm 4 \text{ kcal/mol}$, this value being an average of three independent determinations.

He obtained these three values by the following methods: (A) He calculated ΔH_{298}° of SH(g) as $34.9 \pm 4.5 \text{ kcal/mol}$ from ΔH_{298}° of thiobenzyl alcohol (g), ΔH_{298}° of the benzyl radical (g) and the heat of dissociation (D_0°) of thiobenzyl alcohol reported by Sehon and Darwent (2). (B) A value of $35.2 \pm 4.5 \text{ kcal/mol}$ was calculated from ΔH_{298}° of C_2H_5 (g), ΔH_{298}° of C_2H_5SH (g) and the appearance potential of C_2H_5 reported by Franklin and Lumpkin (3). (C) He calculated that ΔH_{298}° of SH(g) is $33.7 \pm 3 \text{ kcal/mol}$ from ΔH_{298}° of H_2S (g) and the mass spectrographic data for the reactions $H_2S = SH^+ + H + e^-$ and $SH = SH^+ + e^-$ reported by Palmer and Lossing (4). The adopted value of $34.5 \pm 4 \text{ kcal/mol}$ compares with a value of 34.9 kcal/mol obtained from a linear Birge-Sponer extrapolation of the potential function.

Heat Capacity and Entropy

The high resolution spectra of SH(g) have been studied by Ramsay (5) and Johns and Ramsay (6) in the near UV and by Morrow (7) in the vacuum UV. The energy levels of the doublet ground state and of the first excited state ($^2\Sigma$) were reported by Ramsay (5). Six of the seven higher excited levels ($8^2\Sigma$, $9^2\Sigma$, $10^2\Sigma$, $11^2\Sigma$, $12^2\Sigma$, $13^2\Sigma$) were reported by Morrow (7), the last five of which are shown as an average of 75000 cm^{-1} . The remaining electronic level ($14^2\Sigma$) is estimated by analogy with the electronic levels of SD(g) reported by Morrow (7).

Ramsay (5) reported the following rotational and vibrational constants: $B_0 = 9.461 \text{ cm}^{-1}$, $\omega_e = 2702 \text{ cm}^{-1}$, and $\omega_e x_e = 60 \text{ cm}^{-1}$. The value of α_e is calculated from the Morse potential function. The rotational constant B_e is calculated from $B_e = B_0 + \alpha_e/2$. The bond distance is calculated from B_e .

References

1. H. Mackie, Tetrahedron 13, 1159 (1963).
2. A. H. Sehon and B. de B. Darwent, J. Amer. Chem. Soc. 77, 5282 (1955).
3. J. L. Franklin and H. E. Lumpkin, J. Amer. Chem. Soc. 74, 1023 (1952).
4. T. F. Palmer and F. P. Lossing, J. Amer. Chem. Soc. 83, 4661 (1961).
5. D. A. Ramsay, J. Chem. Phys. 20, 1920 (1952).
6. J. W. C. Johns and D. A. Ramsay, Can. J. Phys. 39, 210 (1961).
7. B. A. Morrow, Can. J. Phys. 44, 2447 (1966).

(IDEAL GAS)

SILICON MONOHYDRIDE (SiH₂)

GFW = 29.09397

Ground State Configuration 2¹ Π

$$\Delta H_f^\circ = 89.6 \pm 2 \text{ kcal/mol}$$

$$\Delta H_f^\circ(298.15) = 90 \pm 2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 47.306 \pm 0.05 \text{ gibbs/mol}$$

Electronic Levels and Degeneracies

State	E_i , cm ⁻¹	g_i
-------	--------------------------	-------

$X^2\Pi$	0	2
----------	---	---

4_2^-	142.83	2
---------	--------	---

A_2^+	{21510}	4
---------	---------	---

2_2^-	{24730}	2
---------	---------	---

B_2^+	30808	2
---------	-------	---

C_2^+	30842	2
---------	-------	---

D_2^+	48510	4
---------	-------	---

E_2^+	52399	2
---------	-------	---

$\omega_e X_e$	$= 35.51 \text{ cm}^{-1}$	
----------------	---------------------------	--

σ	$= 1$	
----------	-------	--

ω_e	$= 2041.8 \text{ cm}^{-1}$	
------------	----------------------------	--

B_e	$= 7.4986 \text{ cm}^{-1}$	
-------	----------------------------	--

σ_e	$= 0.219 \text{ cm}^{-1}$	
------------	---------------------------	--

r_e	$= 1.5201 \text{ \AA}$	
-------	------------------------	--

Heat of Formation		
-------------------	--	--

Verma (1) has derived an upper limit to the dissociation energy of 24680 cm ⁻¹ (70.56 kcal) from predissociation in the B ₂ ⁺ state. With JANAF values for Si(g) and H(g) this yields $\Delta H_f^\circ(\text{SiH}_2, g) \geq 87.73 \text{ kcal/mol}$. We adopt a value of $\Delta H_f^\circ(\text{SiH}_2, g) = 90 \pm 2 \text{ kcal/mol}$, assuming that the predissociation has a 2 kcal barrier similar to that in the predissociation of the A ¹ Π state of AlH. Hildenbrand (5) has applied an ionic-covalent correction to the linear Birge-Sponer extrapolation of the ground state dissociation energy and obtains D ₀ (SiH ₂ , g) = 70 kcal in excellent agreement with the predissociation value.		
-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	--	--

Heat Capacity and Entropy		
---------------------------	--	--

The observed electronic levels and rotational and vibrational constants are from Herzberg et al. (2), Klymning and Lindgren (3), and Verma (1). The estimated levels are from the calculations of Jordan (4). The upper states are all assumed to have ground state molecular constants. This approximation introduces negligible error when the first state is as high as 21000 cm ⁻¹ and has the same multiplicity as the ground state.		
------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	--	--

References		
------------	--	--

1. R. D. Verma, Can. J. Phys. 43, 2136 (1965).		
------------------------------------------------	--	--

2. G. Herzberg, A. Lagerqvist, and B. J. McKenzie, Can. J. Phys. 47, 1891 (1969).		
-----------------------------------------------------------------------------------	--	--

3. L. Klymning and B. Lindgren, Ark. Fysik 33, 73 (1966).		
-----------------------------------------------------------	--	--

4. P. C. Jordan, J. Chem. Phys. 44, 3400 (1966).		
--------------------------------------------------	--	--

5. D. L. Hildenbrand, Douglas Advanced Research Labs., Huntington Beach, Calif., private communication, Dec. 30, 1969.		
------------------------------------------------------------------------------------------------------------------------	--	--

Silicon Monohydride (SiH₂)

(Ideal Gas) GFW = 29.09397

T, °K	Cp ^a	S ^b	gibbs/mol -(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH ^c	ΔG ^d	Log Kp
0	0.000	INFINITE	INFINITE	2.205	89.576	89.576	INFINITE
100	7.804	39.135	53.839	1.470	89.667	87.265	-190.717
200	7.371	44.403	47.968	.713	90.062	84.571	-92.415
298	7.191	47.306	47.306	.000	90.000	81.689	-60.026
300	7.190	47.350	47.306	.013	89.998	81.839	-59.619
400	7.180	48.414	47.587	.731	89.661	79.138	-43.239
500	7.285	51.026	48.120	1.453	89.690	76.477	-33.428
600	7.451	52.348	48.719	2.100	89.509	73.851	-26.900
700	7.634	53.531	49.125	2.590	89.297	71.251	-21.500
800	7.817	54.562	49.416	3.717	89.117	68.686	-16.764
900	7.983	55.493	50.485	4.507	88.969	66.141	-14.061
1000	8.129	56.342	51.029	5.313	88.792	63.613	-13.903
1100	8.257	57.122	51.548	6.132	88.613	61.104	-12.140
1200	8.369	57.842	52.047	6.967	88.427	58.613	-10.477
1300	8.465	58.520	52.515	7.805	88.237	56.133	-9.017
1400	8.550	59.150	52.967	8.656	88.056	53.670	-7.768
1500	8.624	59.743	53.399	9.515	87.857	51.222	-6.664
1600	8.690	60.301	53.813	10.381	87.649	48.785	-5.664
1700	8.748	60.830	54.213	11.250	87.432	46.270	-4.764
1800	8.801	61.331	54.592	12.113	87.208	43.720	-3.914
1900	8.848	61.809	54.960	13.013	86.978	41.140	-3.105
2000	8.891	62.264	55.314	13.907	86.742	38.540	-2.335
2100	8.931	62.698	55.655	14.791	86.500	35.920	-1.605
2200	8.967	63.115	55.985	15.664	86.253	33.290	-0.915
2300	9.001	63.514	56.303	16.528	86.000	30.650	-0.265
2400	9.033	63.898	56.612	17.386	85.742	28.000	0.345
2500	9.063	64.267	56.911	18.231	85.479	25.350	0.955
2600	9.092	64.623	57.201	19.058	85.212	22.700	1.565
2700	9.119	64.967	57.482	19.859	84.940	20.050	2.175
2800	9.146	65.299	57.755	20.649	84.663	17.400	2.785
2900	9.172	65.620	58.021	21.428	84.381	14.750	3.395
3000	9.198	65.932	58.279	22.197	84.095	12.100	3.995
3100	9.228	66.238	58.531	22.958	83.805	9.450	4.595
3200	9.249	66.527	58.776	23.709	83.510	6.800	5.195
3300	9.275	66.812	59.016	24.450	83.210	4.150	5.795
3400	9.301	67.089	59.249	25.182	82.905	1.500	6.395
3500	9.328	67.359	59.477	25.908	82.595	-1.150	6.995
3600	9.355	67.622	59.700	26.622	82.280	-3.800	7.595
3700	9.384	67.879	59.917	27.329	81.960	-6.450	8.195
3800	9.413	68.130	60.130	28.030	81.635	-9.100	8.795
3900	9.443	68.375	60.338	28.725	81.305	-11.750	9.395
4000	9.474	68.614	60.542	29.415	80.970	-14.400	9.995
4100	9.506	68.848	60.742	30.100	80.630	-17.050	10.595
4200	9.540	69.078	60.938	30.780	80.285	-19.700	11.195
4300	9.575	69.303	61.130	31.455	79.935	-22.350	11.795
4400	9.611	69.523	61.318	32.125	79.580	-25.000	12.395
4500	9.648	69.740	61.503	32.790	79.220	-27.650	12.995
4600	9.687	69.952	61.684	33.455	78.855	-30.300	13.595
4700	9.727	70.161	61.862	34.115	78.485	-32.950	14.195
4800	9.768	70.366	62.037	34.770	78.110	-35.600	14.795
4900	9.811	70.568	62.209	35.420	77.730	-38.250	15.395
5000	9.854	70.767	62.378	36.065	77.345	-40.900	15.995
5100	9.899	70.962	62.545	36.705	76.955	-43.550	16.595
5200	9.946	71.155	62.709	37.340	76.560	-46.200	17.195
5300	9.993	71.345	62.870	37.970	76.160	-48.850	17.795
5400	10.042	71.532	63.028	38.595	75.755	-51.500	18.395
5500	10.091	71.717	63.185	39.215	75.345	-54.150	18.995
5600	10.141	71.899	63.339	39.830	74.930	-56.800	19.595
5700	10.193	72.079	63.490	40.440	74.510	-59.450	20.195
5800	10.245	72.257	63.640	41.045	74.085	-62.100	20.795
5900	10.298	72.432	63.788	41.645	73.655	-64.750	21.395
6000	10.351	72.606	63.933	42.240	73.220	-67.400	21.995

Dec. 31, 1960; Dec. 31, 1969

Zirconium Hydride (ZrH)

(Ideal Gas) Mol. wt. = 92.228

ZIRCONIUM HYDRIDE (ZrH) (IDEAL GAS)

MOL. WT. = 92.228

T, °K.	C _p ^o	S ^o - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	INFINITE	-2.077	123.652	123.652	INFINITE
100	6.962	44.006	57.868	123.751	120.907	-264.236
200	6.978	48.835	52.282	123.624	118.046	-129.046
300	7.096	51.638	51.638	123.400	115.432	-84.610
400	7.499	51.682	51.638	123.396	115.283	-84.053
500	7.348	53.756	51.919	123.135	112.750	-61.601
600	7.632	55.426	52.459	122.864	110.186	-48.160
700	7.891	56.841	53.074	122.586	107.676	-39.219
800	8.286	58.169	53.710	122.311	105.218	-32.460
900	8.427	60.153	54.913	121.774	100.399	-24.379
1000	8.543	61.048	55.483	121.510	98.038	-21.425
1100	8.639	61.866	56.026	121.236	95.704	-19.014
1200	8.787	62.549	56.549	120.959	93.423	-17.018
1300	8.787	63.222	57.049	120.679	91.194	-15.453
1400	8.845	63.976	57.512	119.451	89.059	-13.902
1500	8.896	64.588	57.963	119.167	86.898	-12.560
1600	8.942	65.163	58.304	118.875	84.757	-11.577
1700	8.977	65.707	58.610	118.575	82.634	-10.623
1800	9.009	66.222	58.890	118.268	80.537	-9.797
1900	9.053	66.710	59.149	117.952	78.461	-9.022
2000	9.084	67.175	59.397	117.628	76.368	-8.345
2100	9.113	67.619	60.312	117.296	74.313	-7.734
2200	9.140	68.043	60.693	116.952	72.440	-7.196
2300	9.165	68.448	61.039	116.598	70.647	-6.731
2400	9.191	68.841	61.303	116.191	68.971	-6.371
2500	9.214	69.216	61.612	115.728	67.108	-5.866
2600	9.237	69.578	61.911	115.206	65.360	-5.494
2700	9.259	69.927	62.202	114.628	63.626	-5.150
2800	9.279	70.264	62.478	114.000	61.909	-4.837
2900	9.300	70.590	62.758	109.549	60.199	-4.537
3000	9.320	70.906	63.024	109.188	58.502	-4.262
3100	9.339	71.212	63.283	108.827	56.816	-4.005
3200	9.357	71.509	63.533	108.465	55.145	-3.766
3300	9.377	71.797	63.778	108.102	53.486	-3.544
3400	9.396	72.077	64.022	107.740	51.836	-3.332
3500	9.414	72.350	64.256	107.376	50.197	-3.134
3600	9.432	72.615	64.484	107.011	48.566	-2.948
3700	9.449	72.874	64.708	106.646	46.949	-2.773
3800	9.464	73.127	64.927	106.281	45.342	-2.608
3900	9.484	73.372	65.139	105.914	43.746	-2.454
4000	9.501	73.613	65.348	105.548	42.153	-2.303
4100	9.518	73.847	65.552	105.180	40.573	-2.163
4200	9.535	74.077	65.753	104.813	39.003	-2.029
4300	9.552	74.302	65.949	104.446	37.444	-1.903
4400	9.568	74.521	66.141	104.078	35.886	-1.786
4500	9.585	74.736	66.330	103.707	34.337	-1.668
4600	9.601	74.947	66.515	103.337	32.802	-1.558
4700	9.617	75.154	66.697	102.967	31.274	-1.454
4800	9.633	75.357	66.875	102.596	29.756	-1.354
4900	9.650	75.555	67.050	102.222	28.246	-1.254
5000	9.666	75.751	67.222	101.848	26.744	-1.160
5100	9.682	75.942	67.391	101.471	25.250	-1.072
5200	9.698	76.130	67.557	101.094	23.764	-0.989
5300	9.713	76.315	67.720	100.716	22.286	-0.910
5400	9.730	76.497	67.882	100.337	20.816	-0.836
5500	9.745	76.676	68.040	99.956	19.354	-0.766
5600	9.761	76.851	68.196	99.574	17.900	-0.700
5700	9.773	77.024	68.349	99.191	16.454	-0.638
5800	9.788	77.194	68.500	98.806	15.016	-0.580
5900	9.803	77.362	68.649	98.420	13.586	-0.526
6000	9.824	77.527	68.796	98.038	12.160	-0.474

June 30, 1963

Ground State Configuration [2T] $\Delta H_f^o = [123.7] \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = [51.638] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^o_{298.15} = [123.4] \text{ kcal. mole}^{-1}$

Electronic Levels and Multiplicities

E_1	E_1
0	[4]
$\omega_e X_e = [19] \text{ cm.}^{-1}$	$\epsilon = 1$
$\omega_e = [1400] \text{ cm.}^{-1}$	$r_e = [1.821] \text{ \AA}$
$B_e = [5.1] \text{ cm.}^{-1}$	$\alpha_e = [0.09] \text{ cm.}^{-1}$

Heat of Formation.

ΔH_f^o was estimated as 123.7 kcal. mole⁻¹ by J. S. Gordon, AstroSystems International, Livingston, New Jersey, private communication, January 10, 1963. $\Delta H_f^o_{298.15}$ was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. r_e was calculated from the relationship $r_e = (16.858778/\mu B_e)^{1/2} \text{ \AA}$.

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	ln f(T)/T	ln f(T)/T	ln f(T)/T	ln f(T)/T	ln f(T)/T	ln f(T)/T	Log K _p
100	6.494	31.251	31.208	0.013	0.000	0.000	0.000	0.000	0.000	0.000
200	6.492	31.208	31.208	0.013	0.000	0.000	0.000	0.000	0.000	0.000
300	6.494	31.251	31.208	0.013	0.000	0.000	0.000	0.000	0.000	0.000
400	6.495	31.267	31.480	0.707	0.000	0.000	0.000	0.000	0.000	0.000
500	6.493	31.496	31.495	1.406	0.000	0.000	0.000	0.000	0.000	0.000
600	6.494	31.604	31.573	2.106	0.000	0.000	0.000	0.000	0.000	0.000
700	6.494	31.685	31.615	2.804	0.000	0.000	0.000	0.000	0.000	0.000
800	6.494	31.715	31.715	3.514	0.000	0.000	0.000	0.000	0.000	0.000
900	6.494	31.746	31.746	4.226	0.000	0.000	0.000	0.000	0.000	0.000
1000	6.494	31.762	31.756	4.944	0.000	0.000	0.000	0.000	0.000	0.000
1100	6.494	31.762	31.756	5.670	0.000	0.000	0.000	0.000	0.000	0.000
1200	6.494	31.762	31.756	6.404	0.000	0.000	0.000	0.000	0.000	0.000
1300	6.494	31.762	31.756	7.148	0.000	0.000	0.000	0.000	0.000	0.000
1400	6.494	31.762	31.756	7.892	0.000	0.000	0.000	0.000	0.000	0.000
1500	6.494	31.762	31.756	8.636	0.000	0.000	0.000	0.000	0.000	0.000
1600	6.494	31.762	31.756	9.380	0.000	0.000	0.000	0.000	0.000	0.000
1700	6.494	31.762	31.756	10.124	0.000	0.000	0.000	0.000	0.000	0.000
1800	6.494	31.762	31.756	10.868	0.000	0.000	0.000	0.000	0.000	0.000
1900	6.494	31.762	31.756	11.612	0.000	0.000	0.000	0.000	0.000	0.000
2000	6.494	31.762	31.756	12.356	0.000	0.000	0.000	0.000	0.000	0.000
2100	6.494	31.762	31.756	13.100	0.000	0.000	0.000	0.000	0.000	0.000
2200	6.494	31.762	31.756	13.844	0.000	0.000	0.000	0.000	0.000	0.000
2300	6.494	31.762	31.756	14.588	0.000	0.000	0.000	0.000	0.000	0.000
2400	6.494	31.762	31.756	15.332	0.000	0.000	0.000	0.000	0.000	0.000
2500	6.494	31.762	31.756	16.076	0.000	0.000	0.000	0.000	0.000	0.000
2600	6.494	31.762	31.756	16.820	0.000	0.000	0.000	0.000	0.000	0.000
2700	6.494	31.762	31.756	17.564	0.000	0.000	0.000	0.000	0.000	0.000
2800	6.494	31.762	31.756	18.308	0.000	0.000	0.000	0.000	0.000	0.000
2900	6.494	31.762	31.756	19.052	0.000	0.000	0.000	0.000	0.000	0.000
3000	6.494	31.762	31.756	19.796	0.000	0.000	0.000	0.000	0.000	0.000
3100	6.494	31.762	31.756	20.540	0.000	0.000	0.000	0.000	0.000	0.000
3200	6.494	31.762	31.756	21.284	0.000	0.000	0.000	0.000	0.000	0.000
3300	6.494	31.762	31.756	22.028	0.000	0.000	0.000	0.000	0.000	0.000
3400	6.494	31.762	31.756	22.772	0.000	0.000	0.000	0.000	0.000	0.000
3500	6.494	31.762	31.756	23.516	0.000	0.000	0.000	0.000	0.000	0.000
3600	6.494	31.762	31.756	24.260	0.000	0.000	0.000	0.000	0.000	0.000
3700	6.494	31.762	31.756	25.004	0.000	0.000	0.000	0.000	0.000	0.000
3800	6.494	31.762	31.756	25.748	0.000	0.000	0.000	0.000	0.000	0.000
3900	6.494	31.762	31.756	26.492	0.000	0.000	0.000	0.000	0.000	0.000
4000	6.494	31.762	31.756	27.236	0.000	0.000	0.000	0.000	0.000	0.000
4100	6.494	31.762	31.756	27.980	0.000	0.000	0.000	0.000	0.000	0.000
4200	6.494	31.762	31.756	28.724	0.000	0.000	0.000	0.000	0.000	0.000
4300	6.494	31.762	31.756	29.468	0.000	0.000	0.000	0.000	0.000	0.000
4400	6.494	31.762	31.756	30.212	0.000	0.000	0.000	0.000	0.000	0.000
4500	6.494	31.762	31.756	30.956	0.000	0.000	0.000	0.000	0.000	0.000
4600	6.494	31.762	31.756	31.700	0.000	0.000	0.000	0.000	0.000	0.000
4700	6.494	31.762	31.756	32.444	0.000	0.000	0.000	0.000	0.000	0.000
4800	6.494	31.762	31.756	33.188	0.000	0.000	0.000	0.000	0.000	0.000
4900	6.494	31.762	31.756	33.932	0.000	0.000	0.000	0.000	0.000	0.000
5000	6.494	31.762	31.756	34.676	0.000	0.000	0.000	0.000	0.000	0.000
5100	6.494	31.762	31.756	35.420	0.000	0.000	0.000	0.000	0.000	0.000
5200	6.494	31.762	31.756	36.164	0.000	0.000	0.000	0.000	0.000	0.000
5300	6.494	31.762	31.756	36.908	0.000	0.000	0.000	0.000	0.000	0.000
5400	6.494	31.762	31.756	37.652	0.000	0.000	0.000	0.000	0.000	0.000
5500	6.494	31.762	31.756	38.396	0.000	0.000	0.000	0.000	0.000	0.000
5600	6.494	31.762	31.756	39.140	0.000	0.000	0.000	0.000	0.000	0.000
5700	6.494	31.762	31.756	39.884	0.000	0.000	0.000	0.000	0.000	0.000
5800	6.494	31.762	31.756	40.628	0.000	0.000	0.000	0.000	0.000	0.000
5900	6.494	31.762	31.756	41.372	0.000	0.000	0.000	0.000	0.000	0.000
6000	6.494	31.762	31.756	42.116	0.000	0.000	0.000	0.000	0.000	0.000
6100	6.494	31.762	31.756	42.860	0.000	0.000	0.000	0.000	0.000	0.000
6200	6.494	31.762	31.756	43.604	0.000	0.000	0.000	0.000	0.000	0.000
6300	6.494	31.762	31.756	44.348	0.000	0.000	0.000	0.000	0.000	0.000
6400	6.494	31.762	31.756	45.092	0.000	0.000	0.000	0.000	0.000	0.000
6500	6.494	31.762	31.756	45.836	0.000	0.000	0.000	0.000	0.000	0.000
6600	6.494	31.762	31.756	46.580	0.000	0.000	0.000	0.000	0.000	0.000
6700	6.494	31.762	31.756	47.324	0.000	0.000	0.000	0.000	0.000	0.000
6800	6.494	31.762	31.756	48.068	0.000	0.000	0.000	0.000	0.000	0.000
6900	6.494	31.762	31.756	48.812	0.000	0.000	0.000	0.000	0.000	0.000
7000	6.494	31.762	31.756	49.556	0.000	0.000	0.000	0.000	0.000	0.000
7100	6.494	31.762	31.756	50.300	0.000	0.000	0.000	0.000	0.000	0.000
7200	6.494	31.762	31.756	51.044	0.000	0.000	0.000	0.000	0.000	0.000
7300	6.494	31.762	31.756	51.788	0.000	0.000	0.000	0.000	0.000	0.000
7400	6.494	31.762	31.756	52.532	0.000	0.000	0.000	0.000	0.000	0.000
7500	6.494	31.762	31.756	53.276	0.000	0.000	0.000	0.000	0.000	0.000
7600	6.494	31.762	31.756	54.020	0.000	0.000	0.000	0.000	0.000	0.000
7700	6.494	31.762	31.756	54.764	0.000	0.000	0.000	0.000	0.000	0.000
7800	6.494	31.762	31.756	55.508	0.000	0.000	0.000	0.000	0.000	0.000
7900	6.494	31.762	31.756	56.252	0.000	0.000	0.000	0.000	0.000	0.000
8000	6.494	31.762	31.756	56.996	0.000	0.000	0.000	0.000	0.000	0.000
8100	6.494	31.762	31.756	57.740	0.000	0.000	0.000	0.000	0.000	0.000
8200	6.494	31.762	31.756	58.484	0.000	0.000	0.000	0.000	0.000	0.000
8300	6.494	31.762	31.756	59.228	0.000	0.000	0.000	0.000	0.000	0.000
8400	6.494	31.762	31.756	59.972	0.000	0.000	0.000	0.000	0.000	0.000
8500	6.494	31.762	31.756	60.716	0.000	0.000	0.000	0.000	0.000	0.000
8600	6.494	31.762	31.756	61.460	0.000	0.000	0.000	0.000	0.000	0.000
8700	6.494	31.762	31.756	62.204	0.000	0.000	0.000	0.000	0.000	0.000
8800	6.494	31.762	31.756	62.948	0.000	0.000	0.000	0.000	0.000	0.000
8900	6.494	31.762	31.756	63.692	0.000	0.000	0.000	0.000	0.000	0.000
9000	6.494	31.762	31.756	64.436	0.000	0.000	0.000	0.000	0.000	0.000
9100	6.494	31.762	31.756	65.180	0.000	0.000	0.000	0.000	0.000	0.000
9200	6.494	31.762	31.756	65.924	0.000	0.000	0.000	0.000	0.000	0.000
9300	6.494	31.762	31.756	66.668	0.000	0.000	0.000	0.000	0.000	0.000
9400	6.494	31.762	31.756	67.412	0.000	0.000	0.000	0.000	0.000	0.000
9500	6.494	31.762	31.756	68.156	0.000	0.000	0.000	0.000	0.000	0.000
9600	6.494	31.762	31.756	68.900	0.000	0.000	0.000	0.000	0.000	0.000
9700	6.494	31.762	31.756	69.644	0.000	0.000	0.000	0.000	0.000	0.000
9800	6.494	31.762	31.756	70.388	0.000	0.000	0.000	0.000	0.000	0.000
9900	6.494	31.762	31.756	71.132	0.000	0.000	0.000	0.000	0.000	0.000
10000	6.494	31.762	31.756	71.876	0.000	0.000	0.000	0.000	0.000	0.000

March 31, 1961

$$D_0^0 = 105.286 \pm 0.15 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 298.15 = 0$$

$$S_{298.15}^0 = 31.21 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\omega_e = 4405.3 \text{ cm.}^{-1}$$

$$\omega_e x_e = 12$$



MOL. WT. = 112.21874

POTASSIUM HYDROXIDE, DIMERIC ($\text{K}_2\text{O}_2\text{H}_2$) (IDEAL GAS)

Point Group C_{2h} $\Delta H_f^\circ = -154.3 \pm 5 \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = [78.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = -157.4 \pm 5 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies	
ω , cm^{-1}	ω , cm^{-1}
[273](1)	[3700](1)
[150](1)	[3700](1)
[255](1)	[1250](1)
[150](1)	[1250](1)
[255](1)	[1250](1)
[258](1)	[1250](1)

Bond Distance: K-O = $[2.43] \text{ \AA}$ O-H = $[0.98] \text{ \AA}$
 Bond Angle: K-O-K = $[90^\circ]$ K-O-H = $[110^\circ]$
 Products of the Moments of Inertia: $I_A I_B I_C = [3.7587] \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$
 $\sigma = 2$

Heat of Formation.

See KOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. F. Porter, J. Chem. Phys. **29**, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **31**, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 \AA larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschl and W. A. Chupka, J. Chem. Phys. **33**, 533 (1960), have also postulated a model for $\text{Li}_2(\text{OH})_2(\text{g})$ which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100° . The last one was adopted for the molecular configuration of $\text{K}_2(\text{OH})_2$, but the bond angle O-K-O was modified to 90° (i.e. a square planar configuration for potassium and oxygen atoms). The bond angle K-O-K in $\text{K}_2(\text{OH})_2(\text{g})$ was assumed to be 110° . The bond distance K-O in $\text{K}_2(\text{OH})_2(\text{g})$ was estimated 10% longer than that in KOH(g). The bond distance O-H was estimated to be the same in $\text{H}_2\text{O}(\text{g})$. The three principal moments of inertia are $I_A = [17.5202] \times 10^{-39}$, $I_B = [38.5534] \times 10^{-39}$ and $I_C = [55.6452] \times 10^{-39} \text{ g. cm.}^2$. The first six selected vibrational frequencies were taken to be equal to those for $\text{K}_2\text{P}_2(\text{g})$ (see $\text{K}_2\text{P}_2(\text{g})$ table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.



Potassium Hydroxide, Dimeric ($\text{K}_2\text{O}_2\text{H}_2$)
 (Ideal Gas) Mol. Wt. = 112.21874

T. °K.	C_p°	S°	ΔH_f°	ΔH_f°	ΔF_f°	Log K _P
0	13.000	INFINITE	-4.415	-154.317	-154.317	INFINITE
100	17.684	60.000	-4.415	-154.317	-154.317	1.741
200	17.684	70.956	-4.415	-154.317	-154.317	2.272
298	19.465	78.366	-4.415	-154.317	-154.317	2.767
300	19.496	78.487	-4.415	-154.317	-154.317	2.772
400	21.073	84.315	-4.415	-154.317	-154.317	3.229
500	22.452	89.170	-4.415	-154.317	-154.317	3.663
600	23.578	93.366	-4.415	-154.317	-154.317	4.073
700	24.488	97.072	-4.415	-154.317	-154.317	4.461
800	25.239	100.392	-4.415	-154.317	-154.317	4.834
900	25.879	103.403	-4.415	-154.317	-154.317	5.195
1000	26.435	106.159	-4.415	-154.317	-154.317	5.546
1100	26.925	108.702	-4.415	-154.317	-154.317	5.888
1200	27.362	111.063	-4.415	-154.317	-154.317	6.219
1300	27.751	113.269	-4.415	-154.317	-154.317	6.539
1400	28.100	115.339	-4.415	-154.317	-154.317	6.848
1500	28.412	117.288	-4.415	-154.317	-154.317	7.146
1600	28.693	119.131	-4.415	-154.317	-154.317	7.433
1700	28.943	120.878	-4.415	-154.317	-154.317	7.709
1800	29.168	122.539	-4.415	-154.317	-154.317	7.975
1900	29.370	124.122	-4.415	-154.317	-154.317	8.232
2000	29.552	125.633	-4.415	-154.317	-154.317	8.481
2100	29.716	127.079	-4.415	-154.317	-154.317	8.721
2200	29.864	128.464	-4.415	-154.317	-154.317	8.954
2300	29.998	129.795	-4.415	-154.317	-154.317	9.181
2400	30.119	131.074	-4.415	-154.317	-154.317	9.402
2500	30.230	132.306	-4.415	-154.317	-154.317	9.618
2600	30.330	133.494	-4.415	-154.317	-154.317	9.829
2700	30.422	134.640	-4.415	-154.317	-154.317	10.035
2800	30.505	135.748	-4.415	-154.317	-154.317	10.237
2900	30.582	136.820	-4.415	-154.317	-154.317	10.435
3000	30.652	137.858	-4.415	-154.317	-154.317	10.629
3100	30.717	138.864	-4.415	-154.317	-154.317	10.819
3200	30.776	139.840	-4.415	-154.317	-154.317	11.005
3300	30.831	140.788	-4.415	-154.317	-154.317	11.187
3400	30.881	141.709	-4.415	-154.317	-154.317	11.365
3500	30.928	142.605	-4.415	-154.317	-154.317	11.539
3600	30.972	143.477	-4.415	-154.317	-154.317	11.709
3700	31.012	144.326	-4.415	-154.317	-154.317	11.875
3800	31.050	145.154	-4.415	-154.317	-154.317	12.038
3900	31.085	145.961	-4.415	-154.317	-154.317	12.197
4000	31.117	146.748	-4.415	-154.317	-154.317	12.352
4100	31.148	147.517	-4.415	-154.317	-154.317	12.504
4200	31.176	148.268	-4.415	-154.317	-154.317	12.652
4300	31.203	149.002	-4.415	-154.317	-154.317	12.797
4400	31.228	149.719	-4.415	-154.317	-154.317	12.939
4500	31.252	150.421	-4.415	-154.317	-154.317	13.078
4600	31.274	151.108	-4.415	-154.317	-154.317	13.215
4700	31.295	151.781	-4.415	-154.317	-154.317	13.349
4800	31.314	152.440	-4.415	-154.317	-154.317	13.481
4900	31.333	153.086	-4.415	-154.317	-154.317	13.611
5000	31.350	153.719	-4.415	-154.317	-154.317	13.739
5100	31.367	154.340	-4.415	-154.317	-154.317	13.864
5200	31.382	154.950	-4.415	-154.317	-154.317	13.987
5300	31.397	155.547	-4.415	-154.317	-154.317	14.108
5400	31.411	156.134	-4.415	-154.317	-154.317	14.227
5500	31.424	156.711	-4.415	-154.317	-154.317	14.343
5600	31.437	157.277	-4.415	-154.317	-154.317	14.457
5700	31.449	157.834	-4.415	-154.317	-154.317	14.568
5800	31.460	158.381	-4.415	-154.317	-154.317	14.677
5900	31.471	158.919	-4.415	-154.317	-154.317	14.783
6000	31.482	159.446	-4.415	-154.317	-154.317	14.887

Lithium Hydroxide, Dimeric ($\text{Li}_2\text{O}_2\text{H}_2$)
(Ideal Gas) Mol. Wt. = 47.89274

LITHIUM HYDROXIDE, DIMERIC ($\text{Li}_2\text{O}_2\text{H}_2$)
(IDEAL GAS) MOL. WT. = 47.89274

T, °K	C _p ^o	cal. mole ⁻¹ deg ⁻¹	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	INFINITE	-	3.463	-178.587	-178.587	INFINITE
100	9.116	50.762	77.218	-2.666	-179.480	-177.613	-177.613	388.173
200	13.582	64.563	100.430	-1.854	-180.430	-178.450	-178.450	536.615
298	16.882	64.563	100.430	-1.854	-180.430	-178.450	-178.450	126.534
300	16.935	64.668	100.430	-1.854	-180.430	-178.450	-178.450	125.715
400	19.420	68.895	100.430	-1.854	-180.430	-178.450	-178.450	92.598
500	21.319	74.443	100.430	-1.854	-180.430	-178.450	-178.450	72.576
600	22.761	78.463	100.430	-1.854	-180.430	-178.450	-178.450	59.111
700	23.673	82.059	100.430	-1.854	-180.430	-178.450	-178.450	48.462
800	24.762	85.307	100.430	-1.854	-180.430	-178.450	-178.450	42.206
900	25.937	88.267	100.430	-1.854	-180.430	-178.450	-178.450	36.549
1000	26.123	90.986	100.430	-1.854	-180.430	-178.450	-178.450	32.014
1100	26.666	93.502	100.430	-1.854	-180.430	-178.450	-178.450	28.298
1200	27.143	95.843	100.430	-1.854	-180.430	-178.450	-178.450	25.196
1300	27.565	98.033	100.430	-1.854	-180.430	-178.450	-178.450	22.568
1400	27.939	100.090	100.430	-1.854	-180.430	-178.450	-178.450	20.312
1500	28.271	102.029	100.430	-1.854	-180.430	-178.450	-178.450	18.356
1600	28.568	103.863	100.430	-1.854	-180.430	-178.450	-178.450	16.642
1700	28.833	105.603	100.430	-1.854	-180.430	-178.450	-178.450	14.787
1800	29.069	107.258	100.430	-1.854	-180.430	-178.450	-178.450	12.940
1900	29.282	108.835	100.430	-1.854	-180.430	-178.450	-178.450	11.290
2000	29.472	110.342	100.430	-1.854	-180.430	-178.450	-178.450	9.807
2100	29.644	111.785	100.430	-1.854	-180.430	-178.450	-178.450	8.466
2200	29.798	113.167	100.430	-1.854	-180.430	-178.450	-178.450	7.247
2300	29.938	114.495	100.430	-1.854	-180.430	-178.450	-178.450	6.136
2400	30.064	115.772	100.430	-1.854	-180.430	-178.450	-178.450	5.118
2500	30.178	117.001	100.430	-1.854	-180.430	-178.450	-178.450	4.182
2600	30.283	118.187	100.430	-1.854	-180.430	-178.450	-178.450	3.319
2700	30.378	119.332	100.430	-1.854	-180.430	-178.450	-178.450	2.521
2800	30.464	120.438	100.430	-1.854	-180.430	-178.450	-178.450	1.781
2900	30.544	121.509	100.430	-1.854	-180.430	-178.450	-178.450	1.091
3000	30.616	122.545	100.430	-1.854	-180.430	-178.450	-178.450	0.449
3100	30.683	123.550	100.430	-1.854	-180.430	-178.450	-178.450	-
3200	30.745	124.525	100.430	-1.854	-180.430	-178.450	-178.450	-1.152
3300	30.801	125.472	100.430	-1.854	-180.430	-178.450	-178.450	-1.715
3400	30.854	126.393	100.430	-1.854	-180.430	-178.450	-178.450	-2.243
3500	30.902	127.288	100.430	-1.854	-180.430	-178.450	-178.450	-2.740
3600	30.947	128.159	100.430	-1.854	-180.430	-178.450	-178.450	-3.209
3700	30.989	129.007	100.430	-1.854	-180.430	-178.450	-178.450	-3.651
3800	31.028	129.834	100.430	-1.854	-180.430	-178.450	-178.450	-4.069
3900	31.064	130.641	100.430	-1.854	-180.430	-178.450	-178.450	-4.466
4000	31.097	131.428	100.430	-1.854	-180.430	-178.450	-178.450	-4.841
4100	31.129	132.196	100.430	-1.854	-180.430	-178.450	-178.450	-5.198
4200	31.158	132.946	100.430	-1.854	-180.430	-178.450	-178.450	-5.537
4300	31.186	133.680	100.430	-1.854	-180.430	-178.450	-178.450	-5.861
4400	31.212	134.397	100.430	-1.854	-180.430	-178.450	-178.450	-6.171
4500	31.236	135.099	100.430	-1.854	-180.430	-178.450	-178.450	-6.466
4600	31.259	135.786	100.430	-1.854	-180.430	-178.450	-178.450	-6.746
4700	31.280	136.458	100.430	-1.854	-180.430	-178.450	-178.450	-7.013
4800	31.300	137.117	100.430	-1.854	-180.430	-178.450	-178.450	-7.267
4900	31.319	137.762	100.430	-1.854	-180.430	-178.450	-178.450	-7.510
5000	31.337	138.395	100.430	-1.854	-180.430	-178.450	-178.450	-7.744
5100	31.354	139.016	100.430	-1.854	-180.430	-178.450	-178.450	-7.973
5200	31.370	139.625	100.430	-1.854	-180.430	-178.450	-178.450	-8.197
5300	31.386	140.223	100.430	-1.854	-180.430	-178.450	-178.450	-8.416
5400	31.400	140.810	100.430	-1.854	-180.430	-178.450	-178.450	-8.630
5500	31.414	141.386	100.430	-1.854	-180.430	-178.450	-178.450	-8.838
5600	31.427	141.952	100.430	-1.854	-180.430	-178.450	-178.450	-9.041
5700	31.439	142.508	100.430	-1.854	-180.430	-178.450	-178.450	-9.239
5800	31.451	143.055	100.430	-1.854	-180.430	-178.450	-178.450	-9.433
5900	31.462	143.593	100.430	-1.854	-180.430	-178.450	-178.450	-9.623
6000	31.473	144.127	100.430	-1.854	-180.430	-178.450	-178.450	-9.808

Dec. 31, 1960; Mar. 31, 1966

Point Group C_{2h}
S_{298.15} = [64.6] cal. deg⁻¹ mole⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω_e , cm ⁻¹	ω_e , cm ⁻¹	ω_e , cm ⁻¹
[465](1)	[3700](1)	[3700](1)
[305](1)	[3700](1)	[3700](1)
[407](1)	[1250](1)	[1250](1)
[385](1)	[1250](1)	[1250](1)
[640](1)	[1250](1)	[1250](1)
[460](1)	[1250](1)	[1250](1)

Bond Distances: Li-O = [1.76] Å O-H = [0.96] Å

Bond Angles: Li-O-Li = [90]° Li-O-H = [110]°

Product of the Moments of Inertia: I_AI_BI_C = [4.56956] X 10⁻¹¹⁵ g.³ cm.⁶

Heat of Formation.

J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have studied the Li₂O(c)-H₂O(g) equilibrium by the mass-spectrometric method. Using the reported equilibrium constants in the temperature range from 1100° to 1450°K. the heat of reaction Li₂OH₂(g) → 2LiOH(g) at 298° has been calculated by the second law and the third law methods as 63.2 and 63.7 kcal. mole⁻¹, respectively. (The third law drift is 0.5 ± 1.5 e.u.) Combination of the third law value (ΔH_f^o 298 = 63.7 kcal. mole⁻¹) with the heat of formation of lithium hydroxide(g) (ΔH_f^o 298 = -58.8 kcal. mole⁻¹) gives the heat of formation of dimeric lithium hydroxide (g) (ΔH_f^o 298 = -181.4 kcal. mole⁻¹) which has been adopted in the tabulation.

J. B. Berkowitz-Matuck and A. Buchler, J. Phys. Chem. 67, 1386 (1963), have also studied the Li₂O(c)-H₂O(g) equilibrium by the transpiration method, and reported two equilibrium constants (K₁₀₉₅^o = 0.105 and K₁₄₄₅^o = 0.357) for the reaction Li₂O(c) + H₂O(g) → Li₂OH₂(g). Using the third law method, the heat of reaction has been calculated from the equilibrium constants as 12.7 kcal. mole⁻¹ at 298.15°K. The heat of formation of Li₂OH₂(g) can be derived as ΔH_f^o 298 = -186.2 ± 3.5 kcal. mole⁻¹ which is different from the adopted value of Berkowitz, Meschi and Chupka, loc. cit. Berkowitz-Matuck and Buchler attempted to explain the difference by inferring that the solid-gas equilibrium was not properly established in the measurement of Berkowitz, Meschi and Chupka, however, the absence of drift in the third law analysis does not support this conclusion.

Heat Capacity and Entropy.

S. H. Bauer, R. M. Diner and R. P. Porter, J. Chem. Phys. 29, 991 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 31, 630 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for Li₂(OH)₂(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the bond angle O-Li-O = 100°. The last one was adopted for the molecular configuration of Li₂(OH)₂(g), but the bond angle O-Li-O was modified to 90° (i.e. a square planar configuration for lithium and oxygen atoms). The bond angle Li-O-H in Li₂(OH)₂(g) was assumed to be 110°. The bond distance Li-O in Li₂(OH)₂(g) was estimated 10% longer than that in LiOH(g). The bond distance O-H was estimated to be the same in H₂O(g). The three principal moments of inertia are: I_A = [9.445] X 10⁻³⁹, I_B = [3.789] X 10⁻³⁹ and I_C = [12.6035] X 10⁻³⁹ g. cm.²

The first six selected vibrational frequencies were taken to be equal to those for Li₂P₂(g) (see Li₂P₂(g) table) and the rest were O-H stretching and bending frequencies.

H₂Li₂O₂



Magnesium Dihydride (MgH₂)

(Crystal) Mol. Wt. = 26.336

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	-	16,250	-	INFINITE
100	3.053	1.027	-	17,056	-	14,543
200	6.043	4.030	-	17,756	-	12,072
298	8.450	7.431	-	18,200	-	6.436
300	8.487	7.483	-	18,208	-	6.354
400	10.550	10.556	-	18,502	-	5.065
500	12.576	12.576	-	18,706	-	3.966
600	13.200	14.065	9.405	18,906	1.123	3.409
700	14.230	17.080	10.352	18,927	4.465	1.394
800	15.080	18.038	11.317	18,891	7.804	2.132
900	15.750	18.834	12.277	18,841	11.143	2.740
1000	16.250	20.341	13.220	20,857	14.483	3.200
1100	16.637	24.109	14.140	20,740	18.186	3.613
1200	16.910	25.569	15.032	20,623	21.719	3.955
1300	17.151	26.932	15.896	20,517	25.283	4.244
1400	17.360	28.411	16.730	20,408	28.784	4.494
1500	17.500	29.413	17.536	20,309	32.040	4.691
1600	17.620	30.547	18.314	19,473	40.605	5.446
1700	17.708	31.618	19.065	21,339	46,245	5.945
1800	17.800	32.632	19.781	23,114	51,853	6.295
1900	17.898	33.597	20.493	24,869	57,381	6.606
2000	18.000	34.518	21.171	26,634	62,992	6.888

MAGNESIUM DIHYDRIDE (MgH₂)

(CRYSTAL)

MOL. WT. = 26.336

ΔH_f^o = -16.3 ± 2.2 kcal. mole⁻¹
ΔH_f^o 298.15 = -18.2 ± 2.2 kcal. mole⁻¹
S_{298.15}^o = 7.43 ± 0.20 cal. deg.⁻¹ mole⁻¹
T_d = [560]°K.

Heat of Formation.

The heat of hydrolysis of MgH₂(c) was measured by G. C. Sinke and D. R. Stull, Thermal Laboratory, The Dow Chemical Company, private communication, July, 1956. The value of ΔH_f^o 298.15 was calculated to be -19.1 ± 2 kcal. mole⁻¹. From the decomposition pressure measurements for MgH₂(c) reported by P. H. Ellinger, et al., J. Am. Chem. Soc. 77, 2647 (1955) and J. F. Stampfer, Jr., C. E. Holley, Jr. and J. F. Suttle, J. Am. Chem. Soc. 82, 3504 (1960), the values of ΔH_f^o 298.15 for MgH₂(c) were found to be -17.9 ± 1.0 and -17.7 kcal. mole⁻¹, respectively. The value used was the average of these three.

Heat Capacity and Entropy.

The low temperature heat capacities (25-300°K.) was measured by G. C. Sinke and D. L. Hildenbrand, Thermal Laboratory, The Dow Chemical Company, private communication, February 1958. Above 300°K. the C_p values were estimated by comparison with those for MgF₂(c). S_{298.15} was obtained from G. C. Sinke and D. L. Hildenbrand, loc. cit., using S₂₅^o (extrap.) = 0.037 cal. deg.⁻¹ mole⁻¹.

Temperature of Decomposition.

T_d was estimated from the value of ΔF_f^o in the table.



Magnesium Dihydroxide (Mg(OH)₂)

(Crystal)

GFW = 58.32674

T, °K	Cp ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log Kp
0	∞	∞	INFINITE	2.726	-218.431	-218.431	INFINITE
100	5.167	2.320	27.633	2.561	-219.873	-213.300	866.166
200	13.592	8.670	16.652	1.596	-220.769	-206.489	225.597
298	18.437	15.100	15.100	∞	-221.000	-199.257	146.059
300	18.500	15.214	15.100	∞	-221.003	-199.122	145.060
400	21.300	20.939	15.862	2.031	-221.025	-191.520	104.806
500	23.400	25.924	17.387	4.269	-220.859	-184.534	60.660
600	25.300	30.362	19.076	9.106	-220.568	-177.257	44.560
700	27.000	34.281	20.744	12.101	-219.553	-170.291	34.110
800	28.400	37.100	22.074	14.101	-218.900	-163.018	26.534
900	30.200	41.561	24.849	15.041	-218.900	-155.989	37.679
1000	31.800	44.826	26.685	16.141	-220.264	-148.557	32.533

Dec. 31, 1960; Dec. 31, 1966; Mar. 31, 1967

MAGNESIUM DIHYDROXIDE (Mg(OH)₂)

(CRYSTAL)

OPW = 58.32674

S_{298.15} = 15.10 gibbs/molT_d = [541]°KΔH_f^o = -218.43 ± 0.5 kcal/molΔH_f^o_{298.15} = -221.0 ± 0.5 kcal/mol

Heat of Formation.

The adopted value is an average of -221.10 and -220.86 kcal/mol obtained from ΔH_f^o₂₉₈ = 9.08 and 8.84 kcal/mol for the dehydration reaction Mg(OH)₂(c) = MgO(c) + H₂O(l). The two values correspond to naturally occurring brucite and to synthetic Mg(OH)₂ prepared from MgO by hydration at 177°C under a steam pressure of about 9 atm. The enthalpies of reaction are derived from studies of Taylor and Wells on the heats of solution of various samples of Mg(OH)₂ and MgO in aqueous HCl. These studies show that the heat of dehydration is quite dependent on the nature of the MgO sample; e.g., values for synthetic Mg(OH)₂ vary monotonically from 9.79 to 8.84 kcal/mol for MgO ignited at temperatures from 450 to 1425°C, respectively. The authors ascribe this difference primarily to increase in particle size at the higher ignition temperatures. We have adopted the results at 1425°C, since they are reasonably consistent with the high temperature samples on which the JANAF heat of formation for MgO is based. The uncertainty is estimated as ± 0.5 kcal/mol.

Shomate and Huffman have confirmed the heat of solution of MgO (ignited at 1000°C) within about 0.3 kcal. Their value may be combined with the heat of solution for synthetic Mg(OH)₂, determined under similar conditions by Torgeson and Sahaana, to obtain ΔH_f^o = 8.85 kcal/mol for the dehydration reaction. At the other extreme, the heat of solution data of Glaue and Archibald lead to ΔH_f^o = 9.74 kcal/mol; however, this value corresponds to MgO ignited at 350°C. The MgO sample was microcrystalline and had significant excess O₂, as suggested by Glaue and Archibald and later confirmed by data of T. H. K. Barron et al., Proc. Roy. Soc. (London) A250, 70 (1959). Glaue and Archibald intentionally used the microcrystalline form which would be similar to the product in their decomposition pressure measurements (190 and 212°C). Thus, it is not surprising that third law analysis of their decomposition pressures yields essentially the same heat of formation as their solution data (see summary below). Decomposition data at higher pressures have been reported by H. S. Pyfe, Am. J. Sci. 255, 729 (1956); D. M. Roy and R. Roy, ibid. 255, 573 (1957); O. C. Kennedy, ibid. 254, 567 (1956); G. M. Zhabrova and B. M. Madenatski, J. Gen. Chem. USSR (Eng. Transl.) 23, 1129 (1954); and L. G. Berg and I. S. Rassonakaya, Dokl. Akad. Nauk SSSR 91, 865 (1951). These data do not significantly affect the heat of formation, however, because of uncertainties in the attainment of equilibrium and in reduction to standard state values.

Source	Mg(OH) ₂ Sample ²	Temp. of MgO Formation, °C	Heat of Dehydration ΔH _f ^o _{298.15} (kcal/mol)	ΔH _f ^o _{298.15}
1. Taylor & Wells (1939)	Brucite	1425	9.08	-221.10
	Synthetic	1425	8.84	-220.86
	Synthetic	1000	9.18	-221.20
2. Torgeson (1948) - Shomate (1943)	Synthetic	450	9.79	-221.81
	Synthetic	1000	8.65	-220.87
3. Glaue & Archibald (1937)	Synthetic*	350	9.74	-221.74
	Xp data	190, 212	20.13**	-221.62

*Prepared by reaction of KOH with MgCl₂(aq) at 210°C, rather than by hydration of MgO.**For Mg(OH)₂(c) = MgO(c) + H₂O(g) rather than Mg(OH)₂(c) = MgO(c) + H₂O(l).

References.

1. K. Taylor and L. S. Wells, J. Res. Natl. Bur. Std. 21, 133 (1938).
2. D. R. Torgeson and Th. G. Sahaana, J. Am. Chem. Soc. 70, 2156 (1948); C. H. Shomate and E. H. Huffman, ibid. 65, 1625 (1943).
3. W. F. Glaue and R. C. Archibald, J. Am. Chem. Soc. 59, 561 (1937).

Heat Capacity and Entropy.

Low temperature heat capacities are from the data (22-321°K) of Glaue and Archibald, loc. cit., who used a synthetic, microcrystalline sample prepared by reaction of KOH with aqueous MgCl₂ at 210°C. The entropy is derived from the heat capacities using S₂₉₈^o = 0.027 eu. Above 321°K the heat capacities are extrapolated graphically. Enthalpy data (393-667°K) reported by F. N. Lashchenko and D. I. Kompan'skii, Zh. Fizik. Khim. 9, 628 (1935), were stated to be based on a calorimeter temperature close to room temperature. Within this uncertainty and the experimental scatter of about ± 5%, the enthalpy data are consistent with the selected values.

Temperature of Decomposition.

T_d is calculated as the temperature at which ΔH_f^o = 0 for Mg(OH)₂(c) = MgO(c) + H₂O(g).

Magnesium Dihydroxide (Mg(OH)₂)
(Ideal Gas) GFW = 58.32674

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	0.00	INFINITE	INFINITE	- 3.551	- 134.556	- 134.556	INFINITE
100	10.768	51.319	77.706	- 3.639	- 135.251	- 133.577	291.932
200	13.455	59.653	66.758	- 1.421	- 135.894	- 131.770	143.992
298	15.403	65.408	60.00	0.000	- 136.300	- 129.556	94.967
300	15.435	65.503	59.808	0.029	- 136.308	- 129.515	94.351
400	17.067	74.063	57.238	3.402	- 137.026	- 124.770	54.537
500	18.067	77.439	56.680	5.255	- 137.297	- 122.294	44.545
600	19.694	80.418	56.148	7.189	- 137.536	- 119.772	37.394
700	20.320	83.090	55.602	9.191	- 137.763	- 117.221	32.023
800	20.738	85.315	55.046	11.166	- 137.983	- 114.588	28.686
900	21.000	87.140	54.476	13.132	- 138.193	- 111.850	24.485
1000	21.156	88.796	53.887	15.520	- 140.352	- 108.992	21.655
1100	21.790	91.709	53.241	17.719	- 140.762	- 106.113	19.326
1200	22.176	93.498	52.581	19.954	- 140.961	- 103.217	17.352
1300	22.519	94.986	51.906	22.156	- 141.141	- 100.308	15.642
1400	22.816	96.248	51.216	24.351	- 141.303	- 97.383	13.798
1500	23.095	97.362	50.516	26.514	- 141.443	- 94.763	11.858
1600	23.336	98.261	49.866	28.639	- 141.564	- 92.439	9.823
1700	23.549	99.082	49.251	29.184	- 141.665	- 89.599	12.239
1800	23.739	100.034	48.507	31.548	- 141.746	- 84.498	10.863
1900	23.903	101.034	47.761	33.311	- 141.809	- 79.413	9.642
2000	24.060	102.052	47.015	35.330	- 141.857	- 68.259	7.569
2100	24.195	103.086	46.269	38.742	- 141.892	- 64.212	6.683
2200	24.317	104.058	45.488	41.168	- 141.910	- 59.163	5.877
2300	24.426	105.941	44.682	43.605	- 141.915	- 54.122	5.143
2400	24.524	107.633	43.854	46.053	- 141.909	- 49.089	4.460
2500	24.614	109.086	43.007	48.510	- 141.897	- 44.070	3.853
2600	24.694	109.953	42.147	50.975	- 141.872	- 39.047	3.282
2700	24.768	110.886	41.270	53.449	- 141.835	- 34.035	2.755
2800	24.834	111.786	40.381	55.929	- 141.787	- 29.034	2.266
2900	24.891	112.650	39.478	58.415	- 141.727	- 24.029	1.811
3000	24.951	113.505	38.561	60.909	- 141.655	- 19.037	1.397
3100	25.002	114.324	37.631	63.405	- 141.572	- 14.048	.990
3200	25.049	115.119	36.681	65.908	- 141.478	- 9.068	.619
3300	25.092	115.890	35.715	68.415	- 141.375	- 4.086	.271
3400	25.131	116.634	34.736	70.926	- 141.260	- 0.927	.000
3500	25.168	117.369	33.746	73.441	- 141.131	5.050	.366
3600	25.202	118.079	32.749	75.960	- 140.989	10.829	.657
3700	25.234	118.770	31.756	78.481	- 140.835	15.796	.933
3800	25.263	119.443	30.762	81.006	- 140.662	20.762	1.194
3900	25.290	120.094	29.768	83.534	- 140.478	25.728	1.441
4000	25.315	120.740	28.764	86.064	- 140.284	30.678	1.676
4100	25.339	121.365	27.756	88.597	- 140.081	35.638	1.900
4200	25.361	121.976	26.741	91.132	- 139.868	40.592	2.112
4300	25.382	122.573	25.719	93.669	- 139.645	45.548	2.315
4400	25.401	123.158	24.688	96.208	- 139.412	50.500	2.508
4500	25.419	123.728	23.649	98.749	- 139.170	55.454	2.693
4600	25.436	124.287	22.602	101.292	- 138.919	60.414	2.870
4700	25.452	124.834	21.548	103.837	- 138.659	65.368	3.040
4800	25.467	125.370	20.489	106.383	- 138.390	70.324	3.202
4900	25.481	125.890	19.425	108.928	- 138.112	75.277	3.357
5000	25.495	126.410	18.356	111.479	- 137.826	80.231	3.507
5100	25.508	126.915	17.281	114.029	- 137.531	85.191	3.651
5200	25.520	127.411	16.202	116.580	- 137.228	90.145	3.789
5300	25.531	127.897	15.119	119.133	- 136.916	95.118	3.922
5400	25.541	128.377	14.034	121.686	- 136.594	100.090	4.050
5500	25.552	128.843	12.944	124.241	- 136.263	105.042	4.174
5600	25.562	129.304	11.849	126.797	- 135.923	110.004	4.293
5700	25.571	129.756	10.754	129.354	- 135.575	114.983	4.409
5800	25.580	130.201	9.659	131.911	- 135.220	119.955	4.520
5900	25.588	130.639	8.564	134.468	- 134.858	124.926	4.626
6000	25.596	131.068	7.469	137.026	- 134.489	129.919	4.732

June 30, 1967



MAGNESIUM DIHYDROXIDE [Mg(OH)₂]

(IDEAL GAS)

GFW = 58.32674

Point Group [C_{2h}]

ΔH_f^o = [-134.6 ± 3] kcal/mol

S_{298.15} = [65.4] gibbs/mol

ΔH_f^o = [-136.3 ± 3] kcal/mol

Ground State Quantum Weight = [2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹	ω, cm ⁻¹	σ = [2]
[3200](1)	[600](1)	[1400](1)	
[1200](1)	[240](1)	[360](1)	
[700](1)	[3300](1)	[100](1)	
Bond Distances: Mg-O = [1.80] Å			
Bond Angles: Mg-O-H = [105°]			
Product of the Moments of Inertia: I _A I _B I _C = [95.6929] x 10 ⁻¹¹⁷ g cm			
O-H = [10.97] Å			
O-Mg-O = [180°]			
I _A I _B I _C = [95.6929] x 10 ⁻¹¹⁷ g cm			

Heat of Formation

Vapor densities of magnesium-bearing species over magnesium oxide were determined, using the transpiration method, by C. A. Alexander, J. S. Ogden and A. Levy, J. Chem. Phys. **33**, 3057 (1963). The MgO reacted with water vapor present in the carrier gas to form a gaseous product, presumably Mg(OH)₂. The authors eliminated MgOH (and other species requiring the formation of gaseous oxygen) as a likely product by holding constant the partial pressure of water but varying the ratio of oxygen and argon in the carrier gas. Experiments with different partial pressures of water indicated that each mole of water produced an equivalent number of moles of product in the vapor. This eliminates [Mg(OH)₂] as a possible product, but not, for example, (MgO)₂H₂O. Species of the latter type are quite unlikely with magnesium, so the reaction is considered to be MgO(c) + H₂O(g) = Mg(OH)₂(g). Equilibrium data (1653-2020°K) given graphically by Alexander et al. yield ΔH_f^o = 67.6 ± 1.9 kcal/mol by second law analysis and ΔH_f^o = 65.2 kcal/mol with a drift of -1.5 ± 1 eu by third law analysis.

Heat Capacity and Entropy

The infrared spectra of Mg(OH)₂(c) were observed in the region 365-3700 cm⁻¹ by C. Cabannes-Ott, Ann. Chim. (Paris) **5**, 903-60 (1960). The vibrational frequencies of the gas are estimated by comparison with those for Mg(OH)₂(c), H₂O(g), H₂O₂(g), MgO(g) and MgF₂(g), and are adjusted to give reasonable agreement between the second and third law heats of reaction. The bond distances are estimated by comparison with those of MgF₂(g), MgO(g) and H₂O(g). The O-Mg-O angle is assumed to be 180°, while the Mg-O-H angle is assumed to be the same as that in H₂O(g). The three principal moments of inertia are I_A = 2.713 x 10⁻⁴⁰, I_B = 18.6455 x 10⁻³⁹ and I_C = 18.9168 x 10⁻³⁹ g cm².





(IDEAL GAS)

MOLYBDIC ACID (H_2MoO_4)

Point Group $[C_{2v}]$

$S_{298.15}^\circ = [84.97 \pm 2.0] \text{ gibbs/mol}$

Ground State Quantum Weight = 11

$\Delta H_f^\circ = -201.5 \pm 1.0 \text{ kcal/mol}$

$\Delta H_f^\circ_{298.15} = -203.4 \pm 1.0 \text{ kcal/mol}$

GFW = 161.9535

Molybdic Acid
(Ideal Gas)

GFW = 161.9535

T, K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	16.000	INFINITE	INFINITE	5.326	201.456	201.456	INFINITE
100	16.260	62.711	104.590	4.168	202.582	197.987	432.657
200	16.520	64.470	104.590	4.168	203.400	197.987	432.657
298	16.893	64.470	104.590	4.000	203.400	186.110	137.932
300	24.951	84.871	104.590	4.066	203.400	186.076	137.013
400	27.562	92.684	104.590	2.680	203.476	182.950	99.959
500	29.440	98.050	104.590	5.537	203.396	177.625	77.727
600	30.761	104.342	90.291	0.591	203.223	172.726	62.915
700	31.769	109.367	92.678	11.682	202.993	167.680	52.346
800	32.576	113.665	95.038	14.902	202.727	162.633	44.429
900	33.216	117.340	97.326	16.192	202.435	157.636	38.279
1000	33.743	121.066	99.267	21.561	202.124	152.675	33.467
1100	34.168	124.305	101.634	24.936	201.805	147.746	29.354
1200	34.566	127.297	103.650	28.377	201.482	142.845	26.016
1300	34.942	130.077	105.377	31.650	201.168	137.972	23.195
1400	35.173	132.673	107.421	35.353	200.865	133.123	20.781
1500	35.418	135.108	109.166	38.693	200.560	128.292	18.692
1600	35.633	137.401	110.879	42.436	200.317	123.483	16.867
1700	35.821	139.567	112.503	46.009	200.074	118.687	15.258
1800	35.987	141.619	113.064	49.599	199.862	113.907	13.830
1900	36.133	143.569	113.566	53.206	199.676	109.136	12.553
2000	36.264	145.426	114.013	56.826	199.522	104.378	11.406
2100	36.380	147.198	114.409	60.459	199.400	99.623	10.368
2200	36.483	148.893	114.756	64.101	199.317	94.874	9.425
2300	36.576	150.517	121.058	67.754	199.270	90.159	8.564
2400	36.660	152.075	122.318	71.416	199.269	85.377	7.775
2500	36.735	153.573	123.539	75.086	199.329	80.640	7.050
2600	36.803	155.015	124.722	78.763	199.453	75.984	6.379
2700	36.865	156.405	125.870	82.446	199.657	71.130	5.758
2800	36.921	157.747	126.984	86.136	199.947	66.365	5.180
2900	36.972	159.044	128.066	89.830	200.327	61.564	4.640
3000	37.019	160.298	129.121	93.530	200.704	56.752	4.120
3100	37.062	161.512	130.147	97.234	201.145	51.933	3.633
3200	37.101	162.690	131.145	100.942	201.655	47.117	3.177
3300	37.137	163.832	132.119	104.654	202.235	42.315	2.746
3400	37.171	164.941	133.068	108.370	202.880	37.520	2.344
3500	37.201	166.019	133.994	112.086	203.602	32.741	1.963
3600	37.230	167.068	134.898	115.810	204.400	28.000	1.602
3700	37.256	168.088	135.761	119.534	205.274	23.300	1.261
3800	37.281	169.082	136.645	123.261	206.223	18.640	0.937
3900	37.303	170.050	137.489	126.990	207.247	14.020	0.631
4000	37.324	170.995	138.315	130.721	208.347	9.440	0.339
4100	37.344	171.917	139.123	134.495	209.522	4.900	0.061
4200	37.363	172.817	139.915	138.190	210.774	0.395	-0.204
4300	37.380	173.697	140.690	141.927	212.102	-4.120	-0.457
4400	37.396	174.556	141.450	145.666	213.506	-8.655	-0.699
4500	37.411	175.397	142.195	149.407	214.984	-13.330	-0.930
4600	37.425	176.219	142.926	153.148	216.536	-18.050	-1.151
4700	37.439	177.024	143.643	156.892	218.168	-22.760	-1.363
4800	37.451	177.812	144.347	160.636	219.879	-27.450	-1.567
4900	37.463	178.585	145.037	164.380	221.668	-32.120	-1.762
5000	37.474	179.342	145.718	168.129	223.534	-36.780	-1.952
5100	37.485	180.084	146.383	171.877	225.476	-41.430	-2.138
5200	37.495	180.812	147.038	175.626	227.494	-46.070	-2.320
5300	37.504	181.526	147.682	179.376	229.588	-50.700	-2.498
5400	37.513	182.227	148.315	183.127	231.758	-55.320	-2.672
5500	37.522	182.916	148.938	186.878	233.994	-59.940	-2.842
5600	37.530	183.592	149.551	190.631	236.296	-64.550	-3.008
5700	37.538	184.256	150.154	194.384	238.664	-69.150	-3.170
5800	37.545	184.909	150.747	198.139	241.098	-73.740	-3.328
5900	37.551	185.551	151.332	201.893	243.598	-78.320	-3.482
6000	37.556	186.182	151.907	205.644	246.162	-82.890	-3.632

June 30, 1970

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[2000] (1)	[100] (1)	[800] (1)	[250] (1)
[1000] (1)	[180] (1)	[950] (1)	[250] (1)
[700] (1)	[100] (1)	[3600] (1)	[200] (1)
[800] (1)	[3600] (1)	[200] (1)	[250] (1)

Bond Distance: Mo-O = $[1.83 \pm 0.05] \text{ \AA}$ O-H = $[0.95 \pm 0.05] \text{ \AA}$
Bond Angle: O-Mo-O = $[109.5^\circ]$ H-O-Mo = $[104.5^\circ]$
O-Mo-OH plane perpendicular to O=MoO plane $\sigma = [2]$

Product of the Moments of Inertia: $I_A I_B I_C = [1.5399 \times 10^{-113}] \text{ g cm}^6$

Heat of Formation

The enhanced volatility of metallic molybdenum and molybdenum trioxide in the presence of water vapor at high temperatures has been investigated by several workers (1, 2, 3) using transpiration techniques. Glemser and Haeseler (1) and Butten (2) have shown that the major volatilization reaction of the oxide is:
 $\text{A. MoO}_3(\text{c}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{MoO}_3(\text{OH})_2(\text{g})$
For the reaction of metallic molybdenum with water vapor, Balton and Jordan (3) reported the existence of $\text{MoO}_3(\text{OH})_2(\text{g})$ according to the equilibrium:
 $\text{B. Mo(c)} + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{MoO}_3(\text{OH})_2(\text{g}) + 3\text{H}_2(\text{g})$

Second and third law analyses of these equilibrium data are summarized below.

Investigator	Reaction	Range, °K	No. of Points	ΔH_{298}° (kcal/mol)	Drift	$\Delta H_f^\circ(\text{MoO}_3(\text{OH})_2)$ kcal/mol
Glemser and Haeseler (1)	A	873-963	Equation	38.2	3rd Law	-4.2
Butten (2)	A	673-773	Equation	30.0	3rd Law	-204.0 ± 0.5
Balton and Jordan (3)	B	1473-1773	Equation	30.1	3rd Law	-203.7 ± 0.5
						-202.6 ± 0.3

The adopted value, $\Delta H_f^\circ(\text{MoO}_3(\text{OH})_2, \text{g}) = -203.4 \pm 1.0 \text{ kcal/mol}$, is an average of these three results.

Heat Capacity and Entropy

The assumed tetrahedral structure for $\text{MoO}_3(\text{OH})_2$ is from Jordan (4). The O-H bond length and H-O-Mo bond angle are assumed to be the same as for $\text{H}_2\text{O}(\text{g})$. The Mo-O bond length is from the compilation of Sutton (5) and assumed to be the same as for Ag_2MoO_4 . Individual moments of inertia are $I_A = 23.782 \times 10^{-39}$, $I_B = 25.415 \times 10^{-39}$, and $I_C = 25.478 \times 10^{-39} \text{ g cm}^2$.

The vibrational frequencies are estimated by comparison with those for $\text{H}_2\text{SO}_4(\text{g})$ (5, 7) and are adjusted to give $S^\circ(\text{MoO}_3(\text{OH})_2, \text{g}) = 137.4 \text{ gibbs/mol}$ at 1600°K. This entropy value is derived from a second law analysis of the equilibrium data for reaction B reported by Balton and Jordan (3).

References

1. V. O. Glemser and R. V. Haeseler, Z. Anorg. Allgem. Chem., **316**, 168 (1962).
2. J. Butten, J. Catalysis, **10**, 188 (1968).
3. G. R. Balton and A. S. Jordan, J. Phys. Chem., **69**, 2065 (1965).
4. A. S. Jordan, Ph.D. Thesis, The University of Pennsylvania, 1965.
5. L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).
6. P. A. Giguere and R. Savole, J. Amer. Chem. Soc., **85**, 287 (1963).
7. S. M. Chackalal and F. E. Stafford, J. Amer. Chem. Soc., **88**, 723 (1966).



Amidogen (NH₂)

(Ideal Gas) Mol. Wt. = 16.02264

H₂N

T, °K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	-2.373	40.757	40.757	INFINITE
100	7.949	37.792	40.574	-1.578	40.450	41.015	-89.635
200	7.954	43.303	47.219	-0.763	40.291	41.633	-45.492
298	8.024	46.488	46.488	0.000	40.070	42.337	-31.033
300	8.027	46.538	46.488	0.015	40.065	42.351	-30.951
400	8.220	48.271	48.266	0.006	39.894	42.148	-22.971
500	8.492	50.733	47.410	1.661	39.619	44.002	-18.232
600	8.804	52.308	48.009	2.526	39.427	44.897	-16.353
700	9.142	53.691	48.001	3.423	39.259	45.823	-14.306
800	9.441	54.975	48.001	4.340	39.118	46.776	-12.196
900	9.701	56.172	48.001	5.271	38.998	47.756	-10.026
1000	10.180	57.127	50.804	6.323	38.884	48.713	-7.824
1100	10.501	58.112	51.424	7.357	38.798	49.700	-5.874
1200	10.799	59.039	52.021	8.422	38.729	50.695	-4.232
1300	11.071	59.944	52.592	9.517	38.670	51.697	-2.820
1400	11.316	60.824	53.135	10.635	38.620	52.697	-1.620
1500	11.542	61.683	53.680	11.779	38.581	53.704	-0.624
1600	11.743	62.544	54.195	12.943	38.559	54.711	-0.747
1700	11.923	63.001	54.692	14.126	38.534	55.724	-0.863
1800	12.084	63.588	55.173	15.327	38.521	56.752	-0.968
1900	12.229	64.173	55.631	16.545	38.517	57.792	-1.062
2000	12.359	64.575	56.089	17.772	38.482	58.782	-1.142
2100	12.475	65.081	56.527	19.014	38.469	59.776	-1.211
2200	12.580	65.164	56.952	20.267	38.457	60.780	-1.270
2300	12.675	65.265	57.365	21.532	38.446	61.792	-1.320
2400	12.761	65.382	57.760	22.802	38.436	62.802	-1.362
2500	12.838	65.789	58.157	24.082	38.423	63.817	-1.400
2600	12.908	66.294	58.537	25.369	38.412	64.851	-1.435
2700	12.972	66.783	58.907	26.663	38.400	65.871	-1.467
2800	13.031	67.255	59.269	27.963	38.386	66.869	-1.497
2900	13.081	67.711	59.625	29.268	38.373	67.852	-1.525
3000	13.133	68.158	59.965	30.580	38.357	68.826	-1.551
3100	13.177	68.589	60.301	31.895	38.342	69.845	-1.574
3200	13.218	68.908	60.629	33.215	38.324	70.905	-1.595
3300	13.256	69.216	60.949	34.539	38.303	71.995	-1.614
3400	13.291	69.514	61.266	35.866	38.280	73.072	-1.631
3500	13.323	69.810	61.570	37.197	38.259	74.027	-1.642
3600	13.353	70.103	61.870	38.531	38.232	75.051	-1.656
3700	13.381	70.394	62.165	39.868	38.203	76.073	-1.667
3800	13.407	70.683	62.453	41.207	38.172	77.098	-1.676
3900	13.431	70.970	62.735	42.547	38.140	78.116	-1.684
4000	13.453	71.256	63.013	43.883	38.102	79.116	-1.690
4100	13.474	71.541	63.284	45.239	38.062	80.116	-1.694
4200	13.493	71.824	63.551	46.598	38.020	81.204	-1.697
4300	13.511	72.103	63.812	47.958	37.975	82.231	-1.699
4400	13.526	72.379	64.068	49.318	37.928	83.258	-1.700
4500	13.545	72.652	64.322	50.684	37.875	84.278	-1.700
4600	13.560	72.924	64.570	52.051	37.822	85.324	-1.700
4700	13.574	73.193	64.813	53.426	37.765	86.356	-1.700
4800	13.587	73.459	65.053	54.801	37.705	87.394	-1.700
4900	13.600	73.722	65.290	56.176	37.642	88.431	-1.700
5000	13.612	73.983	65.520	57.544	37.576	89.461	-1.700
5100	13.623	74.242	65.748	58.913	37.507	90.505	-1.700
5200	13.633	74.500	65.972	60.283	37.436	91.552	-1.700
5300	13.642	74.756	66.193	61.654	37.360	92.592	-1.700
5400	13.650	75.010	66.412	63.026	37.281	93.628	-1.700
5500	13.657	75.262	66.624	64.392	37.201	94.673	-1.700
5600	13.670	75.513	66.835	65.759	37.117	95.712	-1.700
5700	13.678	75.762	67.043	67.126	37.029	96.763	-1.700
5800	13.686	76.009	67.247	68.493	36.939	97.810	-1.700
5900	13.693	76.254	67.448	69.859	36.848	98.850	-1.700
6000	13.701	76.497	67.648	71.226	36.749	99.891	-1.700

Dec. 31, 1960; Dec. 31, 1985

ANTIDIVEN (NH₂) (IDEAL GAS)

MOL. WT. = 16.02264

ΔH_f⁰ = 40.8 ± 3 kcal. mole⁻¹ΔH_f⁰ 298.15 = 40.1 ± 3 kcal. mole⁻¹S⁰ 298.15 = 46.5 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies
ω, cm.⁻¹3173 (1)
1499 (1)
3220 (1)

Bond Distance: N-H = 1.024 Å

Bond Angle: H-N-H = 103°

Product of the Moments of Inertia: I_AI_BI_C = 8.5 X 10⁻¹²⁰ g.³ cm.⁶σ⁻ = 2

Heat of Formation.

The heat of formation of amidogen at 298.15°K., ΔH_f⁰ (NH₂, g) = 39.8 kcal. mole⁻¹ was obtained from the pyrolysis of N₂H₄ by J. A. Kerr, R. C. Sekhar and A. P. Trotman-Dickenson, J. Chem. Soc. 3217 (1963). They have reinvestigated the rate constants of the thermal decomposition N₂H₄ → 2NH₂ at different temperatures using the same techniques as M. Szwarc, J. Chem. Phys. 17, 505 (1949), and revised the activation energy to 57.1 kcal. mole⁻¹ for the reaction at 874°K. (instead of 60 kcal. mole⁻¹ at 1000°K. reported by Szwarc). The activation energy was assumed to be the same as the dissociation energy of the N-N bond in hydrazine. Using all JANAF auxiliary data, one obtains D₀ (H₂N-NH₂) = 55.4 ± 3 kcal. mole⁻¹ and ΔH_f⁰ 298 (NH₂, g) = 40.1 ± 3 kcal. mole⁻¹.

F. M. Page, Trans. Faraday Soc. 57, 1254 (1961), has measured the electron affinity of NH₂ and has applied the results to calculate the dissociation energy, D₀ (H-NH₂) = 102 ± 3 kcal. mole⁻¹. This value leads to the heat of formation ΔH_f⁰ 298 (NH₂, g) = 40.4 ± 3 kcal. mole⁻¹ which is in good agreement with the value selected. E. R. Lippincott and M. O. Dayhoff, Spectrochim. Acta, 16, 807 (1960) calculated theoretically the dissociation energy D₀ (H₂N-NH₂) = 59 kcal. mole⁻¹ which gives ΔH_f⁰ 298 (NH₂, g) = 41.9 kcal. mole⁻¹.

Heat Capacity and Entropy.

The bond distance and angle were measured from the electronic absorption spectra of NH₂ by K. Dressler and D. A. Ransay, Phil. Trans. Roy. Soc. London Ser. A 252, 553 (1959). The three principal moments of inertia are I_A = 0.1189 X 10⁻⁵⁹ g. cm.², I_B = 0.2149 X 10⁻⁵⁹ g. cm.² and I_C = 0.3338 X 10⁻⁵⁹ g. cm.²

The selected vibrational frequencies were obtained from the infrared spectrum of NH₂ by matrix isolation by D. E. Milligan and M. E. Jacox, J. Chem. Phys. 43, 4487 (1965). K. N. Tanner and R. L. King, Nature 181, 963 (1958) have also determined the vibrational frequencies ω₁ = 3200 cm.⁻¹ and ω₂ = 3280 cm.⁻¹ by flash photolysis and calculated ω₂ = 1060 cm.⁻¹. The symmetric and the antisymmetric stretching frequencies are in good agreement. M. Taubol, Spectrochim. Acta 16, 505 (1960), has observed NH₂ bending frequencies, 1572 cm.⁻¹, 1819 cm.⁻¹ and 1623 cm.⁻¹, in HCONH₂(g), C₆H₅NH₂(g) and CH₃NH₂(g), respectively. In light of these observations and the adopted ω₂, Tanner and King's bending frequency seems to be in error.

H₂N

T, °K.	C _p	S°	(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	0.000	0.000	INFINITE	2.4416	32.580	INFINITE
100	7.950	50.564	-1.621	51.931	53.846	-117.674
200	8.095	48.889	-1.822	51.424	53.948	-61.134
298	8.737	52.223	-2.223	50.900	54.261	-42.719
300	8.753	52.277	-2.223	50.890	58.326	-42.689
400	9.784	54.932	-2.578	50.424	60.878	-33.260
500	10.877	57.234	-2.884	50.056	63.535	-27.770
600	11.882	59.307	-3.118	49.783	66.259	-24.134
700	12.768	61.066	-3.277	49.586	69.021	-21.348
800	13.584	62.556	-3.374	49.444	71.807	-18.916
900	14.331	63.806	-3.434	49.373	74.607	-16.918
1000	14.930	64.831	-3.474	49.334	77.412	-15.938
1100	15.356	65.670	-3.507	49.330	80.220	-15.009
1200	15.729	66.354	-3.529	49.334	83.029	-14.121
1300	16.054	66.917	-3.544	49.342	85.832	-13.275
1400	16.337	67.372	-3.554	49.347	88.632	-12.469
1500	16.587	67.758	-3.563	49.346	91.429	-11.706
1600	16.811	68.077	-3.570	49.344	94.217	-11.007
1700	17.005	68.325	-3.575	49.338	97.001	-10.367
1800	17.175	68.500	-3.578	49.334	100.000	-9.784
1900	17.323	68.618	-3.580	49.330	102.551	-9.253
2000	17.457	68.683	-3.583	49.326	105.316	-8.771
2100	17.581	68.705	-3.585	49.324	108.075	-8.338
2200	17.695	68.725	-3.587	49.322	110.829	-7.954
2300	17.802	68.742	-3.588	49.320	113.578	-7.618
2400	17.899	68.757	-3.589	49.318	116.320	-7.323
2500	17.987	68.769	-3.590	49.316	119.056	-7.071
2600	18.063	68.778	-3.591	49.315	121.781	-6.858
2700	18.130	68.784	-3.592	49.314	124.519	-6.681
2800	18.187	68.788	-3.593	49.313	127.264	-6.538
2900	18.237	68.791	-3.594	49.312	130.016	-6.425
3000	18.280	68.793	-3.594	49.311	132.677	-6.338
3100	18.319	68.794	-3.595	49.310	135.385	-6.271
3200	18.355	68.795	-3.595	49.309	138.092	-6.223
3300	18.388	68.796	-3.596	49.308	140.799	-6.191
3400	18.419	68.797	-3.596	49.307	143.496	-6.164
3500	18.448	68.798	-3.597	49.306	146.192	-6.144
3600	18.475	68.799	-3.597	49.305	148.883	-6.128
3700	18.500	68.799	-3.598	49.304	151.573	-6.118
3800	18.523	68.799	-3.598	49.303	154.264	-6.111
3900	18.545	68.799	-3.599	49.302	156.957	-6.105
4000	18.566	68.799	-3.599	49.302	159.627	-6.101
4100	18.585	68.799	-3.599	49.301	162.304	-6.098
4200	18.603	68.799	-3.599	49.300	164.984	-6.095
4300	18.619	68.799	-3.599	49.299	167.664	-6.093
4400	18.634	68.799	-3.599	49.298	170.345	-6.091
4500	18.648	68.799	-3.599	49.297	173.027	-6.089
4600	18.661	68.799	-3.599	49.296	175.667	-6.087
4700	18.673	68.799	-3.599	49.295	178.335	-6.085
4800	18.684	68.799	-3.599	49.294	181.004	-6.084
4900	18.695	68.799	-3.599	49.293	183.674	-6.083
5000	18.705	68.799	-3.599	49.292	186.344	-6.082
5100	18.715	68.799	-3.599	49.291	189.014	-6.081
5200	18.724	68.799	-3.599	49.290	191.684	-6.080
5300	18.733	68.799	-3.599	49.289	194.354	-6.079
5400	18.741	68.799	-3.599	49.288	197.024	-6.078
5500	18.749	68.799	-3.599	49.287	199.694	-6.077
5600	18.756	68.799	-3.599	49.286	202.364	-6.076
5700	18.763	68.799	-3.599	49.285	205.034	-6.075
5800	18.770	68.799	-3.599	49.284	207.704	-6.074
5900	18.777	68.799	-3.599	49.283	210.374	-6.073
6000	18.783	68.799	-3.599	49.282	213.044	-6.072

Dec. 31, 1965

 $\Delta H_f^0 = 52.6 \pm 5 \text{ kcal. mole}^{-1}$ $\Delta H_f^0 = 298.15 = 50.9 \pm 5 \text{ kcal. mole}^{-1}$ Point Group C_{2v} $S_{298.15}^0 = [52.2] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹
[3095](1)	[3205](1)
[1406](1)	[1495](1)
[1360](1)	[910](1)

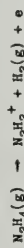
Bond Distance: N-H = [1.014] Å N-N = [1.23] Å

Bond Angle: H-N-N = [100]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.3988] \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The standard enthalpy of formation, ΔH_f^0 298 (N₂H₂) g = 50.9 kcal. mole⁻¹, was calculated from the appearance and ionization potentials of di-imide reported by S. N. Foner and R. L. Hudson, J. Chem. Phys. 29, 442 (1958), using the JANAF ΔH_f^0 (N₂H₂) g = 26.1 kcal. mole⁻¹ in calculation. For example:

 ΔH_f^0 
 $11.0 \pm 0.2 \text{ e.v.}$
 $9.85 \pm 0.1 \text{ e.v.}$
 $1.15 \pm 0.2 \text{ e.v.}$
 $(26.5 \pm 5 \text{ kcal. mole}^{-1})$

From the above heat of formation and that for NH(g) in the JANAF Tables 12-31-65, one can calculate a N-N bond energy of $109.4 \pm 5 \text{ kcal. mole}^{-1}$ at 0°K. This is in agreement with the N-N bond in molecules such as N₂P₂.

Heat Capacity and Entropy.

The bond distances and angle were obtained from a quantum-mechanical calculation by W. Wheland and P. S. K. Chen, J. Chem. Phys. 24, 67 (1956). The three principal moments of inertia are $I_A = [0.3116] \times 10^{-39}$, $I_B = [1.9686] \times 10^{-39}$ and $I_C = [2.2802] \times 10^{-39} \text{ g. cm.}^2$

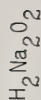
Since there are 12 valency electrons in N₂H₂, A. D. Walsh, J. Chem. Soc. 2288 (1953), has predicted a bent ground state, existing in either a cis or a trans configuration for diimide. E. J. Blau and B. F. Hochheimer, J. Chem. Phys. 41, 1174 (1964), have measured the infrared spectrum of diimide which was frozen in a cold trap as one of the decomposition products of N₂H₄. The spectrum of the solid N₂H₂ at liquid nitrogen temperature agrees with the predicted non-linear planar structure, and the molecule N₂H₂ appears mainly in cis form. They have also assigned six fundamental vibrational frequencies for cis N₂H₂(s) which have been adopted here for gaseous cis N₂H₂. Blau and Hochheimer also observed two gas phase bands (1277 - 1314 and 3050 - 3190 cm.⁻¹). K. Rosengren and G. C. Pimentel, J. Chem. Phys. 43, 507 (1965), have observed these bands in matrix isolation studies. They assigned ω_1 or $\omega_4 = 3074 \text{ cm.}^{-1}$ and $\omega_3 = 1279 \text{ cm.}^{-1}$ which are in satisfactory agreement with the selected frequencies.

Sodium Hydroxide, Dimeric (Na₂O₂H₂)

(Ideal Gas) Mol. Wt. = 79.99434

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₃₉₈)/T	H°-H° ₃₉₈	ΔH _f °	Log K _p
0	0.000	0.000	INFINITE	INFINITE	4.135	-131.754	INFINITE
100	11.929	56.308	86.609	3.230	-132.961	329.711	329.711
200	16.732	66.319	88.610	1.758	-153.946	162.130	162.130
298	18.949	73.442	93.442	0.000	-154.800	106.616	106.616
300	18.985	73.559	93.442	-0.035	-154.815	105.916	105.916
400	20.248	84.070	79.714	2.010	-157.677	60.410	60.410
500	22.248	88.236	77.461	6.465	-158.287	48.002	48.002
600	24.381	91.922	79.269	8.857	-159.203	40.653	40.653
700	26.317	95.230	81.061	11.335	-159.874	38.448	38.448
800	28.000	98.161	83.460	13.840	-160.350	36.410	36.410
1000	32.381	108.981	84.686	16.495	-159.874	25.731	25.731
1100	26.681	103.520	86.103	19.158	-160.168	22.953	22.953
1200	27.324	105.878	87.654	21.869	-160.919	18.732	18.732
1300	27.720	108.081	89.141	24.622	-160.135	16.834	16.834
1400	28.000	110.098	90.569	27.422	-159.874	15.000	15.000
1500	28.381	112.000	91.959	30.255	-159.874	13.423	13.423
1600	28.671	113.937	93.257	33.088	-159.874	12.325	12.325
1700	28.924	115.683	94.526	35.968	-159.874	11.679	11.679
1800	29.151	117.343	95.748	38.872	-159.874	11.279	11.279
1900	29.358	118.926	96.926	41.800	-159.874	10.975	10.975
2000	29.538	120.435	98.064	44.742	-159.874	10.731	10.731
2100	29.704	121.881	99.164	47.705	-159.874	10.540	10.540
2200	29.853	123.266	100.228	50.683	-159.874	10.400	10.400
2300	29.988	124.596	101.259	53.675	-159.874	10.311	10.311
2400	30.111	125.872	102.259	56.680	-159.874	10.262	10.262
2500	30.221	127.100	103.228	59.696	-159.874	10.243	10.243
2600	30.322	128.294	104.169	62.724	-159.874	10.243	10.243
2700	30.414	129.440	105.084	65.761	-159.874	10.262	10.262
2800	30.498	130.547	105.974	68.806	-159.874	10.291	10.291
2900	30.574	131.615	106.840	71.860	-159.874	10.327	10.327
3000	30.642	132.657	107.683	74.921	-159.874	10.364	10.364
3100	30.711	133.663	108.505	77.989	-159.874	10.400	10.400
3200	30.771	134.639	109.306	81.063	-159.874	10.435	10.435
3300	30.826	135.586	110.088	84.143	-159.874	10.470	10.470
3400	30.876	136.504	110.852	87.226	-159.874	10.505	10.505
3500	30.924	137.403	111.598	90.318	-159.874	10.540	10.540
3600	30.968	138.275	112.327	93.413	-159.874	10.575	10.575
3700	31.008	139.124	113.040	96.512	-159.874	10.610	10.610
3800	31.046	139.951	113.737	99.614	-159.874	10.645	10.645
3900	31.082	140.758	114.415	102.720	-159.874	10.680	10.680
4000	31.114	141.546	115.080	105.831	-159.874	10.715	10.715
4100	31.145	142.314	115.743	108.943	-159.874	10.750	10.750
4200	31.173	143.065	116.384	112.059	-159.874	10.785	10.785
4300	31.200	143.799	117.013	115.178	-159.874	10.820	10.820
4400	31.224	144.518	117.626	118.297	-159.874	10.855	10.855
4500	31.249	145.218	118.230	121.423	-159.874	10.890	10.890
4600	31.271	145.906	118.830	124.549	-159.874	10.925	10.925
4700	31.292	146.578	119.413	127.677	-159.874	10.960	10.960
4800	31.312	147.237	119.986	130.808	-159.874	10.995	10.995
4900	31.331	147.884	120.549	133.940	-159.874	11.030	11.030
5000	31.348	148.516	121.102	137.074	-159.874	11.065	11.065
5100	31.365	149.137	121.645	140.209	-159.874	11.100	11.100
5200	31.380	149.746	122.180	143.347	-159.874	11.135	11.135
5300	31.395	150.344	122.706	146.485	-159.874	11.170	11.170
5400	31.409	150.932	123.226	149.623	-159.874	11.205	11.205
5500	31.423	151.508	123.732	152.767	-159.874	11.240	11.240
5600	31.435	152.074	124.233	155.910	-159.874	11.275	11.275
5700	31.447	152.631	124.726	159.054	-159.874	11.310	11.310
5800	31.458	153.176	125.212	162.200	-159.874	11.345	11.345
5900	31.469	153.712	125.691	165.346	-159.874	11.380	11.380
6000	31.480	154.244	126.162	168.495	-159.874	11.415	11.415

Mar. 31, 1966



MOL. WT. = 79.99434

SODIUM HYDROXIDE, DIMERIC (Na₂O₂H₂) (IDEAL GAS)Point Group C_{2h}S°_{298.15} = [73.4] cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

ω _i , cm. ⁻¹	ω _i , cm. ⁻¹
[350](1)	[3700](1)
[209](1)	[3700](1)
[270](1)	[1250](1)
[201](1)	[1250](1)
[294](1)	[1250](1)
[313](1)	[1250](1)

Vibrational Frequencies and Degeneracies

ω_i, cm.⁻¹ω_i, cm.⁻¹

O-H = [0.96] Å

Na-O = [2.17] Å

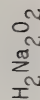
Na-O-H = [110]°

Products of the Moments of Inertia: I_AI_BI_C = [8.156754] X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

See NaOH(g) table for details.

Heat Capacity and Entropy.

S. H. Bauer, R. H. Diner and R. P. Porter, J. Chem. Phys. 29, 921 (1958), have proposed a model for the dimeric alkali hydroxide (g) which consists of a square planar configuration for the alkali and oxygen atoms, with two hydrogen bridges between the oxygens (the hydrogen and oxygen atoms formed a rhombus perpendicular to the alkali-oxygen plane). R. C. Schoonmaker and R. P. Porter, J. Chem. Phys. 31, 830 (1959), have suggested a square planar model without hydrogen bonding with alkali-oxygen bond distances 0.2 Å larger than those assumed for the monomeric alkali hydroxides. J. Berkowitz, D. J. Meschi and W. A. Chupka, J. Chem. Phys. 33, 533 (1960), have also postulated a model for Li₂(OH)₂(g) which consists of a trans configuration with hydrogens above and below the plane of the rhombus, and the angle O-Li-O = 100°. The last one was adopted for the molecular configuration of Na₂(OH)₂, but the bond angle O-Na-O in Na₂(OH)₂(g) was assumed to be 110°. The bond distance O-H was estimated to be the same in H₂O(g). The three principal moments of inertia are I_A = [14.0631] X 10⁻³⁹, I_B = [18.1878] X 10⁻³⁹ and I_C = [31.8449] X 10⁻³⁹ g. cm.²The first six selected vibrational frequencies were taken to be equal to those for Na₂F₂(g) (see Na₂F₂(g) table), and the rest were O-H stretching and bending frequencies which have been suggested by Berkowitz et al., loc. cit.

WATER (H₂O)

(IDEAL GAS)

MOL. WT. = 18.016

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	7.961	0.000	INFINITE	2.367	57.103	57.103	INFINITE	INFINITE
100	7.961	36.396	52.202	1.561	57.433	56.557	123.600	
200	7.961	72.792	45.106	0.815	57.433	56.557	60.792	
298	8.475	45.106	45.106	0.000	57.198	56.557	40.088	
300	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
400	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
500	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
600	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
700	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
800	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
900	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1000	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1100	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1200	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1300	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1400	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1500	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1600	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1700	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1800	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
1900	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2000	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2100	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2200	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2300	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2400	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2500	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2600	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2700	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2800	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
2900	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3000	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3100	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3200	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3300	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3400	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3500	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3600	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3700	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3800	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
3900	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4000	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4100	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4200	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4300	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4400	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4500	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4600	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4700	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4800	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
4900	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5000	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5100	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5200	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5300	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5400	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5500	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5600	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5700	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5800	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
5900	8.475	45.155	45.106	0.015	57.803	54.617	39.786	
6000	8.475	45.155	45.106	0.015	57.803	54.617	39.786	

March 31, 1961

ΔH_f⁰ = -57.103 kcal. mole⁻¹Point Group C_{2v}ΔH_f⁰ 298.15 = -57.7979 kcal. mole⁻¹S_{298.15} = 45.106 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

(W, cm.⁻¹)

3657.05 (1)

1594.59 (1)

3755.79 (1)

Bond Length and Angle O-H distance = 0.9584 Å H-O-H angle = 104.45° σ = 2

Product of Moments of Inertia I_AI_BI_C = 5.7558 × 10⁻¹²⁰ g.³ cm.⁶

Heat of Formation

Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties," 1952.

Heat Capacity and Entropy

A. S. Friedman and L. Haar, J. Chem. Phys. **22**, 2051 (1954), using the infra-red spectra analysis of W. S. Benedict, K. H. Claassen and J. H. Shaw, J. Research Natl. Bur. Standards **49**, 91 (1952), have calculated the thermodynamic functions for water including the anharmonic corrections. Friedman and Haar in comparing their calculation to that of a direct summation by Glatt, Adams, and Johnston, Ohio State University Res. Foundation Tech. Report No. 316-8 (1953), found that the difference between the two calculations was less than the uncertainty in the direct summation.

C_p values from 100° to 5000°K. are from Friedman and Haar. C_p from 5000° to 6000°K. was extrapolated linearly. Using the tabulated functions of Friedman and Haar C_p, S, and H_{298.15}°K. was calculated by the method of Lagrangian curvilinear interpolation, W. J. Taylor, J. Research Natl. Bur. Standards **35**, 151 (1945).

The bond length and angle were obtained from a compilation by L. E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions," The Chem. Soc., Burlington House, London W1, 1958.



Hydrogen Peroxide (H_2O_2)
(Gas) Mol. Wt. = 34.016

INTERIM TABLE

T, °K.	C_p	S°	$-(H^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	0.000	0.000	INFINITE	2.594	31.025	31.025	INFINITE
100	0.013	44.558	62.538	1.798	31.682	29.559	64.598
200	0.013	50.316	54.701	1.877	32.060	27.174	29.093
298	10.305	55.660	55.660	1.000	32.530	25.208	18.477
300	10.330	55.724	55.660	0.019	32.537	25.143	18.330
400	11.580	58.872	56.081	1.116	32.844	22.655	12.377
500	12.560	61.565	56.915	2.325	33.085	20.081	8.777
600	13.310	63.975	57.891	3.621	33.225	17.469	6.363
700	13.870	65.979	58.905	5.000	33.282	14.822	4.830
800	14.300	67.600	59.914	6.369	33.340	12.181	3.328
900	14.690	69.007	60.897	7.639	33.516	9.519	2.311
1000	15.076	71.173	61.848	9.325	33.576	6.850	1.497
1100	15.330	72.910	62.762	10.803	33.622	4.173	0.929
1200	15.510	74.295	63.640	12.590	33.652	1.493	0.529
1300	15.870	75.225	64.483	13.968	33.684	1.186	0.396
1400	16.110	76.010	65.293	15.563	33.703	3.870	0.604
1500	16.330	77.529	66.072	17.185	33.718	6.554	0.955

Hydrogen Peroxide (H_2O_2) (gas)

Mol. Wt. = 34.016

H_f° 298.15 = -32.53 kcal. mole⁻¹

$S_{298.15}^\circ$ = 55.660 cal. deg.⁻¹ mole⁻¹

Point Group C_2

C_p from P. A. Giguère and I. D. Lin, J. Am. Chem. Soc. 77, 6477 (1955). C_p below 298.15°K. estimated.



T, °K	C _p ^a	gbbt/mol	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
0								
298	33.200	37.501	37.501		.000	-194.548	-164.928	170.495
300	33.290	37.707	37.502		.062	-194.535	-164.745	120.016
400	36.700	47.790	36.853		3.575	-194.237	-154.912	84.640
500	38.650	56.206	41.506		7.350	-193.561	-145.155	63.467
600	40.000	63.380	44.569		11.287	-192.691	-135.251	49.175
800	40.830	75.691	51.791		15.340	-191.176	-125.086	32.789
900	41.900	80.015	53.777		17.414	-190.327	-107.422	26.086
1000	42.178	84.445	56.626		27.819	-200.935	-94.950	21.168
1100	42.307	86.471	59.341		32.044	-199.557	-86.620	17.210
1200	42.400	87.553	61.342		35.523	-198.456	-68.412	13.749
1300	42.470	88.679	63.362		38.472	-197.155	-50.326	10.793
1400	42.500	89.702	65.722		40.772	-195.535	-32.326	8.793
1500	42.500	101.634	68.953		46.022	-194.241	-48.428	6.765

Dec. 31, 1960; Dec. 31, 1966

(LIQUID)

SULFURIC ACID (H₂SO₄)

OFW = 98.07754

$$\Delta H_f^{298,15} = -194.548 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 2.56 \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = [13.35] \text{ kcal/mol}$$

$$S_{298,15}^{\circ} = 37.501 \text{ gibbs/mol}$$

$$T_m = 283.55^{\circ}\text{K}$$

$$T_b = [608.6]^{\circ}\text{K}$$

Heat of Formation.

The heat of combustion (ΔH_c°) of rhombic sulfur (c) to H₂SO₄(aq), i.e., S(c, rhombic) + 3/2 O₂(g) + H₂O(l) = H₂SO₄(aq), has been determined by many investigators. Based on the reported ΔH_c° data, values of $\Delta H_f^{298}(\text{H}_2\text{SO}_4, \text{l})$ are derived using heats of solution and dilution for H₂SO₄(l), taken from D. D. Wegman, W. H. Evans, I. Hallow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Technical Note 270-1, Natl. Bur. Std., 1965. The results obtained are presented in the table below. The value of $\Delta H_f^{298}(\text{H}_2\text{SO}_4, \text{l})$ is adopted as -194.548 ± 0.10 kcal/mol, which is the same as that given by Technical Note 270-1, loc. cit.

Investigator	Product	ΔH_c° , kcal/mol	ΔH_f^{298} , kcal/mol
1. McCullough et al. (1963)	H ₂ SO ₄ (70H ₂ O)	-143.58 ± 0.09	-194.400
2. Scott et al. (1956)	H ₂ SO ₄ (75H ₂ O)	-143.98 ± 0.22	-194.775
3. Good et al. (1960)	H ₂ SO ₄ (115H ₂ O)	-143.85 ± 0.06	-194.521
4. Mansson and Sumner (1963)	H ₂ SO ₄ (115H ₂ O)	-143.93 ± 0.07	-194.601

- J. P. McCullough, S. Sumner, H. L. Finke, W. N. Hubbard, J. E. Gross, R. E. Pennington, J. P. Measlerly, W. D. Good and O. Vaddington, *J. Am. Chem. Soc.* **75**, 5075 (1953).
- D. W. Scott, J. P. McCullough, W. N. Hubbard, J. F. Measlerly, I. A. Hosenlopp, F. R. Frow and O. Vaddington, *J. Am. Chem. Soc.* **78**, 5463 (1956).
- J. D. Good, J. L. Lachina and J. P. McCullough, *J. Am. Chem. Soc.* **82**, 5589 (1960).
- M. Mansson and S. Sumner, *Acta Chem. Scand.* **17**, 723 (1963).

Heat Capacity and Entropy.

The heat capacities, 283.46 to 300°K, were measured by W. P. Glaque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Am. Chem. Soc.* **82**, 62 (1960). The Cp values above 300°K are obtained from graphical extrapolation. The value of S°₂₉₈ was reported by Glaque, Hornung, Kunzler and Rubin, loc. cit., based on low temperature heat capacity measurements of H₂SO₄(c).

Melting Data.

T_m and ΔH_m° are taken from T. R. Rubin and W. P. Glaque, *J. Am. Chem. Soc.* **74**, 800 (1952). The value, T_m=283.53°K, has been reported by C. M. Gable, H. P. Betz and S. H. Maron, *J. Am. Chem. Soc.* **72**, 1445 (1950), as well as J. E. Kunzler and W. P. Glaque, *J. Am. Chem. Soc.* **74**, 797 (1952). The heat of melting (ΔH_m°) has also been determined by the following investigators:

ΔH_m° , kcal/mol	Source
2.35	Pickering, <i>Proc. Roy. Soc. (London)</i> 49 , 11 (1891).
2.25	Hantzsch, <i>Z. Physik. Chem.</i> 61 , 262 (1907).
2.24	Krietsch, quoted by Hantzsch, loc. cit.
2.55	Brönsted, <i>Z. Physik. Chem.</i> 58 , 693 (1910).
2.56	Rubin and Glaque, <i>J. Am. Chem. Soc.</i> 74 , 800 (1952).

Vaporization Data.

T_b is the temperature at which the Gibbs energy change (ΔG_r°) for the reaction H₂SO₄(l) = H₂SO₄(g) approaches zero. The difference between ΔH_f° for H₂SO₄(g) and H₂SO₄(l) at T_b is ΔH_v° .

According to G. P. Lucinaki, *Zh. Fiz. Khim.* **30**, 1207 (1956), the total vapor pressure over H₂SO₄(l) reaches one atmosphere at 553°K with a vapor composition of 76.6 mole percent SO₃, 22.6% H₂SO₄, and 0.8% H₂O. This composition implies that the real liquid phase enhances the vapor decomposition by reducing the partial pressure of water vapor.

Sulfuric Acid (H_2SO_4)
(Ideal Gas)

GFW = 98.07754

T, °K	C _p ^a	S ^b	-(C _p ^a -H ₂₉₈)/T	H ^c -H ₂₉₈	ΔH ^c	Log K _p
0	0.000	INFINITE	INFINITE	3.652	-173.425	INFINITE
100	8.985	54.518	82.913	2.840	-174.924	370.138
200	14.549	62.396	70.740	1.670	-176.142	176.452
298	19.266	68.129	65.129	0.000	-177.000	116.945
300	19.343	69.248	64.248	0.036	-177.013	114.145
400	22.505	75.327	60.334	2.157	-178.107	81.845
500	25.506	80.733	71.563	4.595	-178.778	62.346
600	27.410	85.550	73.501	7.235	-179.195	49.304
700	28.943	89.720	75.037	10.067	-179.437	38.568
800	29.962	93.425	77.583	12.993	-179.622	33.309
900	30.469	97.008	79.590	16.036	-179.757	27.466
1000	31.425	100.701	81.539	19.162	-179.844	22.798
1100	32.468	103.744	83.421	22.358	-179.895	18.986
1200	33.479	106.578	85.251	25.633	-179.912	15.915
1300	34.462	109.248	86.979	28.920	-179.910	13.137
1400	35.427	111.808	88.657	32.271	-179.888	10.647
1500	36.372	114.047	90.273	35.692	-179.853	8.467
1600	37.316	116.258	91.828	39.089	-179.807	7.139
1700	38.251	118.444	93.324	42.467	-179.753	6.267
1800	39.177	120.604	94.774	45.837	-179.693	5.427
1900	40.094	122.741	96.179	49.195	-179.628	4.713
2000	40.994	124.859	97.539	52.543	-179.560	4.026
2100	41.879	126.948	98.854	55.881	-179.489	3.367
2200	42.749	129.011	100.124	59.210	-179.415	2.732
2300	43.604	131.051	101.351	62.531	-179.338	2.122
2400	44.444	133.068	102.534	65.844	-179.259	1.535
2500	45.269	135.064	103.672	69.150	-179.178	0.970
2600	46.079	137.041	104.769	72.449	-179.095	0.426
2700	46.874	138.999	105.824	75.743	-179.009	0.000
2800	47.654	140.939	106.841	79.033	-178.922	-0.426
2900	48.419	142.861	107.819	82.319	-178.834	-0.852
3000	49.169	144.767	108.767	85.601	-178.745	-1.278
3100	49.904	146.658	109.684	88.879	-178.656	-1.704
3200	50.624	148.534	110.571	92.153	-178.567	-2.130
3300	51.329	150.396	111.429	95.424	-178.478	-2.556
3400	52.019	152.244	112.258	98.691	-178.389	-2.982
3500	52.694	154.079	113.058	101.954	-178.300	-3.408
3600	53.354	155.901	113.829	105.213	-178.211	-3.834
3700	54.000	157.711	114.571	108.468	-178.122	-4.260
3800	54.631	159.509	115.284	111.719	-178.033	-4.686
3900	55.248	161.294	115.969	114.967	-177.944	-5.112
4000	55.851	163.066	116.626	118.213	-177.855	-5.538
4100	56.440	164.825	117.258	121.456	-177.766	-5.964
4200	57.015	166.571	117.864	124.696	-177.677	-6.390
4300	57.576	168.304	118.444	127.933	-177.588	-6.816
4400	58.124	170.024	118.999	131.167	-177.499	-7.242
4500	58.659	171.731	119.531	134.398	-177.410	-7.668
4600	59.181	173.425	120.041	137.626	-177.321	-8.094
4700	59.690	175.104	120.529	140.851	-177.232	-8.520
4800	60.186	176.768	121.000	144.072	-177.143	-8.946
4900	60.669	178.417	121.454	147.290	-177.054	-9.372
5000	61.139	180.051	121.891	150.505	-176.965	-9.798
5100	61.596	181.671	122.311	153.716	-176.876	-10.224
5200	62.040	183.277	122.716	156.923	-176.787	-10.650
5300	62.471	184.869	123.106	160.126	-176.698	-11.076
5400	62.889	186.447	123.481	163.325	-176.609	-11.502
5500	63.294	188.011	123.841	166.520	-176.520	-11.928
5600	63.686	189.561	124.186	169.711	-176.431	-12.354
5700	64.065	191.096	124.517	172.898	-176.342	-12.780
5800	64.431	192.617	124.834	176.081	-176.253	-13.206
5900	64.784	194.124	125.137	179.260	-176.164	-13.632
6000	65.124	195.617	125.426	182.435	-176.075	-14.058

Dec. 31, 1966

SULFURIC ACID (H_2SO_4)

(IDEAL GAS)

GFW = 98.07754

H_2O_4S

Point Group [C_{2v}]

$S_{298.15}^\circ = [69.1]$ gibbs/mol

Ground State Quantum Weight = 1

$\Delta H_f^\circ = -173.4 \pm 2$ kcal/mol

$\Delta H_{298.15}^\circ = -177.0 \pm 2$ kcal/mol

Vibrational Frequencies and Degeneracies

$\bar{\nu}$, cm ⁻¹	$\bar{\nu}$, cm ⁻¹	$\bar{\nu}$, cm ⁻¹
[3500] (1)	[380] (1)	883 (1)
[1225] (1)	[450] (1)	[400] (1)
1138 (1)	[580] (1)	1450 (1)
834 (1)	3610 (1)	[450] (1)
550 (1)	1159 (1)	568 (1)

Bond Distance: S-O = $[1.42] \text{ \AA}$ S-OR = $[1.53] \text{ \AA}$ O-H = $[0.97] \text{ \AA}$

Bond Angle: O-S-O = $[125]^\circ$ HO-S-OH = $[100]^\circ$ S-O-H = $[105]^\circ$

Product of the Moments of Inertia: $I_A I_B I_C = [4.237 \times 10^{-144}] \text{ g}^3 \text{ cm}^6$

Heat of Formation

The vapor phase equilibria of the H_2SO_4 , H_2O and SO_3 systems have been studied by (1) B. Bodenstein and M. Katayama, Z. Elektrochem. 15, 244 (1909), Z. Physik. Chem. 69, 26 (1909); (2) G. P. Luchinskii, Zh. Fiz. Khim. 30, 1207 (1956), and (3) A. V. Suvorov, R. B. Dobrovin and S. M. Gashler, Russ. J. Inorg. Chem. (English Transl.) 10, 710 (1965). The data of Bodenstein and Katayama and of Suvorov et al. were obtained from PVT studies, while those of Luchinskii were based on vapor pressure measurements. A translation of Luchinskii's paper is not yet available, so it is not known whether he obtained the vapor composition experimentally or by calculation. Using the reported equilibrium values for the reaction $H_2SO_4(g) = H_2O(g) + SO_3(g)$, we evaluate the corresponding enthalpy changes by both the second and third law methods. The results are presented in the table below. The value of ΔH_{298}° for $H_2SO_4(g)$ is adopted as -177 ± 2 kcal/mol.

Investigator	Temp., °K	No. of Points	ΔH_{298}° , kcal/mol	Drift, kcal/mol
1. Bodenstein & Katayama (1909)	596-2-756.2	53	-22.95 \pm 0.66	-24.55 -2.3 \pm 1.0 -176.94
2. Luchinskii (1956)	333-2-473.2	8	-24.02 \pm 0.22	-24.43 -1.2 \pm 0.5 -176.82
3. Suvorov (1965)	583-0-713.0	40	-27.14 \pm 0.45	-24.90 +3.3 \pm 0.6 -177.29

*Calculation based on the third law ΔH_{298}° value.

Heat Capacity and Entropy

The molecular structure and bond angles (O-S-O, HO-S-OH) are estimated by comparison with those for $SO_2(g)$ reported by D. R. Lide, D. E. Mann and R. M. Fristrom, J. Chem. Phys. 26, 754 (1957). The S-O and S-OH bond distances are assumed to be the same as those in $H_2SO_4(c)$, determined by R. Pascard, Compt. Rend. 240, 2162 (1955). The OH distance and S-O-H angle are taken from those for $H_2O(g)$. Electric deflection studies by A. Böhler, J. L. Stauffer and M. Knepper, J. Chem. Phys. 45, 605 (1967), indicate that $H_2SO_4(g)$ is polar, which is consistent with the assumed C_{2v} structure.

The infrared absorption spectrum in the range 4000 to 400 cm⁻¹ of normal and deuterated $H_2SO_4(g)$ above $H_2SO_4(l)$ was observed by S. M. Chackalal and P. E. Stafford, J. Am. Chem. Soc. 89, 723 (1967). The authors assigned nine vibrational frequencies, which are adopted here. The three principal moments of inertia are: $I_A = 1.570 \times 10^{-38}$, $I_B = 1.586 \times 10^{-38}$, and $I_C = 1.702 \times 10^{-38}$ g cm².

Four of the six missing frequencies are obtained from P. A. Giguère and R. Savoie, J. Am. Chem. Soc. 85, 287 (1963), which were estimated by comparison with infrared frequencies for the crystal and Raman values for the liquid. The remaining two frequencies, $\nu_7 = 450$ and $\nu_{14} = 450$ cm⁻¹, are assigned arbitrarily so that the second and third law values for $\Delta H_{298.15}^\circ$ derived from equilibrium data are in reasonable agreement.

H_2O_4S

Tungstic Acid (H₂WO₄)

GFW = 249.86354

(Crystal)

TUNGSTIC ACID (H₂WO₄)

(CRYSTAL)

OPW = 249.86354

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	24.920	34.600	34.600	0.00	-270.500	-239.963	175.697
300	27.500	34.787	34.601	0.050	-270.500	-239.774	174.675
400	31.500	43.082	35.707	2.950	-270.305	-229.552	152.462
500	35.500	50.431	47.929	8.251	-269.763	-219.419	125.958
600	38.200	57.116	40.579	9.822	-268.916	-209.425	76.283
700	40.500	63.219	43.384	13.885	-267.832	-199.591	62.315
800	42.200	66.768	46.216	18.041	-266.611	-189.929	51.866
900	43.500	73.826	49.007	22.338	-265.296	-180.419	43.812
1000	44.500	78.472	51.724	26.748	-263.912	-171.061	37.305

ΔH_f⁰ = UnknownΔH_f^{298.15} = -270.5 ± 0.4 kcal/molS_{298.15}^a = [34.6 ± 6] gibbs/mol

Td = [393]°K

Heat of Formation

V. I. Spitsyn and N. M. Patsukova¹ have measured calorimetrically the heats of reaction (1) and (2) at 298°K as -13.80 ± 0.01 and -13.05 ± 0.02 kcal/mol, respectively. The reactions are given as follows:



Combination of reactions (1) and (2) gives ΔH_f²⁹⁸ = -0.75 ± 0.04 kcal/mol for WO₃(c) + H₂O(l) → H₂WO₄(c), which leads to ΔH_f²⁹⁸(H₂WO₄, c) = -270.5 ± 0.4 kcal/mol.

To obtain WO₃(c) in a form soluble in the calorimetric solution, Spitsyn and Patsukova dehydrated H₂WO₄(c) at the relatively low temperature of 250°C. The resulting WO₃(c) was a very fine lemon-yellow powder which may have excess surface free energy compared with the JANAF standard state. The latter is WO₃ formed at high temperature in a calorimetric bomb. The actual heat of formation of tungstic acid should be less negative if this effect is significant.

The previously accepted value^{2,3,4} -280.2 ± 0.4 kcal/mol, was based on the pressure-temperature-composition studies of G. P. Rutting and B. Kurte⁵ for the WO₃-H₂O system. We suspect that the data do not correspond to equilibrium (see entropy section) for the reaction H₂WO₄(c) → WO₃(c) + H₂O(g).

Heat Capacity and Entropy

C_p300 = 27.0 gibbs/mol is estimated using Kopp's rule. Since the decomposition temperature of H₂WO₄(c) is approximately 400°K, which is relatively low for hydrogen and oxygen to reach their maximum Cp contribution, we estimate Cp400 = 31.0 gibbs/mol for H₂WO₄(c).

The entropy, S₂₉₈^a = 34.6 eu, is estimated so that the decomposition pressure of water is one atmosphere at 120°C. This value is quite uncertain as suggested by comparison with the following estimates. A lower limit may be obtained from S_{283.5}^a = 26.8 eu for H₂SO₄(c). Summation of the entropies for WO₃(c) and H₂O(g) [10.7 eu] yields 28.8 eu, an estimate which is somewhat larger than the lower limit. An upper limit may be obtained by assuming that the pressure of about 14 mm at 190°C corresponds to equilibrium for the reaction H₂WO₄(c) = WO₃(c) + H₂O(g). This pressure, based on the plateau in the temperature-composition data of Rutting and Kurte⁵, yields S₂₉₈^a = 46.5 eu when combined with the adopted ΔH_f²⁹⁸ and JANAF auxiliary data. Since the estimate appears to be unreasonably large, we suggest that this region of the curve may correspond to the reaction WO₃·0.5 H₂O(c) = WO₃(c) + 0.5 H₂O(g). In contrast, the observed pressures⁵ for samples having mole ratios (H₂O/WO₃) of 1.2 - 1.35 leads to S₂₉₈^a = 34 eu, if the reaction is WO₃·H₂O(c) = WO₃(c) + H₂O(g).

Temperature of Decomposition

Td is calculated as the temperature at which the Gibbs energy change of the reaction H₂WO₄(c) → WO₃(c) + H₂O(g) approaches zero.

Spitsyn and Patsukova¹ observed that some dehydration of stoichiometric H₂WO₄(c) occurs at temperatures as low as 90°C. Thermal studies^{6,7} on tungstic acid containing some excess water indicated the start of dehydration somewhere in the region of 60 - 120°C. These temperatures yield a lower limit for Td on the presumption that the experiments correspond to a partial pressure of water of less than one atmosphere.

References

1. V. I. Spitsyn and N. M. Patsukova, Russ. J. Inorg. Chem. (English transl.) **10**, 1304 (1965).
2. D. D. Magman, U.S. Natl. Bur. Std. Report 8919, July 1st, 1965.
3. M. P. Kohler, L. B. Penckertz and R. Barany, U.S. Bur. Mines RI 5973 (1962).
4. U. S. Natl. Bur. Std. Circ. 500, 1952.
5. G. P. Rutting and B. Kurte, Z. Anorg. Chem. **125**, 167 (1953).
6. W. Wanek, Silikaty **5**, 70 (1962).
7. P. P. Kerr and P. Young, Am. Mineral. **29**, 192 (1944).

Dec. 31, 1962; June 30, 1963; Mar. 31, 1967



Tungstic Acid (H₂WO₄)

(Ideal Gas)

GFw = 249.86354

Tungstic Acid (H₂WO₄)

(Ideal Gas)

OPW = 249.86354

T, K	Cp ^a	S ^b	-(G ^c -H ²⁹⁸)/T	H ²⁹⁸ -H ⁰	kcal/mol ΔH ⁰	Log Kp
0	.000	.000	INFINITE	5.038	-214.171	INFINITE
100	14.502	63.357	102.816	3.944	-215.386	460.647
200	20.190	75.182	86.218	2.207	-216.122	274.948
298	24.504	84.103	84.103	.000	-216.500	200.722
300	24.570	84.255	84.100	.045	-216.505	186.155
400	27.446	91.746	85.106	2.656	-216.599	106.713
500	29.394	98.093	87.085	5.504	-216.513	83.048
600	30.811	103.583	89.387	8.518	-216.320	67.281
700	31.903	108.419	91.767	11.655	-216.062	56.030
800	32.757	112.639	94.112	14.804	-215.756	47.484
900	33.417	116.319	96.412	18.204	-215.430	41.059
1000	34.056	120.197	98.615	21.582	-215.078	35.832
1100	34.534	123.466	100.728	25.012	-214.716	31.562
1200	34.932	126.489	102.750	28.486	-214.347	28.010
1300	35.289	129.288	104.693	32.004	-213.974	24.442
1400	35.607	131.883	106.558	35.538	-213.618	20.871
1500	35.787	134.383	108.313	39.105	-213.267	17.291
1600	35.921	136.699	110.016	42.694	-212.929	13.708
1700	36.109	138.887	111.650	46.302	-212.603	10.124
1800	36.349	140.925	113.234	49.936	-212.296	6.531
1900	36.449	142.825	114.776	53.565	-212.006	2.937
2000	36.564	144.798	116.190	57.215	-211.736	12.479
2100	36.595	146.585	117.596	60.877	-211.485	11.378
2200	36.734	148.292	118.922	64.545	-211.259	10.378
2300	36.881	149.928	120.181	68.218	-211.047	9.431
2400	36.992	151.487	121.533	71.916	-210.847	8.531
2500	36.945	153.005	122.742	75.607	-210.709	7.684
2600	37.021	154.456	123.953	79.307	-210.569	7.155
2700	37.072	155.854	125.109	83.012	-210.460	6.500
2800	37.115	157.199	126.212	86.721	-210.364	5.857
2900	37.158	158.506	127.321	90.431	-210.280	5.325
3000	37.196	159.766	128.337	94.152	-210.393	4.796
3100	37.230	160.986	129.411	97.874	-210.482	4.302
3200	37.261	162.169	130.419	101.593	-210.644	3.838
3300	37.289	163.313	131.419	105.306	-210.781	3.400
3400	37.315	164.428	132.419	109.056	-210.899	2.997
3500	37.339	165.512	133.246	112.789	-211.026	2.603
3600	37.361	166.564	134.196	116.524	-211.171	2.235
3700	37.382	167.588	135.095	120.261	-211.173	1.884
3800	37.401	168.584	135.954	124.000	-211.169	1.546
3900	37.418	169.557	136.782	127.740	-211.169	1.214
4000	37.434	170.504	137.633	131.484	-211.212	.904
4100	37.449	171.429	138.446	135.228	-211.244	.609
4200	37.463	172.331	139.242	138.973	-211.284	.328
4300	37.476	173.213	140.022	142.720	-211.318	.060
4400	37.489	174.075	140.782	146.466	-211.348	.000
4500	37.500	174.917	141.535	150.218	-211.453	.000
4600	37.511	175.742	142.270	153.969	-211.523	.674
4700	37.521	176.548	142.991	157.720	-211.604	.189
4800	37.530	177.333	143.693	161.471	-211.685	.000
4900	37.540	178.112	144.393	165.221	-211.779	.000
5000	37.548	178.871	145.075	168.981	-211.678	1.516
5100	37.556	179.615	145.745	172.734	-211.984	3.420
5200	37.564	180.344	146.403	176.492	-222.094	1.869
5300	37.571	181.059	147.049	180.250	-222.219	.000
5400	37.577	181.762	147.687	184.008	-222.359	.000
5500	37.584	182.451	148.312	187.764	-222.457	2.339
5600	37.590	183.129	148.928	191.521	-222.591	65.307
5700	37.595	183.794	149.534	195.282	-222.728	70.451
5800	37.600	184.446	150.131	199.043	-222.868	75.591
5900	37.606	185.091	150.717	202.805	-223.017	80.731
6000	37.611	185.723	151.296	206.563	-223.172	85.871

Dec. 31, 1962; June 30, 1963; Mar. 31, 1967

Point Group [C_{2v}]

S^{298.15} = [84] gibbs/mol

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

w _v , cm ⁻¹	w _v , cm ⁻¹	w _v , cm ⁻¹
[12000]	[100]	[570]
[10000]	[225]	[120]
[6200]	[100]	[1100]
[5600]	[2500]	[1300]
[500]	[630]	[540]

Bond Distances: W-O = [1.81] Å O-H = [0.97] Å

Bond Angle: O-W-O = [109.47]° W-O-H = [105]° σ = [2]

Product of the Moments of Inertia: I_AI_BI_C = [1.443 x 10⁻¹¹³] g³ cm⁶

Heat of Formation

The adopted heat of formation, ΔH²⁹⁸ = -216.5 ± 1.0 kcal/mol, is derived from equilibrium data^{1,2,3,4,5} obtained by the transpiration method. The data are in reasonable agreement and they are summarized below. Beaton and McCarron¹ have concluded that W₃H₂O is the species responsible for the increased volatilization of W(c) and W₃(c) in the presence of water vapor. Based on their data for W(c) and the earlier data for W₃(c), Beaton and McCarron¹ ruled out the possibility of significant amounts of (W₃)₂·H₂O and W₃·2 H₂O.

Investigator	Reaction*	Temp. (°K)	No. of Points	ΔH ²⁹⁸ (kcal/mol)	Drift (eu)	ΔH ²⁹⁸ (kcal/mol)
Beaton & McCarron ¹	A	1473-1773	Equation	14.70	14.63	-216.56
Glemser & Ackermann ²	B	673-1173	6	38.56	41.67	-217.59
Glemser & Haeseler ³	B	1173-1373	Equation	38.27	42.27	-216.99
Glemser & Volz ⁴	B	1373	1	-	43.44	-215.82
Meyer et al. ⁵	B	1393-1518	Equation	26.14	43.51	-215.75

*Reaction A: W(c) + 4H₂O(g) → H₂WO₄(g) + 3H₂(g)

B: W₃(c) + H₂O(g) → H₃WO₄(g)

**Based on the third law value

References

1. G. R. Beaton and R. L. McCarron, J. Phys. Chem. **68**, 1852 (1964).
2. O. Glemser and H. Ackermann, Z. Anorg. Allgem. Chem. **325**, 281 (1963).
3. O. Glemser and R. V. Haeseler, Z. Anorg. Allgem. Chem. **316**, 168 (1962).
4. O. Glemser and H. G. Volz, Naturwissenschaften **43**, 33 (1956).
5. O. Meyer, J. P. Oosterom and W. J. V. Overen, Rev. Trav. Chim. **78**, 417 (1959).

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those for H₂SO₄(g) reported by P. A. Diguere and R. Savoie, J. Am. Chem. Soc. **85**, 287 (1963), and S. M. Chakraborty and P. E. Stafford, J. Am. Chem. Soc. **88**, 723 (1966). These frequencies are also adjusted so that S^{298.15}(H₂WO₄,g) is 136.7 eu as reported by Beaton and McCarron, loc. cit. This entropy was derived from second law analysis of the equilibrium constants for reaction A.

The configuration of W₃ group is assumed to be tetrahedral. The bond angle W-O-H is estimated to be the same as the angle of H₂O(g). The bond distances are assumed to be the same as those in W₃(g) and H₂O(g). The three principal moments of inertia are I_A = 2.328 x 10⁻³⁶, I_B = 2.487 x 10⁻³⁶ and I_C = 2.493 x 10⁻³⁶ g cm².

H₂O W

Phosphorus Hydride (PH₂)
(Ideal Gas) Mol. Wt. = 32.991

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(H° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	2.391	30.594	30.594	30.594	INFINITE
100	7.940	42.029	57.986	-1.597	30.539	28.934	-0.6521	-0.3211
200	8.019	49.550	51.549	-1.800	30.415	27.333	-1.0467	-0.6877
300	8.312	50.800	50.800	-2.000	30.100	25.028	-1.4884	-1.0972
400	8.319	50.851	50.800	-2.015	29.893	25.058	-1.4836	-1.0936
500	8.182	51.310	51.311	-1.867	29.718	24.502	-1.3866	-1.0158
600	8.056	51.013	52.504	-2.705	28.985	22.053	-0.932	-0.8032
700	7.940	50.800	52.504	-2.705	28.985	22.053	-0.932	-0.8032
800	7.825	50.617	54.006	-4.728	27.884	19.536	-0.5971	-0.5971
900	7.710	50.434	54.006	-4.728	27.884	19.536	-0.5971	-0.5971
1000	7.595	50.251	54.006	-4.728	27.884	19.536	-0.5971	-0.5971
1100	7.480	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1200	7.365	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1300	7.250	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1400	7.135	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1500	7.020	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1600	6.905	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1700	6.790	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1800	6.675	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
1900	6.560	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2000	6.445	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2100	6.330	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2200	6.215	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2300	6.100	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2400	5.985	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2500	5.870	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2600	5.755	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2700	5.640	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2800	5.525	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
2900	5.410	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3000	5.295	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3100	5.180	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3200	5.065	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3300	4.950	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3400	4.835	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3500	4.720	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3600	4.605	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3700	4.490	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3800	4.375	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
3900	4.260	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4000	4.145	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4100	4.030	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4200	3.915	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4300	3.800	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4400	3.685	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4500	3.570	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4600	3.455	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4700	3.340	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4800	3.225	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
4900	3.110	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5000	3.000	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5100	2.885	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5200	2.770	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5300	2.655	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5400	2.540	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5500	2.425	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5600	2.310	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5700	2.195	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5800	2.080	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
5900	1.965	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544
6000	1.850	50.068	55.438	-6.917	27.768	16.215	-0.3544	-0.3544

Dec. 31, 1960 Mar. 31, 1963

PHOSPHORUS HYDRIDE (PH₂)

(IDEAL GAS)

Point Group [C_{2v}]
ΔH_f⁰ = [30.6 ± 23] kcal. mole⁻¹
S_{298.15} = [50.8] cal. deg⁻¹ mole⁻¹
ΔH_f⁰ 298.15 = [30.1 ± 23] kcal. mole⁻¹
Ground State Multiplicity = [2]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	[2327] (1)	[1020] (1)	[2322] (1)
---------------------	------------	------------	------------

Bond Distances: P-H = [1.419] Å

Bond Angle: H-P-H = [93.7]°

Product of Moments of Inertia: I_AI_BI_C = [6.95 X 10⁻¹¹³] g.³ cm.⁶

σ = 2

Heat of Formation.

ΔH_f⁰ 298.15 was estimated by V. N. Distefano, R. L. Potter, and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus-I.", American Cyanamid Company. The ΔH_f⁰ 298.15 was estimated by taking 83% of the dissociation energy of PH₂ and using it as the dissociation energy of PH₂. D. Wiles and C. Minkler, J. Phys. Chem. 61, 302 (1957) have estimated the ΔH_f⁰ 298.15 for PH₂(g) to be 30 kcal. mole⁻¹.

Heat Capacity and Entropy.

The vibrational spectra of PH₂ from the flash photolysis of PH₃ has been reported by D. A. Ramsay, Nature 179, 375 (1956) and in N. Y. Acad. Sci. 61, 485, (1957). Similarities between the spectra of NH₂ and PH₂ were found. For NH₂ and NH₃ bond angles and bond distances were reported to be about the same. By analogy then the bond angles and bond distances of PH₂ and PH₃ should be nearly the same. The moments of inertia for PH₂ were therefore calculated from the molecular constants for PH₃. The principal moments were found to be I_A = 3.587 X 10⁻⁴⁰ g. cm.², I_B = 2.959 X 10⁻⁴⁰ g. cm.², and I_C = 6.546 g. cm.² X 10⁻⁴⁰.

Distefano and Potter (loc. cit.) have assumed the ground state degeneracy to be 2, because of the unpaired electron. The vibrational frequencies reported by Distefano and Potter (loc. cit.) have been used. They used a simple force field and the force constants of PH₃ to obtain the vibrational frequencies.

H₂P

H₂P

Hydrogen Sulfide (H₂S)

(Ideal Gas) Mol. Wt. = 34.07994

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	INFINITE	2.381	4.184	4.184	INFINITE	
100	7.579	40.219	1.786	4.312	5.613	12.266	12.266	
200	10.567	49.151	1.785	4.380	7.955	12.266	7.955	
298	8.172	49.151	1.785	4.380	7.955	12.266	7.955	
300	8.176	49.202	49.151	0.15	4.888	7.974	5.809	
400	8.504	51.597	49.476	1.849	5.872	8.918	4.872	
500	8.889	53.536	50.100	1.718	6.615	9.596	4.194	
600	9.306	55.193	50.613	2.628	7.262	10.129	3.689	
700	9.737	56.660	51.546	3.580	7.612	10.538	3.290	
800	10.162	57.988	52.269	4.575	7.812	10.858	3.022	
900	10.567	59.209	52.973	5.612	7.912	11.107	2.673	
1000	10.943	60.342	53.654	6.687	7.912	11.307	2.151	
1100	11.281	61.401	54.311	7.799	7.912	11.468	1.722	
1200	11.584	62.396	54.944	8.943	7.912	11.600	1.364	
1300	11.853	63.334	55.553	10.115	7.912	11.712	1.061	
1400	12.092	64.221	56.141	11.312	7.912	11.807	0.801	
1500	12.303	65.063	56.708	12.532	7.912	11.887	0.575	
1600	12.491	65.863	57.255	13.772	7.912	11.953	0.378	
1700	12.658	66.625	57.784	15.030	7.912	12.007	0.204	
1800	12.808	67.353	58.296	16.303	7.912	12.051	0.050	
1900	12.941	68.049	58.791	17.590	7.912	12.086	0.088	
2000	13.063	68.716	59.271	18.891	7.912	12.112	0.212	
2100	13.171	69.356	59.736	20.203	7.912	12.130	0.323	
2200	13.270	69.971	60.187	21.525	7.912	12.140	0.425	
2300	13.360	70.563	60.625	22.856	7.912	12.143	0.518	
2400	13.444	71.133	61.051	24.197	7.912	12.139	0.603	
2500	13.520	71.684	61.466	25.545	7.912	12.129	0.680	
2600	13.590	72.215	61.869	26.900	7.912	12.114	0.752	
2700	13.655	72.729	62.262	28.263	7.912	12.096	0.818	
2800	13.715	73.227	62.645	29.631	7.912	12.074	0.879	
2900	13.771	73.709	63.018	31.005	7.912	12.048	0.936	
3000	13.824	74.177	63.382	32.385	7.912	12.018	0.989	
3100	13.874	74.631	63.738	33.770	7.912	11.983	1.039	
3200	13.921	75.073	64.085	35.160	7.912	11.943	1.085	
3300	13.965	75.502	64.425	36.554	7.912	11.898	1.129	
3400	14.007	75.919	64.756	37.953	7.912	11.848	1.170	
3500	14.047	76.326	65.081	39.356	7.912	11.793	1.208	
3600	14.085	76.722	65.399	40.762	7.912	11.733	1.246	
3700	14.122	77.108	65.710	42.173	7.912	11.668	1.281	
3800	14.156	77.485	66.015	43.586	7.912	11.598	1.311	
3900	14.190	77.854	66.314	45.004	7.912	11.523	1.332	
4000	14.223	78.213	66.607	46.424	7.912	11.443	1.342	
4100	14.254	78.565	66.895	47.848	7.912	11.358	1.371	
4200	14.285	78.909	67.177	49.275	7.912	11.268	1.399	
4300	14.314	79.245	67.453	50.705	7.912	11.173	1.425	
4400	14.343	79.575	67.725	52.138	7.912	11.073	1.450	
4500	14.371	79.897	67.992	53.574	7.912	10.968	1.474	
4600	14.397	80.213	68.254	55.012	7.912	10.858	1.497	
4700	14.423	80.523	68.512	56.453	7.912	10.743	1.519	
4800	14.450	80.827	68.765	57.897	7.912	10.623	1.539	
4900	14.475	81.125	69.015	59.343	7.912	10.498	1.559	
5000	14.500	81.418	69.260	60.792	7.912	10.368	1.579	
5100	14.523	81.705	69.501	62.243	7.912	10.233	1.597	
5200	14.548	81.988	69.738	63.697	7.912	10.093	1.614	
5300	14.571	82.265	69.972	65.153	7.912	9.948	1.631	
5400	14.594	82.538	70.202	66.611	7.912	9.798	1.648	
5500	14.616	82.806	70.429	68.071	7.912	9.643	1.663	
5600	14.639	83.069	70.652	69.534	7.912	9.483	1.678	
5700	14.661	83.328	70.873	70.999	7.912	9.318	1.693	
5800	14.682	83.584	71.089	72.466	7.912	9.148	1.707	
5900	14.705	83.835	71.303	73.936	7.912	8.973	1.720	
6000	14.725	84.082	71.514	75.407	7.912	8.793	1.733	

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

HYDROGEN SULFIDE (H₂S)

(IDEAL GAS)

MOL. WT. = 34.07994

Point Group C_{2v}ΔH_f^o 0 = -4.18 ± 0.15 kcal. mole⁻¹ΔH_f^o 298.15 = -4.68 ± 0.15 kcal. mole⁻¹S_{298.15}^o = 49.15 cal. deg⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹
2614.56 (1)
1182.68 (1)
2627.48 (1)

Bond Distance: S-H = 1.328 Å

Bond Angle: H-S-H = 92.2°

Moments of Inertia: I_AI_BI_C = 4.69 X 10⁻¹¹⁹ g.³ cm.⁶

σ = 2

Heat of Formation.

The heat of formation of hydrogen sulfide has been calorimetrically measured by H. Zeumer and W. A. Roth, Z. Elektrochem. 40, 777 (1934), and A. P. Kapustinikii and R. T. Kankovskii, Zhur. Fiz. Khim. 32, 2810 (1958), as ΔH_f^o 293 = -4.80 ± 0.15 kcal. mole⁻¹ and ΔH_f^o 298 = -4.94 ± 0.08 kcal. mole⁻¹, respectively. A weighted average of these two values was taken for the standard enthalpy of formation of hydrogen sulfide.

Heat Capacity and Entropy.

The bond distance, angle and vibrational frequencies were obtained from H. C. Allen, Jr. and E. K. Plyler, J. Chem. Phys. 25, 1132 (1956).

J. S. Gordon, private communication, Feb. 7, 1961, has calculated C_p from 298 to 6000°K. by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes second order corrections for vibrational anharmonicity, vibration-rotation interaction, and centrifugal stretching into account. The correction constants were obtained from Allen and Plyler, loc. cit. Below 298°K. the rigid-rotator harmonic oscillator method was used to calculate the functions, but at 298°K. and above Gordon's thermodynamic functions were adopted in this tabulation.

H₂S

Titanium Dihydride (TiH₂)

(Crystal) Mol. Wt. = 49.916

TITANIUM DIHYDRIDE (TiH₂)

(CRYSTAL)

MOL. WT. = 49.916

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞	∞	INFINITE	1.182	-32.508	-32.508	INFINITE
100	3.030	1.512	12.312	1.070	-32.508	-32.508	30.714
200	7.411	7.101	7.101	0.000	-32.508	-32.508	18.418
298	7.411	7.101	7.101	0.000	-32.508	-32.508	18.418
300	7.232	7.146	7.146	0.013	-32.511	-32.509	18.202
400	9.400	9.524	7.411	1.845	-34.993	-21.845	11.935
500	11.300	11.832	8.066	1.883	-35.303	-18.518	8.094
600	12.860	14.035	8.879	3.094	-35.465	-15.144	5.516
700	14.100	16.115	9.765	4.445	-35.510	-11.752	3.669
800	15.090	18.065	10.682	5.806	-35.465	-8.361	2.284
900	15.850	19.888	11.605	7.455	-35.353	-4.977	1.209
1000	16.380	21.598	12.519	9.066	-35.198	-1.611	0.352
1100	16.744	23.166	13.416	10.725	-35.021	1.738	-0.345
1200	17.050	24.637	14.291	12.415	-34.781	5.109	-0.930
1300	17.298	26.012	15.140	14.133	-34.585	8.509	-1.430
1400	17.488	27.301	15.963	15.873	-34.389	11.893	-1.856
1500	17.620	28.512	16.760	17.629	-34.199	15.265	-2.224
1600	17.753	29.654	17.530	19.398	-34.019	18.622	-2.544
1700	17.858	30.734	18.276	21.178	-34.847	21.970	-2.824
1800	17.934	31.757	18.956	22.968	-34.685	25.306	-3.072
1900	17.981	32.728	19.694	24.764	-34.536	28.636	-3.294
2000	18.000	33.650	20.369	26.564	-34.077	32.051	-3.502

$$\Delta H_f^0 = [-32.5 \pm 2.0] \text{ kcal. mole}^{-1}$$
$$\Delta H_f^{298.15} = [-34.5 \pm 2.0] \text{ kcal. mole}^{-1}$$
$$S_{298.15}^0 = 7.101 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

Heat of Formation.

The heat of combustion of TiH_{1.73}(c), the stable species of titanium hydride, was reported to be -247.8 kcal. by A. Sieverts and A. Gotta, Z. anorg. allgem. Chem. 199, 384 (1931). From this data the value of ΔH_f^{298.15} for TiH_{1.73}(c) was calculated to be -29.40 kcal. mole⁻¹. The heat of dissociation of titanium hydride having compositions between the rough limits TiH_{1.75}-TiH_{1.93} was given as 19.15 kcal. per mole of H₂ dissociated by T. R. P. Gibb, Jr., J. McSharry, and R. W. Bragdon, J. Am. Chem. Soc. 73, 1751 (1951). Assuming this value is applicable to compositions between the limits TiH_{1.73}-TiH₂, the difference in the heat of formation of titanium hydride between TiH_{1.73} and TiH₂ was estimated to be -5.17 kcal. mole⁻¹. Thus the value of ΔH_f^{298.15} for TiH₂(c) was calculated.

Heat Capacity and Entropy.

The low temperature C_p for TiH_{1.97}(c), 24-363°K., were measured by B. Stalinski and Z. Bieganski, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 9, No. 5, 243 (1960). This data were adopted for TiH₂(c) due to lack of the measured C_p values. A small but well marked λ-type anomaly with a maximal value of C_p at 288.5°K. in the C_p vs. T curve was observed. S_{298.15} was reported by B. Stalinski and Z. Bieganski, loc. cit., based on S₂₅(extrap.) = 0.065 cal. deg.⁻¹ mole⁻¹.

June 30, 1963



(IDEAL GAS)

AMMONIA (NH₃)

Point Group C_{3v} $\Delta H_f^0 = -9.30 \text{ kcal. mole}^{-1}$ MOL. WT. = 17.03061
 $\Delta H_f^0 = 46.03 \pm 0.1 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = 298.15 = -10.97 \pm 0.1 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

Zero-order "harmonic" ω_e , cm. ⁻¹	Observed Wave Numbers ω_e , cm. ⁻¹
3506 (1)	3577 (2)
1022 (1)	1691 (2)
1022 (1)	950 (1)
1627 (2)	

Bond Length: N-H = 1.0124 Å
 Bond Angle: H-N-H = 106.67°
 Product of the Moments of Inertia: $I_A I_B I_C = 3.4826 \times 10^{-119} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation

A weighted average based on analysis using JANAF functions was selected. Haber, Tammaru and Oeholm, Z. Elektrochem. 21, 206 (1915) obtained $\Delta H_{298}^0 = 11.10$ for NH₃ from 0.5 H₂ + 1.5 H₂ by flow calorimetry. Estimated uncertainty is 1% and the formation value was corrected by 0.025 kcal. for non-ideality of NH₃. Becker and Roth, ibid. 20, 836 (1934) measured ΔH_f^0 for NH₃ from the heat of formation of H₂O and (NH₄)₂CO₃, and the necessary ΔH_{298}^0 leading to $\Delta H_{298}^0 = 182.9 \pm 0.24$ for 3H₂O(l) + N₂(g) → 2NH₃(g) + 2H₂O(l). Equilibrium data from Larson and Dodge, J. Am. Chem. Soc. 45, 2918 (1923) and Haber, Tammaru and Ponnaz, Z. Elektrochem. 21, 89 (1915) were analyzed as tabulated by Stephenson and McMahon, J. Am. Chem. Soc. 61, 437 (1939) from the non-ideality corrections of Gillespie and Beattie, Phys. Rev. 56, 743 (1930). Data (1000-3000 atm) from Winchester and Dodge, A.I.Ch.E. Journal 2, 128 (1915) were assumed ideal. High-temperature calorimetry of the direct decomposition includes Haber and Tammaru, Z. Elektrochem. 21, 191 (1915) and Wittig and Schmatz, ibid. 63, 470 (1959).

Method

Source	Method	ΔH_f^0 298 (kcal. mole ⁻¹)	Drift (e.u.)
Haber, Tammaru, Oeholm (1915)	Flow calorimetry at 298°K	-11.07	
Becker, Roth (1934)	Indirect calorimetry at 294°K	-11.02±0.12	
Larson, Dodge (1923)	K _p from K _p (10-1000 atm, 600-800°K)	-10.88(-10.82±0.03)*	-0.17±0.05
Haber, Tammaru, Ponnaz (1915)	K _p from K _p (30 atm, 800-1200°K)	-10.89(-10.95±0.05)*	0.04±0.05
Haber, Maschke (1915)	K _p (1 atm, 900-1400°K)	-10.87(-10.60±0.1)*	-0.22±0.08
Haber, Tammaru (1915)	Flow calorimetry (759-952°K)	-10.87	
Wittig, Schmatz (1959)	Flow calorimetry at 823°K	-10.98	

*Third law values for equilibrium data are followed by second law values in parentheses.

Heat Capacity and Entropy

The functions are an approximation of the non-rigid rotator anharmonic oscillator based on calculations of Harrison and Kobe, Chem. Eng. Progr. 49, No. 7, 349 (1953) and Yungman, Gurvich and Ritscheva, Trudy Gosudarst. Inst. Priklad. Khim. 49, 20 (1962). In these calculations anharmonicity of ν_2 associated with inversion doubling was treated by summation over the energy levels. Both calculations include rotational distortion corrections while Yungman, et al., also allow for anharmonicity and vibration-rotation interaction of the other fundamentals. JANAF functions agree with the results to within 0.02 e.u. in the range 298-1500°K.

Two sets of rigid rotator harmonic oscillator functions were also tested for consistency with the ammonia data (see below). These were obtained from molecular dimensions and either calculated zero order frequencies (ω_e) or observed wave numbers (ω_e) obtained by Benedict and Plyler, Can. J. Phys. 35, 1235 (1957) from high resolution infrared studies. Herzberg, "Infrared and Raman Spectra", pp. 503-4, 1945 states that ω_e should be used and the RRHO⁰ functions give better, but not perfect, agreement with the observed C_p^0 for NH₃. Principal moments of inertia are $I_A = 4.414 \times 10^{-40}$ and $I_B = I_C = 2.809 \times 10^{-40} \text{ cm.}^2$. Electron diffraction studies by Bastiansen and Besley, Acta Chem. Scand. 18, 2077 (1964) give slightly different constants (bond distance 1.015 Å and angle = 109.1°).

T, °K	Heat Capacity, C _p		Entropy, S°	
	Observed	JANAF	Observed	JANAF
253.15	8.271(a)	8.269	239.72	44.23(b,c)
298.15	8.521(a)	8.515	239.15	44.21
423.15	9.422(a)	9.423	288.15	46.03
800.	12.070-2(f)	12.225	800.	55.99

(a) M. S. Osborne, H. P. Stinson, T. S. Slichter, Jr., and G. S. Crago, NBS Sci. Papers 20, 85 (1924-6) measured C_p of gaseous NH₃ (258 to 423°K and 0.5 to 20 atm) within an estimated maximum error of 0.3% (about 0.03 cal. deg.⁻¹ mole⁻¹) and obtained C_p by use of a suitable equation of state.

(b) R. Overstreet and W. P. Giauque, J. Am. Chem. Soc. 59, 254 (1937) determined the entropy of the real gas at the normal boiling point as $S_{239.72}^0 = 44.06 \pm 0.10 \text{ cal. deg}^{-1} \text{ mole}^{-1}$.

(c) (S-S)_{239.72} = 0.17 cal. deg.⁻¹ mole⁻¹ from the virial coefficient equation derived by Hirschfelder, McCure and Weeks, J. Chem. Phys. 10, 201 (1942) from the PVT data of Meyers and Jessup, Refrig. Eng. 11, 345 (1925).

(d) Combination of ΔH_f^0 800 = -12.85 kcal. mole⁻¹ from the calorimetric measurement of F. E. Wittig and W. Schmatz, Z. Elektrochem. 63, 470 (1959) with ΔH_f^0 = 9.315 kcal. mole⁻¹ from equilibrium data (f).

(e) Second law analysis of the equilibrium data (f).

(f) K_p values based on the equilibrium data of Haber, Tammaru and Ponnaz and of Larson and Dodge were analyzed by regression analysis to give $\Delta H_{800}^0 = 9.315 \pm 0.004$, $\Delta H_{800}^0 = -12.666 \pm 0.017$ and ΔC_p 800 = -2.51 ± 0.20.

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

Hydronium Unipositive Ion (H₃O⁺)

(Ideal Gas) GFW = 19.02276

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ₃₀₀)/T	cal/mol H ^o - H ₃₀₀	cal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	8.400	45.924	4.000	136.900	144.983	-106.275
300						
350	8.411	45.076	4.015	136.890	145.020	-105.647
400	8.401	46.465	4.261	136.873	145.050	-104.980
450	8.473	50.599	4.602	136.905	149.112	-99.177
500						
550	8.604	52.405	4.764	136.999	151.145	-95.055
600	10.271	54.150	4.847	136.147	153.159	-97.618
700	11.271	58.157	5.129	137.117	157.117	-92.364
800	12.459	62.129	5.409	138.084	161.084	-87.118
900	13.602	66.064	5.684	139.043	165.043	-81.872
1000						
1100	13.514	59.734	5.144	140.178	160.944	-81.977
1200	13.994	60.631	5.341	140.526	162.618	-79.653
1300	14.457	61.554	5.529	140.873	164.293	-77.328
1400	14.857	62.504	5.729	141.299	165.973	-75.002
1500	15.239	63.493	5.932	141.716	167.657	-72.676
1600						
1700	15.590	64.417	6.144	142.140	169.340	-70.350
1800	15.920	65.282	6.362	142.600	171.020	-68.024
1900	16.240	66.100	6.584	143.096	172.704	-65.698
2000	16.710	67.894	6.861	143.536	174.388	-63.372
2100						
2200	16.930	69.615	7.097	144.510	178.390	-59.165
2300	17.111	70.943	7.341	145.007	179.992	-56.839
2400	17.280	71.913	7.585	145.506	181.594	-54.513
2500	17.432	72.630	7.800	146.010	183.196	-52.187
2600						
2700	17.772	73.324	8.048	147.031	186.181	-47.980
2800	17.899	73.997	8.293	147.542	187.678	-45.654
2900	18.124	75.285	8.537	148.054	189.176	-43.328
3000	18.223	75.901	8.740	149.078	192.050	-39.121
3100						
3200	18.314	76.500	8.946	149.592	193.474	-36.795
3300	18.398	77.083	9.156	150.102	194.893	-34.469
3400	18.470	77.653	9.366	150.612	196.312	-32.143
3500	18.615	78.741	9.596	151.623	199.019	-27.936
3600						
3700	18.677	79.266	9.806	152.127	200.363	-25.610
3800	18.735	79.779	10.016	152.634	201.707	-23.284
3900	18.839	80.768	10.252	153.142	203.051	-20.958
4000	18.886	81.246	10.454	153.650	204.395	-18.632
4100						
4200	18.930	81.712	10.656	154.158	205.739	-16.306
4300	18.971	82.169	10.858	154.667	207.083	-13.980
4400	19.045	83.053	11.045	155.071	208.427	-11.654
4500	19.079	83.482	11.246	155.480	209.771	-9.328
4600						
4700	19.111	83.901	11.447	155.901	211.115	-7.002
4800	19.170	84.714	11.634	156.324	212.459	-4.676
4900	19.217	85.112	11.836	156.750	213.803	-2.350
5000	19.222	85.500	12.040	157.177	215.147	0.000
5100						
5200	19.246	85.881	12.246	157.604	216.491	2.324
5300	19.260	86.255	12.452	158.031	217.835	4.648
5400	19.310	86.594	12.658	158.458	219.179	6.972
5500	19.330	87.337	13.110	160.084	223.750	8.891
5600						
5700	19.348	87.686	13.316	161.400	224.877	8.776
5800	19.365	88.028	13.521	161.833	226.017	8.660
5900	19.398	88.405	13.726	162.261	227.156	8.544
6000	19.413	89.023	14.130	163.076	229.338	8.354

June 30, 1966

HYDRONIUM UNIPosITIVE ION (H₃O⁺) (IDEAL GAS)

OPW = 19.02276

Point Group [C_{3v}]

S_{298.15} = [45.92] gibbs/mol

ΔH_f^o = 139.1 ± 3 kcal/mol

Ground State Quantum Weight = 1

ΔH_f^o = 138.9 ± 3 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
(3760)(1)	(3870)(2)
(1050)(1)	(1550)(2)

Bond Distance: H-O = [0.95] Å

Bond Angle: H-O-H = [109]°

Product of the Moments of Inertia: I_AI_BI_C = [2.59] X 10⁻¹¹⁹ g³ cm⁶

σ = 3

Heat of Formation

The proton affinity of water has been measured by the ion impact method as -169 kcal/mol by V. L. Tal'rose and E. L. Frankvitch, Doklady Akad. Nauk SSSR 111, 376 (1956), J. Am. Chem. Soc. 80, 2344 (1958). The selected heat of formation of hydronium ion, ΔH_f^o(H₃O⁺, g) = 139.1 kcal/mol, was derived from the ΔH_f^o = -169 kcal/mol for H₂O(g) + H⁺(g) → H₃O⁺(g), using the JANAF ΔH_f^o(H₂O, g) = -57.1 and ΔH_f^o(H⁺, g) = 385.2 kcal/mol.

The values of 195 and 207 kcal/mol for the heat of formation of H₃O⁺(g) have also been reported by P. M. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, 1957, and R. R. Berner and P. A. Long, J. Phys. Chem. 65, 1565 (1961), respectively. These two values were based on the electron impact studies which may involve unaccounted excitations and excess energy in the fragments. Other literature values have been reviewed by D. M. Bishop, J. Chem. Phys. 43, 4453 (1965).

J. A. Green and T. M. Sugden, Ninth Symposium (International) on Combustion, Academic Press, New York, 1963, based on the studies of the positive ions in flames by mass spectrometry, prefer the value derived from the proton affinity of water obtained by Tal'rose and Frankvitch, rather than the electron impact data. From the approximate equilibrium constant calculations for the reaction HCO⁺(g) + H₂O(g) ⇌ H₃O⁺(g) + CO(g), D. G. Clifton, AD44078, G. M. Defense Research Laboratory, General Motors Corp., Santa Barbara, Calif., July 1964, has also found that the heat of formation of H₃O⁺(g) derived from the proton affinity of water, not from the electron impact data, leads to agreement with the experimental data given by Green and Sugden.

Heat Capacity and Entropy

Since the molecule H₃O⁺(g) has the same number of valence electrons as NH₃(g), a pyramidal molecular configuration (C_{3v}) is assumed for H₃O⁺(g) in the tabulation. D. G. Clifton, J. Chem. Phys. 41, 3656 (1964), has obtained a bond distance O-H of 0.95 Å from an application of covalent bond radii and the effect of electric charge, and a bond angle H-O-H of 109° by extrapolating a plot of bond length versus bond angle for NH₃(g) and PH₃(g) to 0.95 Å. Both values are adopted in the tabulation. The three principal moments of inertia are I_A = 0.4004 X 10⁻³⁹, I_B = I_C = 0.2445 X 10⁻³⁹ g cm². D. M. Bishop, loc. cit., has calculated theoretically the bond distance H-O of 0.95 Å and the bond angle H-O-H of 114° 26' with a planar D_{3h} molecular configuration. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton.



Orthophosphoric Acid (H_3PO_4)
(Crystal) Mol. Wt. = 97.999

T. °K.	C _p	S°	$-(F^\circ - H^\circ_{298})/T$	ΔH°_f	ΔF°_f	Log K _P
6	0.003	0.00	INFINITE	-297.541	-297.541	INFINITE
100	10.249	8.255	28.510	-297.541	-297.541	350.225
200	18.139	17.830	28.510	-297.541	-297.541	92.583
298	25.384	26.421	26.421	-301.530	-264.604	103.491
300	25.486	26.421	26.421	-301.537	-264.604	103.491
300	33.000	26.421	26.421	-301.537	-264.604	103.491
500	33.230	41.823	28.615	-301.537	-264.604	103.491
600	35.700	47.915	32.151	-301.365	-227.096	82.716
700	37.400	53.555	34.813	-300.945	-214.749	67.044
800	38.800	58.649	37.479	-320.867	-207.781	56.760
900	39.500	63.265	40.092	-320.079	-193.691	47.932
1000	40.600	67.853	42.622	-319.274	-179.690	39.269
1100	40.600	71.292	45.056	-318.453	-165.773	32.934
1200	41.000	74.842	47.393	-317.613	-151.929	27.669
1300	41.400	78.140	49.632	-316.767	-138.156	23.225
1400	41.700	81.219	51.780	-315.916	-124.449	19.426
1500	42.000	84.106	53.840	-315.068	-110.800	16.143

ORTHOPHOSPHORIC ACID (H_3PO_4)
(CRYSTAL)
MOL. WT. = 97.999

$$\Delta H^\circ_f 0 = -297.5 \pm 0.3 \text{ kcal. mole}^{-1}$$

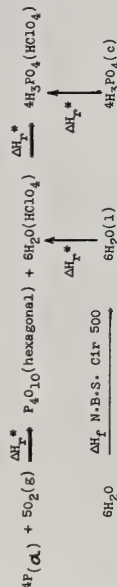
$$\Delta H^\circ_m = 3.100 \text{ kcal. mole}^{-1}$$

$$S^\circ_{298.15} = 26.42 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 315.51^\circ \text{K}$$

Heat of Formation.

The heat of formation was determined by W. S. Holmes (private communication July 5, 1962, Albright and Wilson (WPA) Ltd., Oldbury, Birmingham, Great Britain (in press by Paraday Society)). W. S. Holmes measured the enthalpy of combustion of white phosphorus (α form) in oxygen in a bomb calorimeter. The product, P_4O_{10} (hexagonal), was hydrolyzed in 10N perchloric acid to give H_3PO_4 . Measurement of the enthalpy of solution of $H_3PO_4(c)$ then enabled the ΔH°_f 298.15 to be calculated according to the following cycle:



* All ΔH°_f 's were measured.

E. P. Egan, Jr. and B. B. Luff, J. Phys. Chem., 65, 523 (1961), from partial molal heat contents of H_3PO_4 solutions found that a smooth extrapolation to 100% H_3PO_4 would give them a ΔH°_f 298.15 for $H_3PO_4(c)$ which was 755 cal. mole⁻¹ greater than the ΔH°_f 298.15 reported in the National Bureau of Standards Circular 500. The Circular 500 (loc. cit.) heat of formation refers to the work of Thomson, "Thermochemische Untersuchungen," Vol. 2, Barth, Leipzig (1882-1886). The heats of formation summarized:

ΔH°_f 298.15	Source
-305.7 \pm 0.3 kcal. mole ⁻¹	W. S. Holmes (loc. cit.)
-306.2 kcal. mole ⁻¹	Circular 500 (loc. cit.)
-305.4 kcal. mole ⁻¹	Egan and Luff (loc. cit.)
The selected ΔH°_f 298.15, -305.7 \pm 0.3 kcal. mole ⁻¹ , was corrected by +4.17 kcal. mole ⁻¹ , which is the ΔH°_f 298.15 of white (α) phosphorus.	

Heat Capacity and Entropy.

Third law entropy was calculated from the low temperature heat capacities measured by E. P. Egan, Jr. and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).

Melting.

The heat of fusion, ΔH°_m , was reported by E. P. Egan, Jr. and B. B. Luff, J. Phys. Chem. 65, 523 (1961) from ΔH°_m data measured by E. P. Egan, Jr. and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957). The melting point $T_m = 315.51^\circ \text{K}$ was taken from the work of W. H. Rose and R. N. Jones, J. Am. Chem. Soc. 47, 2185 (1925).

H_3O_4P

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o	Log K _p
0						
100						
200						
298	48.000	34.993	0.000	-298.810	-264.440	193.830
300	48.000	35.289	34.983	-298.776	-264.227	192.480
400	48.000	49.088	16.876	-296.572	-252.986	136.218
500	48.000	59.809	40.431	-295.253	-242.190	105.856
600	48.000	68.561	44.413	-293.614	-231.733	84.405
700	48.000	75.960	48.404	-292.056	-221.543	69.165
800	48.000	82.369	52.258	-290.489	-211.684	59.247
900	48.000	88.023	55.924	-288.889	-202.020	49.832
1000	48.000	93.080	59.391	-287.253	-193.739	42.340
1100	48.000	97.655	62.685	-285.589	-185.822	36.242
1200	48.000	101.832	65.758	-283.899	-178.247	31.187
1300	48.000	105.674	68.682	-282.188	-171.001	26.931
1400	48.000	109.231	71.453	-280.459	-164.071	23.301
1500	48.000	112.542	74.083	-278.709	-157.445	20.171
1600	48.000	115.640	76.589	-276.927	-151.121	17.445
1700	48.000	118.540	78.969	-275.120	-145.079	15.031
1800	48.000	121.294	81.244	-273.289	-139.324	12.933
1900	48.000	123.889	83.421	-271.429	-133.841	11.047
2000	48.000	126.351	85.507	-269.536	-128.612	9.357

June 30, 1962

Orthophosphoric Acid (H₃PO₄) (Liquid)

Mol. Wt. = 97.999
ΔH_f^o 298.15 = -298.81 ± 0.5 kcal. mole⁻¹
S_{298.15}^o = 35.0 cal. deg.⁻¹ mole⁻¹
T_m = 315.61°K
ΔH_m = 3.100 kcal. mole⁻¹
Heat of Formation. Calculated from ΔH_f^o 298.15 for H₃PO₄(c) and ΔH_m^o given by E. P. Egan, Jr., and B. B. Luff, J. Phys. Chem. 65, 523 (1961) using the ΔH_m data reported by E. P. Egan, Jr., and Z. T. Wakefield, J. Phys. Chem. 61, 1500 (1957).

Heat Capacity and Entropy. The heat capacity is estimated. The entropy at 298.15°K. is calculated using S_{298.15}^o of H₃PO₄(c) and the ΔH_m at 298.15°K.

Melting Data. T_m reported by W. H. Ross and R. M. Jones, J. Am. Chem. Soc. 47, 2165 (1925). ΔH_m from E. P. Egan, Jr., and Z. T. Wakefield (loc. cit.).

Phosphine (PH₃)

(Ideal Gas) Mol. Wt. = 33.999

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	keal. mole ⁻¹ ΔH _f ^o	Log K _p
0	∞	∞	∞	∞	∞
100	7.949	57.622	2.423	6.945	INFINITE
200	8.111	56.877	1.628	6.511	13.514
298	8.168	56.877	1.628	6.511	4.452
300	8.168	56.877	1.628	6.511	4.452
400	8.487	50.238	0.16	5.458	6.077
500	8.987	52.997	0.500	4.827	3.486
600	9.487	55.347	1.319	4.262	2.987
700	10.110	57.468	2.169	3.776	2.694
800	10.817	59.277	3.067	3.350	2.504
900	11.595	60.927	4.011	2.976	2.333
1000	12.439	62.518	5.000	2.654	2.188
1100	13.346	64.054	6.144	2.387	2.068
1200	14.315	65.545	7.454	2.185	1.973
1300	15.346	66.990	8.930	2.045	1.900
1400	16.439	68.390	10.574	1.973	1.843
1500	17.595	69.745	12.388	1.955	1.800
1600	18.815	71.055	14.372	1.985	1.768
1700	20.099	72.320	16.526	2.062	1.745
1800	21.447	73.540	18.850	2.185	1.728
1900	22.859	74.714	21.344	2.352	1.715
2000	24.335	75.842	24.000	2.562	1.705
2100	25.875	76.924	26.817	2.815	1.697
2200	27.479	77.960	29.792	3.112	1.690
2300	29.147	78.950	32.926	3.454	1.684
2400	30.879	79.894	36.219	3.841	1.678
2500	32.675	80.792	39.672	4.274	1.673
2600	34.535	81.644	43.284	4.754	1.668
2700	36.459	82.450	47.054	5.281	1.663
2800	38.447	83.210	50.982	5.854	1.658
2900	40.499	83.924	55.068	6.474	1.653
3000	42.615	84.592	59.312	7.140	1.648
3100	44.795	85.214	63.714	7.852	1.643
3200	47.039	85.792	68.272	8.610	1.638
3300	49.347	86.326	73.086	9.414	1.633
3400	51.719	86.816	78.156	10.264	1.628
3500	54.155	87.262	83.482	11.160	1.623
3600	56.655	87.664	89.064	12.102	1.618
3700	59.219	88.022	94.902	13.090	1.613
3800	61.847	88.336	101.000	14.124	1.608
3900	64.539	88.606	107.358	15.204	1.603
4000	67.295	88.832	114.074	16.330	1.598
4100	70.115	89.014	121.146	17.502	1.593
4200	72.999	89.152	128.574	18.720	1.588
4300	75.947	89.246	136.358	19.984	1.583
4400	78.959	89.296	144.498	21.294	1.578
4500	82.035	89.302	153.000	22.650	1.573
4600	85.175	89.264	161.864	24.052	1.568
4700	88.379	89.182	171.090	25.500	1.563
4800	91.647	89.056	180.678	27.000	1.558
4900	94.979	88.886	190.628	28.552	1.553
5000	98.375	88.672	201.040	30.156	1.548
5100	101.835	88.414	211.914	31.812	1.543
5200	105.359	88.112	223.250	33.520	1.538
5300	108.947	87.766	235.048	35.280	1.533
5400	112.599	87.376	247.308	37.092	1.528
5500	116.315	86.942	260.030	38.956	1.523
5600	120.087	86.464	273.214	40.872	1.518
5700	123.915	85.942	286.860	42.840	1.513
5800	127.799	85.376	301.068	44.860	1.508
5900	131.739	84.766	315.838	46.932	1.503
6000	135.735	84.112	331.170	49.056	1.498

June 30, 1962

PHOSPHINE (PH₃)

ΔH_f^o 0 = +7.0 ± 0.4 kcal mole⁻¹

Point Group C_{3v}

Vibrational Levels and Multiplicities
ω, cm⁻¹

992 (1) 2327.7 (2) 1122.4 (2)

H-P-H angle = 93° 50'

I_A = I_B = 6.29 × 10⁻⁴⁰ g cm²

I_C = 7.24 × 10⁻⁴⁰ g cm²

σ = 3

Heat of Formation

The heat of formation was derived by S. R. Gunn and L. G. Green, J. Phys. Chem., **65**, 779 (1961). In order to obtain the ΔH_f^o 298.15 they measured the heat of explosive decomposition of phosphine gas. There is a good deal of uncertainty about the heat of formation of PH₃(g), for instance:

ΔH_f^o 298.15
+3.6 kcal mole⁻¹

+6.3 kcal mole⁻¹

-2.34 kcal mole⁻¹

+1.6 kcal mole⁻¹

Source
The heat of reaction between gaseous PH₃ and saturated bromine water. M. J. Ogier, Ann. Chim. Phys., **20**, 5 (1880).

The heat of combustion of PH₃(g) in O₂(g) to form H₃PO₄. M. P. Lemoult, Compt. Rend., **115**, 374 (1907).

Equilibrium data of W. N. Ipatiev, and A. W. Frost, Ber. dtsh. chem. Ges., **63B**, 1104 (1930). Their data showed a wide variation in ΔH, as much as 11 kcal mole⁻¹.

National Bureau of Standards, Report No. 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," 1 January 1962 (page 80-91).

The heats of formation have been reviewed by T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth's Scientific Publications, London, (1958); and by F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of The Chemical Substances," Reinhold Publishing Corp., New York (1936).

The heat of formation selected was, +1.3 ± 0.4 kcal mole⁻¹, as reported by Gunn and Green (loc. cit.). The selected heat of formation was based on white (g) phosphorus and thus required an adjustment for the red (V) phosphorus reference state.

Heat Capacity and Entropy

The Fundamental wave number and degeneracy assignments are from the infrared spectral data by V. N. McConaghie and H. H. Nielsen, J. Chem. Phys., **21**, 1836, (1953). The molecular constants are those obtained from infrared data by H. H. Nielsen, J. Chem. Phys., **20**, 759 (1952). Nielsen (loc. cit.) has reported the molecular constants after calculating the Coriolis coupling effect between the wave numbers 2 and 4, or (892 cm⁻¹) and (1122.4 cm⁻¹).

H₃P

(IDEAL GAS)

MOL. WT. = 33.999

ΔH_f^o 298.15 = +5.5 ± 0.4 kcal/mole⁻¹

S_{298.15}^o = 50.24 cal deg⁻¹ mole⁻¹

H₃P

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	$-(H^{\circ}-H^{\circ}_{298})/T$ °K. ⁻¹	$H^{\circ}-H^{\circ}_{298}$ kcal. mole ⁻¹	ΔF°	Log K _p
0					
100	14.540	27.000	.000	-26.780	19.689
200	19.570	27.121	.036	-26.846	19.811
300	21.271	27.960	.209	-27.001	19.933
400	22.960	29.331	.429	-27.268	20.055
500	24.640	31.130	.673	-27.536	20.177
600	26.310	33.352	.941	-27.804	20.299
700	27.970	36.000	1.233	-28.072	20.421
800	29.630	39.072	1.549	-28.340	20.543
900	31.290	42.576	1.899	-28.608	20.665
1000	32.950	46.512	2.283	-28.876	20.787
1100	34.610	50.880	2.699	-29.144	20.909
1200	36.270	55.680	3.149	-29.412	21.031
1300	37.930	60.912	3.633	-29.680	21.153
1400	39.590	66.576	4.151	-29.948	21.275
1500	41.250	72.672	4.703	-30.216	21.397
1600	42.910	79.200	5.289	-30.484	21.519
1700	44.570	86.160	5.909	-30.752	21.641
1800	46.230	93.552	6.563	-31.020	21.763
1900	47.890	101.376	7.251	-31.288	21.885
2000	49.550	109.632	7.973	-31.556	22.007

March 31, 1962

Ammonium Iodide (NH₄I)
(Crystal)

Mol. Wt. = 144.95

$\Delta H^{\circ}_{f, 298.15} = -40.30$ kcal. mole⁻¹

$S^{\circ}_{298.15} = 27.0 \pm 1.5$ cal. deg.⁻¹ mole⁻¹

$\Delta H^{\circ}_{f, 798} = 40.280$ kcal. mole⁻¹

$T_m = 280^{\circ}\text{K}$

$\Delta H^{\circ}_{t, 280} = 0.70$ kcal. mole⁻¹

$T_m = 824^{\circ}\text{K}$

$\Delta H^{\circ}_{m, 280} = [5.0]$ kcal. mole⁻¹

$\Delta H^{\circ}_{f, 298.15}$, T_m , and T_m . Taken from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties". $S^{\circ}_{298.15}$ was taken from K. K. Kelley, U. S. Bureau of Mines Bulletin 594, (1960). Sublimation data from N. W. Luft, Ind. Chemist, 31, 502 (1955).

Heat Capacity. Data extrapolated from Simon, Simson, and Ruhemann Z. Phys. Chemie, 129, 339 (1927).

Hydrazine (N₂H₄)

(Liquid)

Mol. Wt. = 32.04528

T, °K.	C _p	S° - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	20.850	5.028	49.091	4.406	11.611	19.797
100	22.250	19.910	31.166	2.451	11.857	27.880
200	23.650	36.226	20.090	0.000	12.100	35.694
298	24.650	42.218	31.861	5.179	13.054	26.163
300	24.650	42.218	31.861	5.179	13.054	26.163
400	26.600	56.226	20.090	0.000	12.100	35.694
500	27.860	62.218	31.861	5.179	13.054	26.163
600	30.060	67.492	34.034	8.075	13.838	21.509

HYDRAZINE (N₂H₄)

(LIQUID)

MOL. WT. = 32.04528

S_{298.15} = 29.05 ± 0.1 cal. deg.⁻¹ mole⁻¹
 T_m = 274.69°K.
 T_b = 386.9°K.

ΔH_f^o 298.15 = 12.10 ± 0.1 kcal. mole⁻¹
 ΔH_m^o = 3.025 kcal. mole⁻¹
 ΔH_v^o = 9.70 kcal. mole⁻¹

Heat of Formation.

A. M. Hughes, R. J. Corruccini and E. C. Gilbert, J. Am. Chem. Soc. **61**, 2659 (1939), measured the heats of combustion of hydrazine and hydrazine monohydrate. The data, adjusted as suggested by L. G. Cole and E. C. Gilbert, J. Am. Chem. Soc. **73**, 5423 (1951), are summarized below. Heats of solution determined by V. C. Bushnell, A. M. Hughes and E. C. Gilbert, J. Am. Chem. Soc. **59**, 2142 (1937) interrelate N₂H₄(l) and N₂H₄·H₂O(l). An intermediate value was selected from the resulting heats of formation.

Source	Reaction	ΔH _f ^o 298	ΔH _f ^o 298
Hughes	N ₂ H ₄ (l) + O ₂ (g) → N ₂ (g) + 2H ₂ O(l)	-148.68 ± 0.06	12.05
Hughes	N ₂ H ₄ ·H ₂ O(l) + O ₂ (g) → N ₂ (g) + 3H ₂ O(l)	-147.00 ± 0.06	—
Bushnell	N ₂ H ₄ (l) + H ₂ O(l) → N ₂ H ₄ ·H ₂ O(l)	-1.80	12.17*

*From combination of second and third reactions.

Heat Capacity and Entropy.

Heat capacities (12-340°K) of hydrazine crystal and liquid were determined by D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc. **71**, 2293 (1949). Values beyond the experimental range for the liquid were extrapolated linearly. The entropy was obtained from the heat of melting and the smoothed heat capacities of the crystal using S₁₂^o = 0.023 cal. deg.⁻¹ mole⁻¹.

Melting Data.

Taken from Scott et al., loc. cit.

Vaporization Data.

The normal boiling point and heat of vaporization are those calculated for the ideal gas from these tables. The boiling point found for the real gas (387.3°K) by W. Hieber and A. Woerner, Z. Elektrochem. **40**, 252 (1934) is in good agreement. The selected heat of vaporization, ΔH_v^o 298 = 10.69 kcal. mole⁻¹, is based on the vapor pressure data of Scott et al., loc. cit., series III. Vapor pressure measurements of Hieber and Woerner, loc. cit., and E. T. Chang and N. A. Gokcen, AD-458286, Defense Documentation Center, January, 1964, are in satisfactory agreement as shown below.

Source	Temp. Range °K.	ΔH _v ^o 298 (kcal. mole ⁻¹) 2nd Law	ΔH _v ^o 298 (kcal. mole ⁻¹) 3rd Law	3rd Law Drift e.u.
Scott, et al. (1949)	275-345	10.683 ± 0.003	10.696	0.05 ± 0.01
Chang, Gokcen (1964)	276-325	10.40 ± 0.03	10.68	0.91 ± 0.09
Hieber, Woerner (1934)	293-357	10.82 ± 0.03	10.71	-0.33 ± 0.07

The second law-third law consistency of Scott et al. reflects the use of these data in selection of the gas phase functions (see H₂N₂ gas).

Hydrazine (N₂H₄)

(Ideal Gas) Mol. Wt. = 32.04528

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	(H ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹	ΔH _f ^o	Log K _p
							ΔF _f ^o
0	∞.000	∞.000	∞.000	∞.000	26.155	26.155	INFINITE
100	8.214	46.625	66.140	1.956	24.751	28.778	- 62.891
200	9.718	52.717	58.058	1.068	23.730	33.192	- 36.268
300	12.145	57.030	57.030	∞.000	22.790	38.042	- 27.884
400	12.194	57.106	57.106	∞.023	22.776	38.136	- 27.781
500	12.747	60.971	60.971	1.352	23.698	43.375	- 23.317
600	16.861	64.498	58.484	2.957	21.522	48.772	- 21.317
700	18.538	67.726	59.843	4.730	21.183	54.257	- 19.762
800	19.910	70.690	60.654	6.654	20.975	59.787	- 18.666
900	21.111	73.470	63.897	8.652	20.849	65.461	- 17.816
1000	23.030	78.348	65.925	13.124	20.897	70.901	- 17.216
1100	23.894	80.583	66.570	15.469	21.002	76.460	- 16.709
1200	24.552	82.690	67.781	17.882	21.156	82.011	- 16.293
1300	25.042	84.682	68.782	20.358	21.345	87.573	- 15.945
1400	25.462	86.570	70.193	22.900	21.576	93.150	- 15.689
1500	26.367	88.330	71.946	25.551	21.826	98.745	- 15.464
1600	26.836	90.097	72.665	28.211	22.094	104.352	- 15.261
1700	27.234	91.737	73.451	30.976	22.382	109.975	- 15.072
1800	27.560	93.260	74.290	33.746	22.689	115.612	- 14.785
1900	27.820	94.688	75.079	36.504	22.998	121.264	- 14.478
2000	28.238	96.220	76.624	39.251	23.321	126.936	- 14.145
2100	28.525	97.635	77.952	42.001	23.651	132.621	- 13.797
2200	28.766	98.955	79.433	44.755	23.985	138.319	- 13.439
2300	28.960	100.180	80.958	47.504	24.324	144.024	- 13.074
2400	29.117	101.320	82.429	50.243	24.666	149.746	- 12.709
2500	29.334	102.684	83.859	53.078	25.011	155.473	- 12.348
2600	29.515	103.838	85.261	55.904	25.357	161.204	- 11.984
2700	29.660	104.955	86.648	58.726	25.703	166.940	- 11.615
2800	29.775	106.034	88.004	61.536	26.049	172.681	- 11.242
2900	29.855	107.084	89.336	64.336	26.397	178.426	- 10.865
3000	30.026	108.100	90.644	67.124	26.741	184.176	- 10.482
3100	30.128	109.086	91.927	69.897	27.086	189.931	- 10.097
3200	30.221	110.044	93.184	72.654	27.428	195.691	- 9.712
3300	30.297	110.974	94.414	75.394	27.767	201.456	- 9.327
3400	30.367	111.881	95.619	78.119	28.105	207.226	- 8.942
3500	30.430	112.763	96.804	80.822	28.437	212.999	- 8.557
3600	30.528	113.622	97.959	83.504	28.767	218.777	- 8.172
3700	30.591	114.459	99.087	86.174	29.091	224.556	- 7.787
3800	30.630	115.274	100.190	88.836	29.409	230.336	- 7.402
3900	30.704	116.073	101.269	91.483	29.729	236.116	- 7.017
4000	30.755	116.851	102.318	94.116	30.040	241.896	- 6.632
4100	30.802	117.611	103.338	96.736	30.347	247.676	- 6.247
4200	30.884	118.354	104.333	99.346	30.647	253.456	- 5.862
4300	30.927	119.079	105.304	101.936	30.940	259.236	- 5.477
4400	30.970	119.790	106.254	104.504	31.235	265.016	- 5.092
4500	30.993	120.486	107.184	107.044	31.518	270.796	- 4.707
4600	30.998	121.167	108.094	109.564	31.799	276.576	- 4.322
4700	31.030	121.834	108.974	112.064	32.073	282.356	- 3.937
4800	31.089	122.484	109.824	114.544	32.340	288.136	- 3.552
4900	31.108	123.128	110.644	116.994	32.605	293.916	- 3.167
5000	31.116	123.756	111.434	119.424	32.862	299.696	- 2.782
5100	31.141	124.373	112.194	121.834	33.113	305.476	- 2.397
5200	31.184	124.979	112.924	124.224	33.360	311.256	- 2.012
5300	31.210	125.574	113.624	126.594	33.600	317.036	- 1.627
5400	31.210	126.155	114.294	128.944	33.834	322.816	- 1.242
5500	31.230	126.728	114.934	131.274	34.061	328.596	- 0.857
5600	31.249	127.291	115.544	133.584	34.283	334.376	- 0.472
5700	31.266	127.844	116.124	135.874	34.500	340.156	- 0.087
5800	31.286	128.384	116.674	138.144	34.714	345.936	0.308
5900	31.302	128.924	117.194	140.394	34.914	351.716	0.703
6000	31.318	129.464	117.684	142.624	35.113	357.496	1.098

Dec. 31, 1960; Dec. 31, 1955

HYDRAZINE (N₂H₄)

(IDEAL GAS)

Point Group C₂
 $S_{298,15}^{\circ} = 57.03 \pm 0.4$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{\circ} = 26.16$ kcal. mole⁻¹
 $\Delta H_f^{\circ} = 22.79 \pm 0.2$ kcal. mole⁻¹
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ν , cm. ⁻¹	ν , cm. ⁻¹	ν , cm. ⁻¹	ν , cm. ⁻¹
---------------------------	---------------------------	---------------------------	---------------------------

3350	875	3280	
------	-----	------	--

1312	377	[93]	
------	-----	------	--

1098	3350	966	
------	------	-----	--

Bond Distances: N-H = 1.022 Å N-N = 1.449 Å
 Bond Angle: H-N-H = 109.4° H-N-N = 112.0°
 Torsional angle between two NH₂ groups ≥ 90° from eclipsed position.
 Product of the Moments of Inertia: I_AI_BI_C = 7.307 X 10⁻¹¹⁷ g.³ cm.³

Heat of Formation.

This was obtained from the heat of formation of the liquid and the selected heat of vaporization, $\Delta H_{298}^{\circ} = 10.69$ kcal. mole⁻¹, derived from the vapor pressure data (Series III) of D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem. Soc. **71**, 2293 (1949). Other vapor pressure data from W. Kieber and A. Woerner, Z. Elektrochem. **40**, 252 (1934) and E. T. Chang and N. A. Ockers, AD-458288, Defense Documentation Center, January, 1964, are in satisfactory agreement (see N₂H₄ liquid table).

Heat Capacity and Entropy.

Functions were calculated from the constants given above using the rigid rotator harmonic oscillator method. The entropy was increased by R ln 2 because two rotameric forms are implied by use of the torsional frequency. Small but arbitrary adjustments were made in the assignment of the bending mode frequencies in order to reproduce the vapor pressure data of Scott et al., loc. cit., as closely as possible. Calculated values of $S_{298}^{\circ} = 57.03$ and $S_{340}^{\circ} = 58.70$ cal. deg.⁻¹ mole⁻¹ may be compared with 56.99 and 59.69, respectively, derived from the data of Scott et al.. Internal rotation calculations would require a complex potential function in order to fit the data. The barrier to inversion (990 cm.⁻¹ ~ 2.8 kcal.) is slightly less than the barrier to internal rotation at the trans position (1110 cm.⁻¹ ~ 3.2 kcal.) according to analyses of the microwave data by T. Kasuya, Sci. Papers, Inst. Phys. Chem. Res. (Tokyo) **55**, No. 1, 1-39 (1962) and T. Kasuya and T. Kojima, J. Phys. Soc. Japan **18**, 364-8 (1963).

From matrix isolation and gas phase infrared studies, E. Catalano, R. H. Sanborn and J. W. Frazer, J. Chem. Phys. **39**, 2265 (1963), have suggested possible uncertainties in the assignment of the bending mode frequencies in the region from 1630 to 740 cm.⁻¹. The question hinges on the uncertain existence of a gas phase fundamental at about 1600 cm.⁻¹ as observed by P. A. Diguere and I. D. Liu, J. Chem. Phys. **20**, 136 (1952). No corresponding matrix band was found and the gas phase band appeared to be due to absorption on the cell windows. A vapor phase Raman frequency at 1564 cm.⁻¹ was observed, however, by Yu. I. Kotov and V. M. Tatevskii, Opt. i Spektroskopiya **15**, 65 (1963). Catalano et al. suggest one assignment based on the uncertain fundamental and a tentative alternative assignment excluding it. The two assignments give entropies that are 0.26 cal. deg.⁻¹ mole⁻¹ lower and 0.12 higher than the third law value. The lower calculated entropy is probably more reasonable, but the higher value could be more easily modified to agree with the third law value. Thus the alternative assignment was adopted with ν_{11} arbitrarily increased from ~810 to 835 cm.⁻¹.

The structural constants are based primarily on the electron diffraction study of Y. Morino, T. Iijima and Y. Murata, Bull. Chem. Soc. Japan **33**, 46 (1960). Related analyses of the infrared fine structure of the torsional frequency (377 cm.⁻¹), A. Yamaguchi, I. Ichihara, T. Shimomouchi and S. Mizushima, Spectrochim. Acta **16**, 1471 (1960), and of the microwave spectra, Kasuya and Kojima, loc. cit., are in close agreement. The microwave data give an H-H angle of 106° and a torsional angle of 90°2'. Principal moments of inertia of the adopted structure are I_A = 0.574 X 10⁻³⁹, I_B = 3.573 X 10⁻³⁹ and I_C = 3.563 X 10⁻³⁹ g.² cm.²





(Ideal Gas) Mol. Wt. = 32.122

Silane (SiH_4) (Ideal Gas)

Mol. Wt. = 32.122
 $\Delta H_f^\circ 298.15 = 7.3 \pm 0.3 \text{ kcal. mole}^{-1}$
 $S^\circ 298.15 = 48.789 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Point Group T_d

Vibrational Frequencies and Degeneracies

$\omega_{cm.}^{-1}$	Deg.
2183 (3)	910 (3)
978 (2)	2187 (1)

Si-H distance = 1.457 Å H-Si-H angle = $109^\circ 28'$ $\sigma = 12$
 Product of Moments of Inertia $I_{AB} I_C = 0.84659 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation, $\Delta H_f^\circ 298.15$ was determined by S. Gunn and L. Greene, J. Phys. Chem. **65**, 773 (1961). A value of 7.8 kcal. mole⁻¹ was selected by J. S. Gordon, Thiel Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960.

Heat Capacity and Entropy. Molecular constants were taken from J. S. Gordon, op. cit., G. Janz and Y. Mikawa, Bull. Chem. Soc. Japan, **34**, 1495 (1961) reported slightly different values for the vibrational levels.

T, K.	C _p ^o	S ^o	- (F° - H ₂₉₈ °) / T	H° - H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	10.000	INFINITE	2.519	10.085	10.085	INFINITE	
100	12.303	35.008	2.473	8.228	11.811	11.811	
200	14.139	50.059	2.473	6.394	17.254	7.541	
298	16.236	68.789	2.473	4.614	21.473	7.093	
300	16.252	68.789	2.473	4.614	21.473	7.093	
400	18.344	82.664	2.473	3.322	24.093	6.581	
500	19.386	94.885	2.473	2.449	26.449	6.422	
600	20.206	106.970	2.473	1.856	28.516	6.297	
700	20.924	118.925	2.473	1.457	31.190	6.194	
800	21.525	130.777	2.473	1.149	34.564	6.113	
900	22.032	142.521	2.473	0.912	38.602	6.041	
1000	22.461	154.170	2.473	0.730	43.402	5.979	
1100	22.825	165.732	2.473	0.594	48.963	5.924	
1200	23.137	177.215	2.473	0.496	55.365	5.875	
1300	23.405	188.626	2.473	0.426	62.620	5.846	
1400	23.637	199.971	2.473	0.374	70.746	5.831	
1500	23.836	211.284	2.473	0.335	79.746	5.825	
1600	24.014	222.562	2.473	0.306	89.620	5.820	
1700	24.169	233.807	2.473	0.282	100.366	5.815	
1800	24.305	245.018	2.473	0.262	112.079	5.811	
1900	24.425	256.193	2.473	0.245	124.754	5.807	
2000	24.532	267.332	2.473	0.231	138.396	5.804	
2100	24.628	278.437	2.473	0.219	152.004	5.801	
2200	24.713	289.507	2.473	0.209	165.579	5.798	
2300	24.791	300.541	2.473	0.201	180.116	5.795	
2400	24.860	311.541	2.473	0.194	194.614	5.792	
2500	24.923	322.507	2.473	0.188	210.074	5.789	
2600	24.980	333.437	2.473	0.183	226.494	5.786	
2700	25.032	344.332	2.473	0.178	243.874	5.783	
2800	25.079	355.193	2.473	0.174	262.214	5.780	
2900	25.123	366.018	2.473	0.170	281.514	5.777	
3000	25.163	376.807	2.473	0.166	301.774	5.774	
3100	25.200	387.560	2.473	0.162	323.004	5.771	
3200	25.233	398.277	2.473	0.158	345.204	5.768	
3300	25.263	408.957	2.473	0.154	368.374	5.765	
3400	25.290	419.604	2.473	0.150	392.514	5.762	
3500	25.314	430.218	2.473	0.146	417.624	5.759	
3600	25.334	440.800	2.473	0.142	443.704	5.756	
3700	25.350	451.351	2.473	0.138	470.754	5.753	
3800	25.363	461.872	2.473	0.134	498.774	5.750	
3900	25.374	472.363	2.473	0.130	527.764	5.747	
4000	25.384	482.824	2.473	0.126	557.724	5.744	
4100	25.391	493.255	2.473	0.122	588.654	5.741	
4200	25.396	503.656	2.473	0.118	620.554	5.738	
4300	25.400	514.027	2.473	0.114	653.424	5.735	
4400	25.403	524.368	2.473	0.110	687.264	5.732	
4500	25.405	534.679	2.473	0.106	722.074	5.729	
4600	25.406	544.960	2.473	0.102	757.854	5.726	
4700	25.407	555.211	2.473	0.100	794.604	5.723	
4800	25.408	565.432	2.473	0.096	832.324	5.720	
4900	25.408	575.624	2.473	0.092	871.014	5.717	
5000	25.408	585.787	2.473	0.088	910.674	5.714	
5100	25.408	595.920	2.473	0.084	951.304	5.711	
5200	25.408	606.024	2.473	0.080	992.904	5.708	
5300	25.408	616.100	2.473	0.076	1035.474	5.705	
5400	25.408	626.147	2.473	0.072	1079.014	5.702	
5500	25.408	636.166	2.473	0.068	1123.524	5.699	
5600	25.408	646.157	2.473	0.064	1169.004	5.696	
5700	25.408	656.120	2.473	0.060	1215.454	5.693	
5800	25.408	666.054	2.473	0.056	1262.874	5.690	
5900	25.408	675.960	2.473	0.052	1311.264	5.687	
6000	25.408	685.837	2.473	0.048	1360.624	5.684	

December 31, 1960.



T, °K.	C _p	S°	$-(F^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	.000	.000	INFINITE	2.233	.000	.000	.000
100	5.797	6.990	19.148	.000	.000	.000	.000
200	6.519	13.148	19.188	1.208	.000	.000	.000
298	6.687	18.171	.000	.000	.000	.000	.000
300	6.684	18.212	.012	.000	.000	.000	.000
400	6.552	21.570	.000	.000	.000	.000	.000
500	6.495	21.570	1.385	.000	.000	.000	.000
600	6.486	22.752	19.463	1.974	.000	.000	.000
700	6.968	46.034	22.250	16.649	.000	.000	.000
800	4.968	46.498	25.266	17.186	.000	.000	.000
900	4.968	47.253	27.690	16.642	.000	.000	.000
1000	4.968	47.606	28.687	16.139	.000	.000	.000
1100	4.968	48.280	31.338	18.636	.000	.000	.000
1200	4.968	48.712	32.768	19.133	.000	.000	.000
1300	4.968	48.110	34.010	19.630	.000	.000	.000
1400	4.968	47.486	35.152	20.126	.000	.000	.000
1500	4.968	46.821	36.072	20.623	.000	.000	.000
1600	4.968	50.141	36.941	21.120	.000	.000	.000
1700	4.968	50.443	37.727	21.617	.000	.000	.000
1800	4.968	50.726	38.441	22.114	.000	.000	.000
1900	4.968	51.000	39.085	22.611	.000	.000	.000
2000	4.968	51.250	39.596	23.107	.000	.000	.000
2100	4.968	51.492	40.252	23.604	.000	.000	.000
2200	4.968	51.723	40.769	24.101	.000	.000	.000
2300	4.968	51.944	41.250	24.598	.000	.000	.000
2400	4.968	52.156	41.706	25.094	.000	.000	.000
2500	4.968	52.358	42.122	25.591	.000	.000	.000
2600	4.968	52.553	42.519	26.088	.000	.000	.000
2700	4.968	52.741	42.895	26.585	.000	.000	.000
2800	4.968	52.921	43.249	27.082	.000	.000	.000
2900	4.968	53.096	43.576	27.578	.000	.000	.000
3000	4.968	53.264	43.886	28.075	.000	.000	.000
3100	4.968	53.427	44.210	28.572	.000	.000	.000
3200	4.968	53.485	44.501	29.069	.000	.000	.000
3300	4.968	53.738	44.778	29.566	.000	.000	.000
3400	4.968	53.986	45.046	30.062	.000	.000	.000
3500	4.968	54.030	45.294	30.559	.000	.000	.000
3600	4.969	54.170	45.543	31.056	.000	.000	.000
3700	4.969	54.306	45.778	31.553	.000	.000	.000
3800	4.969	54.439	46.005	32.050	.000	.000	.000
3900	4.969	54.568	46.222	32.547	.000	.000	.000
4000	4.970	54.684	46.433	33.044	.000	.000	.000
4100	4.970	54.816	46.636	33.541	.000	.000	.000
4200	4.971	54.936	46.832	34.038	.000	.000	.000
4300	4.972	55.053	47.022	34.535	.000	.000	.000
4400	4.973	55.167	47.206	35.032	.000	.000	.000
4500	4.975	55.279	47.384	35.529	.000	.000	.000
4600	4.976	55.388	47.557	36.027	.000	.000	.000
4700	4.978	55.494	47.724	36.525	.000	.000	.000
4800	4.981	55.600	47.887	37.023	.000	.000	.000
4900	4.983	55.703	48.046	37.521	.000	.000	.000
5000	4.987	55.804	48.200	38.019	.000	.000	.000
5100	4.991	55.903	48.350	38.518	.000	.000	.000
5200	4.996	56.000	48.496	39.018	.000	.000	.000
5300	5.001	56.095	48.639	39.518	.000	.000	.000
5400	5.006	56.188	48.778	40.018	.000	.000	.000
5500	5.014	56.280	48.913	40.519	.000	.000	.000
5600	5.022	56.371	49.046	41.021	.000	.000	.000
5700	5.031	56.460	49.175	41.523	.000	.000	.000
5800	5.041	56.547	49.301	42.027	.000	.000	.000
5900	5.051	56.632	49.424	42.532	.000	.000	.000
6000	5.064	56.718	49.546	43.037	.000	.000	.000

December 31, 1961

MERCURY (Hg)

(REFERENCE STATE)

MOL. WT. = 200.61

The reference state is chosen as follows:

0° to 234.29°K Crystal

234.29° to 629.73°K Liquid

629.73° to 800°K Ideal Gas

$$S^{\circ}_{298.15} = 18.171 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 234.29^{\circ}\text{K}$$

$$T_b = 629.73^{\circ}\text{K}$$

$$\Delta H^{\circ}_V 298.15 = 14.652 \pm 0.015 \text{ kcal. mole}^{-1}$$

$$\Delta H^{\circ}_m = 0.5486 \pm 0.0001 \text{ kcal. mole}^{-1}$$

$$\Delta H^{\circ}_V 629.73 = 14.133 \pm 0.020 \text{ kcal. mole}^{-1}$$

Heat Capacity.

The heat capacities of F. L. Smith and N. M. Wolcott, *Phil. Mag.* **1** (8), 854 (1956), 1.2°-20.2°K. R. H. Buey and W. P. Giauque, *J. Am. Chem. Soc.* **75**, 806 (1953), 15°-350°K. and T. B. Douglas, A. P. Ball, and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **46**, 334 (1951), 300°-770°K. have been smoothly joined. There is fair agreement between the selected values and those of G. L. Fickard and F. E. Simon, *Proc. Phys. Soc. A61*, 1 (1948), L. O. Carpenter and P. H. Oakley, *Phil. Mag.* **12**, 511 (1931), L. O. Carpenter and L. O. Stoodley, *Phil. Mag.* **10**, 249 (1930), E. Cohen, O. I. Krulshner, and A. L. Moenvald, *Z. phys. Chem.* **A86**, 437 (1920), A. L. Dixon and W. H. Rodenbush, *J. Am. Chem. Soc.* **49**, 1162 (1927), F. Simon, *Z. phys. Chem.* **107**, 282 (1923), *Ann. Physik* **68**, 241 (1922), J. N. Brønsted, *Z. Elektrochem.* **19**, 714 (1912), and F. Pollitzer, *Z. Elektrochem.* **17**, 5 (1911).

Melting Data.

From Buey and Giauque, loc. cit.

Boiling Point and Heat of Vaporization.

Calculated from the vapor pressures determined by K. D. Carlson, R. J. Thorn, and P. W. Gilles, private communication, October 1961, F. M. Ernberger and H. W. Fitman, *Rev. Sci. Instrum.* **25**, 584 (1954), F. H. Spedding and J. L. Dye, *J. Phys. Chem.* **59**, 561 (1955), and J. A. Beattie, B. E. Blaisdell, and J. Kaminsky, *Proc. Am. Acad. Arts Sciences* **71**, 375 (1937). Earlier measurements are less accurate and have not been used. Gas imperfection has been allowed for by the method of Buey and Giauque, loc. cit.

(Liquid) Mol. Wt. = 200.61

MOL. WT. = 200.61

(LIQUID)

MERCURY (Hg)

T, °K.	C _p	S° cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔF _f ° kcal. mole ⁻¹	Log K _p
298	6.687	18.171	18.171	.000	.000	.000	.000
300	6.688	18.212	18.171	.012	.000	.000	.000
400	6.552	20.115	18.431	.473	.000	.000	.000
500	6.495	21.570	18.919	1.325	.000	.000	.000
600	6.486	22.752	19.462	2.274	.000	.000	.000
700	6.503	23.738	20.006	3.264	1.784	1.784	1.784
800	6.567	25.411	21.030	4.613	3.069	3.069	3.069
1000	6.742	28.117	21.504	8.163	8.163	8.163	8.163
1100	6.817	28.763	21.953	5.291	13.345	10.324	2.051
1200	6.842	27.359	22.369	5.977	13.500	12.567	2.270
1300	6.842	26.433	23.169	7.370	12.756	16.707	2.408
1500	7.117	28.922	23.436	8.078	12.545	18.604	2.740
1600	7.192	29.383	23.887	8.793	12.327	20.886	2.853
1700	7.267	29.822	24.224	9.516	12.101	22.956	2.951
1800	7.341	30.248	24.557	10.248	11.875	24.956	3.036
1900	7.417	30.638	24.887	10.985	11.650	27.083	3.116
2000	7.492	31.020	25.155	11.730	11.377	29.083	3.178

See notes on reference state for sources of data.

$$\Delta H_f^\circ 298.15 = 0$$

$$S_{298.15}^\circ = 18.171 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 234.29^\circ\text{K}$$

$$T_b = 629.73^\circ\text{K}$$

$$\Delta H_v^\circ 298.15 = 14.651 \pm 0.015 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 0.5486 \pm 0.0001 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^\circ 629.73 = 14.134 \pm 0.020 \text{ kcal. mole}^{-1}$$

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ ΔH° _f kcal. mole ⁻¹	ΔF°	Log K _p
0	.000	INFINITE	1.481	15.404	INFINITE
100	4.968	36.366	12.745	12.745	27.854
200	4.968	38.710	15.493	10.111	10.111
298	4.968	41.794	18.052	7.609	5.577
300	4.968	41.794	.009	7.565	5.511
400	4.968	43.254	5.064	14.849	14.849
500	4.968	44.362	45.357	1.003	14.885
600	4.968	45.266	42.749	18.330	1.282
700	4.968	46.131	41.182	1.996	18.178
800	4.968	46.977	43.581	2.493	.000
900	4.968	47.283	43.960	2.990	.000
1000	4.968	47.606	44.319	3.467	.000
1100	4.968	48.279	44.658	3.984	.000
1200	4.968	48.712	44.978	4.481	.000
1300	4.968	49.109	45.281	4.977	.000
1400	4.968	49.478	45.567	5.474	.000
1500	4.968	49.820	45.840	5.971	.000
1600	4.968	50.141	46.099	6.468	.000
1700	4.968	50.442	46.345	6.965	.000
1800	4.968	50.726	46.581	7.461	.000
1900	4.968	51.095	46.806	7.958	.000
2000	4.968	51.250	47.022	8.455	.000
2100	4.968	51.492	47.229	8.952	.000
2200	4.968	51.723	47.428	9.449	.000
2300	4.968	51.944	47.620	9.945	.000
2400	4.968	52.155	47.804	10.442	.000
2500	4.968	52.358	47.983	10.939	.000
2600	4.968	52.553	48.155	11.436	.000
2700	4.968	52.741	48.321	11.933	.000
2800	4.968	52.921	48.482	12.430	.000
2900	4.968	53.096	48.638	12.926	.000
3000	4.968	53.264	48.790	13.423	.000
3100	4.968	53.427	48.937	13.920	.000
3200	4.968	53.585	49.079	14.417	.000
3300	4.968	53.738	49.218	14.914	.000
3400	4.968	53.886	49.353	15.410	.000
3500	4.968	54.030	49.485	15.907	.000
3600	4.968	54.170	49.613	16.404	.000
3700	4.968	54.306	49.738	16.901	.000
3800	4.968	54.439	49.860	17.398	.000
3900	4.968	54.568	49.979	17.895	.000
4000	4.970	54.693	50.095	18.392	.000
4100	4.970	54.816	50.209	18.889	.000
4200	4.971	54.936	50.320	19.386	.000
4300	4.972	55.053	50.429	19.883	.000
4400	4.973	55.167	50.535	20.380	.000
4500	4.975	55.279	50.639	20.878	.000
4600	4.976	55.386	50.742	21.375	.000
4700	4.978	55.495	50.842	21.873	.000
4800	4.981	55.600	50.940	22.371	.000
4900	4.984	55.703	51.036	22.869	.000
5000	4.987	55.804	51.130	23.368	.000
5100	4.991	55.902	51.223	23.867	.000
5200	4.996	55.999	51.314	24.366	.000
5300	5.001	56.095	51.403	24.866	.000
5400	5.007	56.188	51.491	25.366	.000
5500	5.014	56.280	51.577	25.867	.000
5600	5.022	56.371	51.662	26.369	.000
5700	5.031	56.460	51.745	26.872	.000
5800	5.041	56.547	51.827	27.375	.000
5900	5.052	56.633	51.908	27.880	.000
6000	5.064	56.718	51.987	28.386	.000

December 31, 1961

 $\Delta H_{f0}^{\circ} = 15.404 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f0}^{\circ} = 10.111 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 14.852 \pm 0.015 \text{ kcal. mole}^{-1}$
 $\Delta S_{f298.15}^{\circ} = 41.794 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_{f298.1$

Mercury Moniodide (HgI)

INTERIM TABLE

Mol. Wt. = 327.52

(Ideal Gas)

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	9.549	57.402	17.019	2.531	33.179	33.179	INFINITE
200	9.929	63.477	17.019	1.762	33.176	29.054	-63.495
300	10.155	67.068	17.019	1.283	32.848	25.052	-27.374
400	10.356	69.741	17.019	1.000	31.900	21.459	-15.729
500	10.529	71.768	17.019	0.844	31.393	21.395	-15.586
600	10.677	73.473	17.019	0.768	30.886	20.556	-15.026
700	10.807	74.907	17.019	0.723	30.396	19.848	-14.007
800	10.917	76.126	17.019	0.697	29.926	19.355	-13.986
900	11.007	77.140	17.019	0.682	29.556	18.961	-13.986
1000	11.077	77.925	17.019	0.675	29.268	18.638	-13.986
1100	11.129	78.475	17.019	0.672	29.044	18.368	-13.986
1200	11.167	78.875	17.019	0.670	28.868	18.138	-13.986
1300	11.195	79.150	17.019	0.668	28.728	17.948	-13.986
1400	11.216	79.345	17.019	0.666	28.618	17.788	-13.986
1500	11.231	79.475	17.019	0.665	28.528	17.658	-13.986
1600	11.241	79.545	17.019	0.664	28.453	17.548	-13.986
1700	11.247	79.585	17.019	0.663	28.393	17.458	-13.986
1800	11.250	79.605	17.019	0.662	28.343	17.388	-13.986
1900	11.251	79.615	17.019	0.661	28.303	17.338	-13.986
2000	11.251	79.615	17.019	0.661	28.273	17.298	-13.986
2100	11.251	79.615	17.019	0.661	28.253	17.268	-13.986
2200	11.251	79.615	17.019	0.661	28.243	17.248	-13.986
2300	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
2400	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
2500	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
2600	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
2700	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
2800	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
2900	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3000	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3100	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3200	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3300	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3400	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3500	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3600	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3700	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3800	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
3900	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4000	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4100	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4200	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4300	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4400	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4500	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4600	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4700	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4800	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
4900	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5000	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5100	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5200	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5300	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5400	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5500	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5600	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5700	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5800	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
5900	11.251	79.615	17.019	0.661	28.243	17.238	-13.986
6000	11.251	79.615	17.019	0.661	28.243	17.238	-13.986

December 31, 1961

MERCURY MONIODIDE (HgI)

(IDEAL GAS)

Ground State Configuration ²2

ΔH_f^o 298.15 = 31.9 ± 1.1 kcal mole⁻¹

S_{298.15} = 67.068 cal deg⁻¹ mole⁻¹

Electronic Level and Multiplicity

$\frac{E, \text{ cm}^{-1}}{0}$ $\frac{g_i}{2}$

$\omega_e \nu_e = 1.00 \text{ cm}^{-1}$

$\sigma = 1$

$\alpha_e = [0.0003] \text{ cm}^{-1}$

$r_e = [2.49] \text{ \AA}$

Heat of Formation

K. Wieland and A. Herzog, Helv. Chim. Acta, **32**, 889 (1949) gave 8.3 ± 1.1 kcal for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants were taken from K. Wieland, Zeits. f. Elektrochemie **54**, 761 (1960). Rotational constants were estimated using equation III 123, p. 108, G. Herzberg, "Spectra of Diatomic Molecules," van Nostrand, New York 1950. The bond length was estimated to be 0.985 of the mercuric bond length by analogy with the mercury chlorides.

HgI

MOL. WT. = 327.52

HgI

T. °K.	C _p	$\int_0^T C_p dT$ cal. mole ⁻¹ deg. ⁻¹	$\int_0^T C_p dT$ - (F°-H° ₂₉₈)/T	$\int_0^T C_p dT$ H°-H° ₂₉₈	ΔH_f° kcal. mole ⁻¹	ΔF_f°	Log K _p
0							
100							
200							
298	16.542	43.336	41.336	.000	- 25.200	- 24.427	17.905
300		43.453	41.336	.034	- 25.202	- 24.422	17.791
400	18.600	63.653	44.080	1.944	- 26.125	- 24.014	13.120
500	19.600	88.941	45.609	4.254	- 36.690	- 21.925	9.593
600	20.105	117.917	47.642	6.575	- 38.226	- 18.617	6.781
700	20.105	146.583	49.682	8.575	- 51.789	- 13.615	4.313
800	20.105	174.907	51.732	10.565	- 51.777	- 8.431	2.303
900	20.105	202.911	53.799	12.596	- 50.566	- 3.124	.799
1000	20.105	230.583	56.267	14.606	- 49.958	- 2.114	-.462
1100	20.105	257.769	58.463	16.417	- 48.351	- 7.292	- 1.449
1200	20.105	284.228	60.296	18.027	- 46.747	- 12.414	- 2.261
1300	20.105	310.000	61.728	19.438	- 45.142	- 17.487	- 2.940
1400	20.105	335.118	62.940	20.638	- 43.540	- 22.514	- 3.514
1500	20.105	359.585	63.945	21.639	- 41.939	- 27.496	- 4.006

MERCURY DIIODIDE (HgI₂)

(Crystal)

Mol. Wt. = 454.43

ΔH_f° 298.15 = -25.2 ± 0.4 kcal. mole⁻¹

$S_{298.15}^\circ$ = [43.336] ± 1.5 cal. deg.⁻¹ mole⁻¹

T_c = 402°K

ΔH_t° = 0.601 ± 0.04 kcal. mole⁻¹

T_m = 530°K

ΔH_m° = 4.533 ± 0.05 kcal. mole⁻¹

Heat of Formation. Taken from National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties", (1952).

Heat Capacity and Entropy. The heat capacity was calculated from the heat content data of M. Guinchant, Comp. Rend. 89, 145 (1907) and R. Ewald, Ann. d. Physik (4) 44, 1213 (1914). The entropy was estimated by adjusting its value to provide the best fit of the melting, sublimation and vaporization phenomena.

Transition. The heat and temperature of transition were taken from National Bureau of Standards Circular 500 (loc. cit.).

Melting. The heat of melting was taken from M. Guinchant (loc. cit.), the temperature of melting from National Bureau of Standards Circular 500 (loc. cit.).

Mercury Diiodide (HgI₂)

(Liquid) Mol. Wt. = 454.43

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100								
200								
298	16.592	51.544	51.544	.000	20.662	22.536	16.519	
300	16.600	51.659	51.544	.034	20.668	22.546	16.424	
400	24.400	57.777	52.324	2.161	24.550	22.574	16.372	
500	24.400	63.221	53.776	4.621	34.282	22.672	16.272	
600	24.400	67.670	55.902	7.061	33.391	19.235	7.006	
700	24.400	71.431	57.959	9.501	46.525	15.375	4.600	
800	24.400	74.690	59.763	11.941	65.483	10.995	3.004	
900	24.400	77.563	61.565	14.361	84.403	7.674	1.571	
1000	24.400	80.134	63.313	16.821	103.405	2.614	.281	
1100	24.400	82.460	64.950	19.261	122.369	1.415	.074	
1200	24.400	84.583	66.499	21.701	141.335	5.349	.574	
1300	24.400	86.536	67.966	24.141	160.301	9.198	1.546	
1400	24.400	88.344	69.358	26.581	179.268	12.968	2.526	
1500	24.400	90.026	70.680	29.021	198.239	16.662	3.427	

March 31, 1962

MERCURY DIIODIDE (HgI₂)

(Liquid)

Mol. Wt. = 454.43

ΔH_f^o 298.15 = [-20.862] ± 0.45 kcal. mole⁻¹

ΔF_f^o 298.15 = [51.544] ± 1.5 cal. deg.⁻¹ mole⁻¹

T_m = 530°K

ΔH_m = 4.553 ± 0.05 kcal. mole⁻¹

T_b = 627°K

ΔH_v = 14.141 ± 0.25 kcal. mole⁻¹

Heat of Formation. Calculated from ΔH_f^o 298(c).

Heat Capacity and Entropy. Heat capacity measurements were obtained from the data of M. Guinchant, Comp. Rend. SG, 145 (1907) in the range 540-600°K and were assumed constant above and below this range. A glass type transition was assumed at 353°K below which the heat capacity was that of HgI₂(c). The entropy was calculated from the entropy of the crystal and the measured entropy of fusion.

Fusion and Vaporization. T_m and T_b are taken from National Bur. of Standards (U.S.) Circular 500 (1952). ΔH_m is from the data of M. Guinchant (loc. cit.) and ΔH_v was obtained from the data of E. B. R. Pridoux, J. Chem. Soc. (London) 97, 2032 (1910) and F. M. G. Johnson, J. Amer. Chem. Soc. 33, 777 (1911).

HgI₂

HgI₂

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f	ΔF _f	Log K _p
100	14.000	68.000	INFINITE	2.802	2.802	2.802	2.802	INFINITE
200	14.243	74.556	81.659	1.431	2.621	10.563	11.542	10.344
298	14.608	80.331	80.331	1.000	3.855	14.112	16.112	10.326
300	14.611	80.421	80.421	0.97	3.844	14.178	16.178	10.326
400	14.735	86.444	86.444	1.495	8.299	17.400	21.400	8.162
500	14.796	87.940	87.940	1.695	14.927	18.673	22.673	6.162
600	14.828	92.640	92.640	4.424	18.921	18.618	22.618	4.761
700	14.848	92.528	84.446	5.937	31.062	16.979	21.979	5.301
800	14.861	92.911	85.633	7.423	32.984	14.684	20.984	4.011
900	14.870	92.979	86.717	8.857	34.527	12.400	19.527	2.813
1000	14.877	92.979	87.832	10.337	35.822	10.156	18.156	2.213
1100	14.882	99.648	88.843	11.865	32.738	7.861	15.861	1.562
1200	14.885	100.943	89.798	13.373	32.656	5.604	14.021	1.021
1300	14.886	102.134	90.702	14.862	32.573	3.352	12.573	0.563
1400	14.887	103.243	91.563	16.332	32.490	1.106	11.490	0.163
1500	14.892	104.265	92.372	17.800	32.413	1.131	10.413	0.163
1600	14.894	105.226	93.145	19.329	32.335	3.366	9.366	0.460
1700	14.895	106.129	93.893	20.819	32.258	5.595	8.258	0.719
1800	14.896	106.981	94.567	22.308	32.183	7.818	7.183	0.949
1900	14.897	107.786	95.181	23.797	32.108	10.041	6.108	1.135
2000	14.898	108.550	95.750	25.286	32.035	12.295	5.035	1.339
2100	14.898	109.277	96.226	26.777	31.964	14.468	4.000	1.506
2200	14.899	109.970	97.121	28.267	31.894	16.676	3.000	1.656
2300	14.900	110.632	97.947	29.757	31.825	18.883	2.000	1.794
2400	14.900	111.275	98.780	31.247	31.757	21.090	1.000	1.920
2500	14.900	111.875	99.620	32.737	31.690	23.296	0.000	2.036
2600	14.900	112.459	99.295	34.227	31.625	25.484	2.442	2.142
2700	14.901	113.021	99.793	35.717	31.562	27.680	2.240	2.240
2800	14.901	113.563	100.275	37.207	31.500	29.873	2.332	2.332
2900	14.901	114.095	100.750	38.697	31.438	32.066	2.426	2.426
3000	14.902	114.591	101.192	40.186	31.378	34.251	2.495	2.495
3100	14.902	115.080	101.636	41.678	31.320	36.439	2.569	2.569
3200	14.902	115.553	102.063	43.168	31.263	38.624	2.638	2.638
3300	14.902	116.012	102.479	44.658	31.208	40.809	2.703	2.703
3400	14.902	116.458	102.886	46.148	31.153	42.999	2.763	2.763
3500	14.902	116.889	103.278	47.638	31.100	45.171	2.820	2.820
3600	14.902	117.308	103.661	49.129	31.048	47.348	2.874	2.874
3700	14.903	117.717	104.036	50.619	30.998	49.523	2.925	2.925
3800	14.903	118.114	104.401	52.109	30.949	51.701	2.973	2.973
3900	14.903	118.499	104.758	53.599	30.902	53.876	3.019	3.019
4000	14.903	118.879	105.108	55.090	30.855	56.047	3.062	3.062
4100	14.903	119.246	105.446	56.580	30.810	58.220	3.103	3.103
4200	14.903	119.606	105.779	58.070	30.767	60.392	3.142	3.142
4300	14.903	120.000	106.105	59.551	30.724	62.566	3.179	3.179
4400	14.903	120.398	106.428	61.032	30.681	64.740	3.216	3.216
4500	14.903	120.834	106.746	62.511	30.638	66.914	3.250	3.250
4600	14.903	120.961	107.041	64.031	30.608	69.084	3.281	3.281
4700	14.903	121.262	107.341	65.522	30.571	71.252	3.312	3.312
4800	14.903	121.606	107.635	67.017	30.537	73.395	3.342	3.342
4900	14.903	121.900	107.925	68.508	30.503	75.538	3.370	3.370
5000	14.903	122.204	108.205	69.993	30.472	77.682	3.397	3.397
5100	14.903	122.699	108.483	71.483	30.442	79.891	3.423	3.423
5200	14.904	122.769	108.755	72.974	30.415	82.052	3.448	3.448
5300	14.904	123.072	109.023	74.464	30.389	84.216	3.473	3.473
5400	14.904	123.375	109.288	75.954	30.362	86.380	3.496	3.496
5500	14.904	123.625	109.544	77.444	30.332	88.537	3.518	3.518
5600	14.904	123.893	109.797	78.935	30.323	90.699	3.540	3.540
5700	14.904	124.157	110.047	80.425	30.305	92.862	3.560	3.560
5800	14.904	124.416	110.293	81.916	30.287	95.020	3.580	3.580
5900	14.904	124.676	110.536	83.406	30.268	97.176	3.599	3.599
6000	14.904	124.921	110.772	84.897	30.266	99.330	3.618	3.618

March 31, 1962

MERCURY DIODIDE (HgI₂) (Ideal Gas)

Mol. Wt. = 454.43

ΔH_f° 298.15 = -3.855 ± 0.5 kcal. mole⁻¹S° 298.15 = 80.331 cal. deg. mole⁻¹Point Group = D_{∞h}

Vibrational Levels and Multiplicities

$$\omega_e, \text{ cm.}^{-1}$$

$$\begin{Bmatrix} 156 & \{1\} \\ 33 & \{2\} \\ [233] & \{1\} \end{Bmatrix}$$

Hg-I distance = 2.58 Å

Moment of Inertia = 280.5 X 10⁻³⁹ g. cm.²

σ = 2

Heat of Formation. The heat of formation of the crystal as given in National Bureau of Standards (U.S.) Circular 500, "Selected Values of Chemical Thermodynamic Properties", 1952 was combined with the 3rd law heat of sublimation at 298°K derived from the data of K. Niwa and Z. Shibata, J. Pac. Sci. Hokkaido Imp. Univ. Ser. III 2, 183 (1939); D. W. Magee, Univ. Microfilms No. 14474 Ann Arbor, Mich., and F. M. G. Johnson, J. Amer. Chem. Soc. 53, 777 (1931).

Heat Capacity and Entropy. The vibrational constants were given by W. Klemperer and L. Lindeman, J. Chem. Phys. 25, 397 (1956). The anti-symmetric stretching frequency was estimated by analogy with the bromide and chloride. The bond length was an average of the values given by H. Braune and S. Knoke, Naturwiss. 21, 349 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Farad. Soc. 33, 852 (1937) and P. A. Akshin, V. P. Spiridonov and A. N. Khodachenkov, Zhur. Fiz. Khim. 35, 20 (1959).

Mercury Monoxide (HgO)

(Crystal) Mol. Wt. = 216.61

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	2.176	20.605	20.605	INFINITE
100	6.796	7.371	1.776	20.969	16.741	40.955
200	9.173	12.872	.969	21.119	16.581	17.564
298	10.551	16.795	.000	21.699	13.783	10.250
300	10.551	16.860	.020	21.698	13.935	10.151
400	11.550	20.037	1.126	21.608	11.356	6.206
500	12.340	22.703	1.858	21.429	8.615	3.853
600	12.935	25.008	3.587	21.191	6.315	2.300
700	13.400	26.931	4.995	34.937	2.284	.714
800	13.745	28.551	6.263	34.475	2.347	-.641
900	14.012	30.486	7.652	33.989	6.922	-1.681
1000	14.200	31.973	9.063	33.489	11.440	-2.500

MERCURY MONOXIDE (HgO)

(CRYSTAL)

MOL. WT. = 216.61

$$\Delta H_f^0 298.15 = -21.699 \pm 0.024 \text{ kcal. mole}^{-1} \quad S_{298.15}^0 = 16.795 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_{\text{decomp}} = 749^\circ\text{K.}$$

Heat of Formation.

Obtained from the entropy obtained by T. W. Bauer and H. L. Johnston, J. Am. Chem. Soc. 75, 2217 (1953) and the free energy of formation as determined from the numerous cell measurements described by Bauer and Johnston. The value adopted for $\Delta F_f^0 298.15$ was $-42,707 \pm 14 \text{ cal. mole}^{-1}$.

Heat Capacity and Entropy.

The heat capacity has been measured from 15° to 298°K. by Bauer and Johnston loc. cit. The extrapolation below 15°K was done assuming a T^3 law and gave $S_{15}^0 = 0.264 \text{ e.u.}$ Above 298° the data was extrapolated smoothly and adjusted to give the observed decomposition vapor pressures of G. B. Taylor and G. A. Rullett, J. Phys. Chem. 17, 565 (1913).

Decomposition.

According to Taylor and Rullett, loc. cit., the vapor pressure reaches 1.89 atmospheres at 749°K. This corresponds to the decomposition to 2 Hg(g) + O₂(g), the equilibrium constant being unity at 1.89 atm.

June 30, 1962

HgO

(Ideal Gas) GFW = 216.5894

(Ideal Gas) GFW = 216.5894

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ^o 298	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	0.000	∞	2.153	11.117	11.117	INFINITE
100	6.969	49.187	63.768	11.057	11.057	19.684
200	7.340	54.103	57.837	10.804	7.235	7.906
298	7.859	57.134	54.000	10.000	5.688	4.170
300	7.868	57.183	54.051	9.996	5.662	4.125
400	8.236	59.500	57.446	9.786	4.250	2.332
500	8.469	61.365	59.051	9.605	1.262	
600	8.650	62.923	59.736	9.433	1.560	0.568
700	8.798	64.411	60.111	9.275	2.075	0.256
800	8.924	65.841	60.311	9.130	2.775	0.000
900	9.033	67.224	60.366	8.996	3.722	0.000
1000	9.116	68.564	61.379	8.826	4.671	1.021
1100	9.184	69.865	61.966	8.651	5.622	1.117
1200	9.239	71.128	62.533	8.478	6.581	1.196
1300	9.284	72.362	63.082	8.305	7.550	1.266
1400	9.321	73.577	63.611	8.133	8.488	1.325
1500	9.353	74.772	64.127	7.963	9.448	1.376
1600	9.381	75.948	64.626	7.794	10.409	1.422
1700	9.406	77.105	65.111	7.628	11.366	1.465
1800	9.428	78.244	65.582	7.465	12.316	1.506
1900	9.448	79.366	66.039	7.305	13.260	1.545
2000	9.466	80.473	66.486	7.148	14.200	1.581
2100	9.482	81.567	66.926	6.994	15.136	1.615
2200	9.497	82.648	67.359	6.842	16.069	1.647
2300	9.511	83.716	67.784	6.692	17.000	1.677
2400	9.524	84.772	68.201	6.544	17.929	1.706
2500	9.536	85.817	68.611	6.400	18.857	1.734
2600	9.548	86.852	68.999	6.259	19.784	1.761
2700	9.559	87.877	69.377	6.120	20.710	1.787
2800	9.569	88.892	69.747	5.983	21.636	1.812
2900	9.578	89.897	70.111	5.848	22.562	1.837
3000	9.586	90.892	70.470	5.715	23.488	1.861
3100	9.593	91.877	70.824	5.583	24.414	1.885
3200	9.599	92.852	71.173	5.452	25.340	1.909
3300	9.604	93.817	71.517	5.322	26.266	1.933
3400	9.609	94.772	71.856	5.195	27.192	1.957
3500	9.613	95.717	72.191	5.070	28.118	1.981
3600	9.617	96.652	72.512	4.946	29.044	2.005
3700	9.620	97.577	72.829	4.823	29.970	2.029
3800	9.623	98.492	73.143	4.702	30.896	2.053
3900	9.626	99.397	73.454	4.582	31.822	2.077
4000	9.628	100.292	73.762	4.463	32.748	2.101
4100	9.630	101.177	74.067	4.345	33.674	2.125
4200	9.632	102.052	74.369	4.228	34.600	2.149
4300	9.634	102.917	74.668	4.112	35.526	2.173
4400	9.636	103.772	74.964	4.000	36.452	2.197
4500	9.638	104.617	75.257	3.888	37.378	2.221
4600	9.639	105.452	75.547	3.778	38.304	2.245
4700	9.640	106.277	75.834	3.669	39.230	2.269
4800	9.641	107.092	76.118	3.561	40.156	2.293
4900	9.642	107.897	76.400	3.454	41.082	2.317
5000	9.643	108.692	76.679	3.348	42.008	2.341
5100	9.644	109.477	76.956	3.243	42.934	2.365
5200	9.645	110.252	77.231	3.139	43.860	2.389
5300	9.646	111.017	77.504	3.036	44.786	2.413
5400	9.647	111.772	77.775	2.934	45.712	2.437
5500	9.648	112.517	78.044	2.832	46.638	2.461
5600	9.649	113.252	78.311	2.731	47.564	2.485
5700	9.650	113.977	78.576	2.631	48.490	2.509
5800	9.651	114.692	78.839	2.531	49.416	2.533
5900	9.652	115.397	79.100	2.432	50.342	2.557
6000	9.653	116.092	79.359	2.333	51.268	2.581

June 30, 1967

MERCURY MONOXIDE (HgO)

(IDEAL GAS)

GFW = 216.5894

Ground State Configuration ¹IΔH_{f,0}^o = [11] kcal/molS_{298.15}^o = [57] gibbs/molΔH_{f,298.15}^o = [10] kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
0	1

ω₀X_e = [680] cm⁻¹ω₀X_e = [4.7] cm⁻¹

σ = 1

B_e = [0.336] cm⁻¹r_e = [1.84] Å

Heat of Formation

The heat of formation (ΔH_{f,298}^o) of HgO(g) is estimated to be 10 ± 15 kcal/mol. This value is obtained from the heat of formation of PbO(g) and comparison of the heats of formation of analogous lead and mercury compounds using the method of Karapet'yants (1). The corresponding dissociation energy (D₀) of HgO(g) is 64 ± 15 kcal/mol.

Heat Capacity and Entropy

The equilibrium internuclear separation (r_e) of HgO(g) is estimated from the corresponding quantity for PbO(g) and comparison of Hg-X and Pb-X bond distances for cases in which values of both distances are known. The rotational constant B_e is calculated from r_e. The fundamental vibrational frequency ω₀ is estimated from Guggenheimer's relation for multiple bonded molecules (2). The anharmonic vibrational term ω₀X_e is calculated from ω₀(4ω₀ + 2ω_e). The value of ω₀ is calculated from the Morse potential function. The ground state configuration is estimated from the building-up principle (3), the united atom theory (3), and from analogy with BeO.

References

1. M. Kh. Karapet'yants, Russ. J. Inorg. Chem. (English Transl.) **10**, 837 (1965).
2. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.



Mercury Monoiodide, Dimeric (Hg_2I_2)
(Crystal) Mol. Wt. = 655.04

INTERIM TABLE

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _p
100					
200					
298	25.300	57.670	28.462	26.545	19.457
300	25.323	57.670	28.463	26.532	19.328
400	26.126	62.812	28.463	26.532	14.064
500	27.170	67.228	28.463	26.532	10.109
600	27.740	71.263	28.463	26.532	
700	28.180	76.249	28.463	26.532	7.031
800	28.560	80.507	28.463	26.532	3.881
900	28.890	84.347	28.463	26.532	1.190
1000	29.190	87.777	28.463	26.532	0.1975
1100	29.461	90.777	28.463	26.532	2.302
1200	29.703	93.561	28.463	26.532	3.814
1300	29.923	96.122	28.463	26.532	4.889
1400	30.120	98.491	28.463	26.532	5.765
1500	30.300	102.772	28.463	26.532	6.580
			28.463	26.532	7.113

MERCURY MONOIODIDE, DIMERIC (Hg_2I_2) (Crystal)

Mol. Wt. = 655.04
 $\Delta H_f^\circ 298.15 = -28.462 \pm 0.5 \text{ kcal. mole}^{-1}$
 $S^\circ 298.15 = 57.670 \pm 2.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 563^\circ\text{K}$
 $\Delta H_m = [6.5] \pm 2.0 \text{ kcal. mole}^{-1}$

Heat of Formation. The average value of the cell measurements of W. C. Vosburgh, J. Amer. Chem. Soc. 50, 2386 (1928); E. Cohen Zeits. f. physik. Chemie 94, 210 (1920); T. Yoshida, J. Chem. Soc. Japan 48, 435 (1927); L. W. Øholm, Acta. Soc. Scientiarum Fennicae 41, 1 (1913) and the calorimetric values of R. Varot, Ann. Chim. Phys. (7) 9, 91 (1896) and W. Nernst, Zeits. f. Physik. Chemie 2, 23 (1888) was adopted.

Heat Capacity and Entropy. The heat capacity at 298.15° was taken from National Bureau of Standards (U.S.) Circular 500 (1952) and was estimated above this by analogy with mercurous chloride. The entropy was obtained from the heat and free energy of formation obtained from the cell measurements listed under heat of formation.

Melting. P. Yvon, Comp. Rend. 76, 1607 (1873) gives 563°K for the melting point. The heat of melting was estimated by assuming the entropy of melting per atom to be the same as that for mercuric iodide.



Mercury Moniodide, Dimeric (Hg_2I_2)
(Liquid) Mol. Wt. = 655.04 **INTERIM TABLE**

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _P
0							
100							
200							
298	25.300	66.868		.000	- 23.021	- 23.846	17.479
300	25.323	67.025		.037	- 23.022	- 23.851	17.374
400	32.600	74.872		2.784	- 23.022	- 23.851	16.791
500	32.600	82.167		6.054	- 23.022	- 23.851	16.191
600	32.600	88.020		9.314	- 23.022	- 23.851	15.581
700	32.600	93.116		12.574	- 23.022	- 23.851	14.971
800	32.600	97.458		15.834	- 23.022	- 23.851	14.361
900	32.600	101.309		19.094	- 23.022	- 23.851	13.751
1000	32.600	104.783		22.353	- 23.022	- 23.851	13.141
1100	32.600	107.850		25.613	- 23.022	- 23.851	12.531
1200	32.600	110.587		28.873	- 23.022	- 23.851	11.921
1300	32.600	113.000		32.133	- 23.022	- 23.851	11.311
1400	32.600	115.122		35.393	- 23.022	- 23.851	10.701
1500	32.600	117.961		38.653	- 23.022	- 23.851	10.091

March 31, 1962

MERCURY MONIODIDE, DIMERIC (Hg_2I_2) (Liquid)

Mol. Wt. = 655.04

ΔH°_f 298.15 = [-23.021 ± 2.5] kcal. mole⁻¹

$S^\circ_{298.15}$ = [66.868 ± 8.0] cal. deg.⁻¹ mole⁻¹

T_m = 563°K

ΔH°_m = [6.5 ± 2.0] kcal. mole⁻¹

T_b = [630]°K (decomp.)

Heat of Formation. Calculated from ΔH°_f (crystal) and the estimated heat of melting and heat capacity.

Heat Capacity and Entropy. C_p was estimated as 1.33 times the heat capacity of mercuric iodide. The entropy was calculated from S° crystal, the estimated ΔH°_m and the heat capacities of solid and liquid.

Melting and Vaporization. The melting point was given by P. Yvon, Comp. Rend. 76, 1607 (1873); the heat of melting was estimated from that of mercuric iodide, by assuming the entropies of melting per atom to be equal. Mercurous iodide decomposes to $\text{Hg}(g)$ and $\text{HgI}_2(g)$ at the boiling point which was estimated from the free energy change of the reaction.

Hg_2I_2

Hg_2I_2

Iodine, Monatomic (I)

(Ideal Gas) Mol. Wt. = 126.91

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f kcal. mole ⁻¹	ΔF _f kcal. mole ⁻¹	Log K _f
100	4.900	37.000	INFINITE	25.633	25.633	INFINITE
200	4.968	47.200	1.481	25.633	25.633	4.549
300	4.968	53.184	2.988	25.633	25.633	12.712
400	4.968	57.184	4.314	25.537	16.800	12.314
500	4.968	59.752	5.471	25.537	16.800	12.314
600	4.968	61.658	6.459	18.229	10.787	3.929
700	4.968	62.924	7.272	18.229	10.787	3.929
800	4.968	63.687	7.871	18.229	10.787	3.929
900	4.968	64.073	8.350	18.229	10.787	3.929
1000	4.970	64.196	8.709	18.412	5.775	1.262
1100	4.973	64.070	8.968	18.455	4.509	.896
1200	4.977	63.703	9.168	18.488	3.239	.590
1300	4.984	63.184	9.324	18.542	1.966	.331
1400	4.993	62.571	9.458	18.609	.690	.108
1500	5.004	61.816	9.578	18.688	-.591	.086
1600	5.018	61.039	9.679	18.772	-1.873	.256
1700	5.034	60.144	9.737	18.717	-3.158	.406
1800	5.052	59.132	9.773	18.762	-4.447	.540
1900	5.072	58.006	9.793	18.809	-5.737	.660
2000	5.093	56.667	9.816	18.857	-7.031	.768
2100	5.115	55.116	9.825	18.907	-8.326	.866
2200	5.137	53.454	9.824	18.956	-9.624	.956
2300	5.160	51.683	9.818	19.011	-10.925	1.038
2400	5.182	49.803	9.805	19.066	-12.227	1.113
2500	5.204	47.815	9.785	19.121	-13.532	1.183
2600	5.226	45.720	9.759	19.179	-14.840	1.247
2700	5.247	43.517	9.728	19.238	-16.149	1.307
2800	5.267	41.208	9.692	19.298	-17.460	1.363
2900	5.286	38.894	9.651	19.360	-18.774	1.415
3000	5.304	36.573	9.605	19.422	-20.091	1.464
3100	5.321	34.247	9.556	19.486	-21.409	1.509
3200	5.336	31.916	9.502	19.551	-22.729	1.552
3300	5.351	29.581	9.444	19.616	-24.051	1.593
3400	5.364	27.241	9.381	19.682	-25.376	1.631
3500	5.376	24.896	9.313	19.749	-26.701	1.667
3600	5.387	22.548	9.240	19.816	-28.030	1.702
3700	5.397	20.196	9.162	19.884	-29.360	1.734
3800	5.406	17.841	9.079	19.952	-30.692	1.765
3900	5.414	15.480	8.991	20.020	-32.025	1.795
4000	5.421	13.116	8.898	20.089	-33.362	1.823
4100	5.427	10.752	8.800	20.157	-34.697	1.849
4200	5.432	8.388	8.698	20.225	-36.035	1.875
4300	5.436	6.024	8.591	20.293	-37.377	1.900
4400	5.439	3.660	8.479	20.360	-38.720	1.923
4500	5.442	1.296	8.362	20.427	-40.062	1.946
4600	5.444	57.077	8.239	20.494	-41.406	1.967
4700	5.446	54.719	8.112	20.560	-42.754	1.988
4800	5.446	52.360	7.980	20.626	-44.101	2.008
4900	5.447	50.001	7.843	20.691	-45.450	2.027
5000	5.447	47.642	7.701	20.755	-46.801	2.046
5100	5.446	45.283	7.554	20.820	-48.153	2.063
5200	5.445	42.924	7.402	20.882	-49.507	2.081
5300	5.444	40.565	7.245	20.945	-50.860	2.097
5400	5.442	38.206	7.083	21.006	-52.214	2.113
5500	5.440	35.847	6.916	21.066	-53.572	2.129
5600	5.438	33.488	6.744	21.126	-54.931	2.146
5700	5.436	31.129	6.567	21.185	-56.289	2.158
5800	5.433	28.770	6.385	21.243	-57.648	2.172
5900	5.431	26.411	6.198	21.300	-59.009	2.186
6000	5.428	24.052	6.006	21.356	-60.370	2.199

December 31, 1961

IODINE, MONATOMIC (I)

(IDEAL GAS)

MOL. WT. = 126.91

ΔH_f⁰ = 25.633 ± .010 kcal. mole⁻¹

ΔH_f⁰ 298 = 25.537 kcal. mole⁻¹

Ground State = 2P_{3/2}

S₂₉₈⁰ = 43.184 cal. mole⁻¹ deg.⁻¹

Electronic Levels and Multiplicities

ω, cm. ⁻¹	g _i	ω, cm. ⁻¹	g _i	ω, cm. ⁻¹	g _i
0	4	67082.12	4	68549.77	6
7603.15	2	68586.96	2	68586.00	6
54533.46	6	64990.01	4	68612.02	4
61819.81	4	65844.49	6	71850.	14
60896.27	2	65670.00	8	72750.	24
56092.86	4	66020.64	6	75300.	80
63186.76	2	66355.21	4	77110.	64
64906.34	6	67288.45	4	79210.	128
				81440.	218

Thermodynamic Functions.

Atomic constants were taken from G. E. Moore [U. S. Natl. Bur. Standards Circ. 467, Vol. III (1958)]. The higher levels were averaged. Calculated thermodynamic functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards, 55, 147 (1955)].

Heat of Formation.

The dissociation energy of diatomic iodine is given as D₀⁰ = 12452.5 ± 1.5 cm.⁻¹ by R. D. Verma [J. Chem. Phys. 32, 738 (1960)]. Converting to calories and combining with the heat of sublimation of iodine yields the heat of formation of the ideal monatomic gas. Evans, Munson, and Wagman [loc. cit.] list several investigations of the dissociation energy from equilibrium data. These are all less precise than the spectroscopic value and are not given any weight. The "best" average of the thermal data yields D₀⁰ = 35.568 kcal. mole⁻¹ (spectroscopic = 35.606 kcal. mole⁻¹).

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	78.138	-	INFINITE
100	10.756	13.527	36.237	- 3.038	- 78.250	- 77.922	170.206
200	12.074	20.500	26.565	- 1.213	- 78.301	- 77.574	44.769
298	12.614	25.427	25.427	0.000	- 78.370	- 77.205	56.592
300	12.621	25.505	25.427	- 0.023	- 78.372	- 77.197	56.238
400	12.850	28.172	25.921	1.254	- 86.987	- 75.022	32.792
500	13.232	32.083	24.875	2.604	- 86.196	- 75.023	
600	13.695	34.534	27.853	3.949	- 86.025	- 72.803	26.519
700	14.297	36.686	29.049	5.357	- 85.793	- 70.617	22.046
800	14.975	38.591	29.513	6.918	- 85.513	- 68.482	18.105
900	15.725	40.246	31.175	8.384	- 85.122	- 66.452	14.705
1000	16.550	42.144	32.188	9.956	- 84.684	- 64.501	
1100	17.400	43.746	33.167	11.637	- 83.093	- 61.262	12.172
1200	17.880	45.251	34.112	13.364	- 80.314	- 57.493	10.471
1300	18.255	46.653	35.003	15.055	- 76.483	- 53.151	7.063
1400	17.930	47.970	35.903	16.805	- 71.687	- 48.571	6.765
1500	17.908	48.210	36.749	18.692	- 66.008	- 43.046	5.880
1600	17.960	50.268	37.564	20.486	- 59.166	- 39.575	5.088
1700	17.881	51.457	38.350	22.283	- 51.284	- 35.152	4.269
1800	17.695	52.455	39.097	24.082	- 42.684	- 30.760	3.420
1900	17.403	53.455	39.837	25.882	- 33.484	- 26.447	3.218
2000	16.900	54.382	40.541	27.682	- 24.284	- 22.247	

Dec. 31, 1961; June 30, 1967

$\Delta H_f^\circ = -78.14 \pm 0.1$ kcal/mol	$\Delta H_f^\circ = -78.37 \pm 0.1$ kcal/mol
$\Delta H_{298.15}^\circ = -78.37 \pm 0.1$ kcal/mol	$\Delta H_{298.15}^\circ = -78.37 \pm 0.1$ kcal/mol
$\Delta H_m^\circ = 5.74$ kcal/mol	
$\Delta H_{298.15}^\circ$ (to monomer) = 48.37 kcal/mol	
$\Delta H_{298.15}^\circ$ (to dimer) = 55.84 kcal/mol	

Heat of Formation

The heats of solution of KI(c) have been critically reviewed by V. B. Parker, U. S. Natl. Bur. Std. NBS-RS-2, 1965. Six pertinent results are quoted in the table below. Adopting the best value, $\Delta H_{298}^\circ = 4.86 \pm 0.03$ kcal/mol, reported by Parker, and $\Delta H_f^\circ = -60.32$ and -13.19 kcal/mol for K^+ (H_2O) and I^- (H_2O), respectively, obtained from U.S. Natl. Bur. Std. Tech. Note 270-1, 1965, we obtain ΔH_{298}° (KI, c) = -78.37 ± 0.1 kcal/mol, which is adopted.

ΔH_f° , kcal/mol*	Temperature, °C	n**	Investigator
4.830 \pm 0.05	19	200	J. Thomsen, Thermochemische Untersuchungen, J. Barth Verlag, Leipzig, 1882-86.
4.897 \pm 0.04	25	18	J. Wülf and E. Lange, Z. Physik. Chem. 116, 161 (1925).
4.873	25	500	E. Lange and W. Martin, Z. Physik. Chem. 1480, 233 (1937).
4.790 \pm 0.10	20.5	600	M. M. Popov, S. M. Skuratov, and M. M. Strel'tsova, Zhur. Obshch. Khim. 10, 2023 (1940).
5.020	24.5	18.5	M. Bobtelsky and R. D. Lairech, J. Chem. Soc. 1950, 3612 (1950).
4.830 \pm 0.07	25	75000	A. F. Kapustinskii and S. I. Drakin, Zhur. Fiz. Khim. 28, 581 (1952).

*Values are adjusted to 298.15°K and to infinite dilution.

**n is the number of moles of H_2O per mole of KI(c) in solution.

Heat Capacity and Entropy

The low temperature heat capacities are based on those measured by W. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) A242, 467 (1957), 2.86 - 268.0°K. The adopted values are in good agreement with the Cp values reported by W. W. Scallies, Phys. Rev. 112, 49 (1958), 2 - 7°K. The data of K. Clusius, J. Goldmann, and A. Perlick, Z. Naturforsch. 4A, 424 (1949), 10.27 - 269.9°K, appear to be too low in the temperature range 70 - 270°K and are not used. Low temperature enthalpies, 83 - 273°K, have been measured by F. Koref, Ann. Physik 2, 49 (1911). The value of S_{298}° is derived based on the adopted low temperature heat capacities, using $S_{298}^\circ = 0.0033$ eu.

The high temperature enthalpies were determined by S. M. Skuratov and S. A. Lapushkin, Russ. J. Gen. Chem. (English Transl.) 21, 2485 (1951), 623 - 923°K; A. S. Dworin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 1, 1964, 854 - 954°K; and C. B. Cooper, J. Chem. Phys. 21, 777 (1953), 297 - 973°K. Heat Capacities are derived from the enthalpies by a curve fitting method which requires a smooth joint with the low temperature Cp. Enthalpy values used in the curve fit include smooth values calculated from the equation of Skuratov and the value $H_{954}^\circ - H_{298}^\circ = 9.2$ kcal/mol from Dworin. Deviation of the input values from the selected enthalpies are all less than 0.3 percent, while the deviations of the data of Cooper range from ± 1.0 percent at 570°K to -1.6 percent at 974°K. Since the latter point is 20° above the melting point, there appears to be an error in Cooper's measurement of temperature. Cp above the melting point is obtained by graphical extrapolation.

Melting Data

Tm has been reported to be 953, 952 and 954°K by R. C. Ray and V. Dayal, Trans. Faraday Soc. 32, 741 (1936); T. E. Phipps and E. G. Partridge, J. Am. Chem. Soc. 51, 1331 (1929); and J. W. Johnson and M. A. Bredig, J. Phys. Chem. 52, 604 (1958), respectively. The last value is adopted. The heat of melting was determined by A. S. Dworin and M. A. Bredig, J. Phys. Chem. 54, 269 (1960), using drop calorimetry.

Heat of Sublimation

The difference between ΔH_{298}° for KI(g) and KI(c) is ΔH_{298}° (to monomer). The ΔH_{298}° (to dimer) is calculated as the enthalpy change for the following reaction: $2KI(c) = K_2I_2(g)$.

Potassium Iodide (KI)
(Liquid) GFW = 166.0064

T, °K	C _p ^o	S ^o - (C ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	17.300	27.273	27.273	0.000	- 74.156	54.358
300	17.300	27.380	27.273	+0.32	- 74.764	54.020
400	17.300	32.357	27.952	1.762	- 76.934	40.335
500	17.300	36.217	29.233	3.492	- 81.708	31.735
600	17.300	39.371	30.668	5.222	- 81.153	25.401
700	17.300	42.038	32.106	6.952	- 80.588	21.592
800	17.300	44.348	33.495	8.682	- 80.021	18.458
900	17.300	46.386	34.817	10.412	- 79.455	16.037
1000	17.300	48.208	36.066	12.142	- 78.888	14.114
1100	17.300	49.457	37.264	13.872	- 78.289	12.388
1200	17.300	51.363	38.361	15.602	- 77.680	10.744
1300	17.300	52.747	39.415	17.332	- 77.002	9.198
1400	17.300	54.029	40.414	19.062	- 76.258	7.769
1500	17.300	55.223	41.362	20.792	- 75.448	6.415
1600	17.300	56.339	42.263	22.522	- 74.572	5.125
1700	17.300	57.388	43.122	24.252	- 73.630	3.898
1800	17.300	58.377	43.943	25.982	- 72.625	2.732
1900	17.300	59.312	44.727	27.712	- 71.554	1.625
2000	17.300	60.200	45.479	29.442	- 70.424	0.573
2100	17.300	61.044	46.200	31.172	- 69.236	-0.513
2200	17.300	61.849	46.893	32.902	- 68.000	-1.614
2300	17.300	62.618	47.560	34.632	- 66.725	-2.732
2400	17.300	63.354	48.203	36.362	- 65.412	-3.865
2500	17.300	64.060	48.823	38.092	- 64.063	-5.019

POTASSIUM IODIDE (KI)

(LIQUID)

GFW = 166.0064

$$S_{298.15}^{\circ} = 27.273 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -74.771 \text{ kcal/mol}$$

$$T_m = 954^{\circ}\text{K}$$

$$\Delta H_m^{\circ} = 5.74 \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = 45.62 \text{ kcal/mol}$$

Heat of Formation

The heat of formation, ΔH_{298}° , is obtained from ΔH_{298}° (KI, c) by adding ΔH_m° and the difference between $H_{954}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived as 17.3 gibbs/mol from the enthalpy measurements, 954 - 1014°K, by A. S. Dworkin, private communication, Oak Ridge National Laboratory, Oak Ridge, Tenn., Dec. 1, 1984. This Cp value is adopted in the temperature range 298 - 2500°K. S_{298}° is obtained in a manner analogous to that of the heat of formation.

Melting Data

See KI(c) table for details.

Vaporization Data

The boiling point, Tb = 1618°K, is calculated as the temperature at which the sum of the partial pressures of KI(g) and $K_2I_2(g)$ over KI(l) equals one atmosphere. The value of ΔH_v° is calculated as the heat required to produce one mole of vapor mixture, which contains 78 percent monomer (KI) and 22 percent dimer (K_2I_2) at Tb.

Tb was reported as 1603 and 1590 K by H. von Wartenberg and P. Albrecht, Z. Elektrochem. 21, 162 (1921), and O. Ruff and S. Mugdan, Z. Anorg. Chem. 117, 147 (1921), respectively.

Potassium Iodide (KI)
(Ideal Gas)

GFW = 166.0064

POTASSIUM IODIDE (KI)

(IDEAL GAS)

GFW = 166.0064

IK

T, K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	INFINITE	2.468	-20.176	-20.176	INFINITE
100	8.104	52.335	69.459	1.712	-20.226	-32.378	71.847
200	8.709	54.191	62.512	.868	-29.562	-34.393	39.769
298	8.872	61.704	61.704	.000	-30.000	-35.651	29.065
300	8.874	61.759	61.704	.016	-30.009	-35.710	28.929
400	8.843	62.073	62.073	.000	-31.459	-42.573	19.405
500	8.893	62.325	62.325	1.805	-35.824	-44.573	16.459
600	9.027	67.968	63.457	2.674	-38.898	-45.736	16.659
700	9.055	69.362	64.204	3.610	-39.159	-46.855	14.659
800	9.081	70.572	64.926	4.610	-39.415	-47.837	13.066
900	9.107	71.663	65.514	5.626	-39.510	-48.686	11.896
1000	9.127	72.668	66.066	6.638	-39.532	-50.000	10.859
1100	9.148	73.475	66.882	7.252	-39.105	-49.980	9.930
1200	9.169	74.271	67.465	8.164	-39.184	-49.147	8.951
1300	9.190	75.006	68.017	9.086	-39.177	-48.313	8.122
1400	9.211	75.688	68.541	10.006	-39.210	-47.476	7.411
1500	9.231	76.324	69.039	11.026	-39.242	-46.638	6.795
1600	9.251	76.921	69.513	11.859	-39.272	-45.795	6.255
1700	9.272	77.482	69.966	12.774	-39.301	-44.953	5.779
1800	9.292	78.013	70.398	13.706	-39.330	-44.104	5.355
1900	9.312	78.516	70.816	14.636	-39.358	-43.262	4.976
2000	9.332	78.994	71.209	15.566	-39.387	-42.411	4.635
2100	9.351	79.449	71.591	16.503	-39.415	-41.562	4.325
2200	9.371	79.885	71.958	17.439	-39.444	-40.713	4.044
2300	9.391	80.302	72.312	18.377	-39.472	-39.861	3.788
2400	9.411	80.702	72.653	19.317	-39.500	-39.007	3.552
2500	9.431	81.097	72.993	20.259	-39.529	-38.153	3.335
2600	9.450	81.487	73.302	21.203	-39.558	-37.295	3.135
2700	9.470	81.814	73.610	22.149	-39.526	-36.439	2.950
2800	9.490	82.139	73.919	23.097	-39.495	-35.579	2.777
2900	9.510	82.462	74.228	24.047	-39.464	-34.715	2.616
3000	9.529	82.785	74.536	25.000	-39.433	-33.853	2.466
3100	9.549	83.128	74.756	25.953	-39.402	-32.988	2.326
3200	9.568	83.431	75.022	26.909	-39.370	-32.118	2.194
3300	9.588	83.726	75.281	27.867	-39.339	-31.250	2.070
3400	9.607	84.012	75.534	28.827	-39.308	-30.377	1.953
3500	9.626	84.291	75.780	29.789	-39.276	-29.500	1.842
3600	9.647	84.563	76.020	30.759	-39.245	-28.621	1.738
3700	9.667	84.827	76.255	31.714	-39.214	-27.738	1.638
3800	9.687	85.085	76.484	32.685	-39.183	-26.851	1.544
3900	9.707	85.342	76.708	33.655	-39.152	-25.960	1.455
4000	9.726	85.593	76.926	34.627	-39.121	-25.068	1.369
4100	9.746	85.824	77.140	35.600	-39.090	-24.163	1.288
4200	9.765	86.059	77.350	36.576	-39.059	-23.255	1.210
4300	9.785	86.289	77.555	37.554	-39.028	-22.343	1.136
4400	9.804	86.514	77.754	38.531	-38.997	-21.422	1.064
4500	9.824	86.734	77.953	39.514	-38.966	-20.507	.995
4600	9.844	86.950	78.147	40.494	-38.935	-19.592	.929
4700	9.864	87.162	78.336	41.483	-38.904	-18.680	.865
4800	9.883	87.370	78.522	42.471	-38.873	-17.762	.804
4900	9.903	87.574	78.704	43.460	-38.842	-16.840	.744
5000	9.922	87.775	78.884	44.451	-38.811	-15.910	.687
5100	9.942	87.971	79.061	45.444	-38.780	-14.984	.631
5200	9.962	88.164	79.234	46.440	-38.749	-14.059	.576
5300	9.981	88.354	79.404	47.437	-38.718	-13.134	.523
5400	9.999	88.541	79.571	48.437	-38.687	-12.209	.472
5500	10.021	88.725	79.736	49.437	-38.656	-11.284	.422
5600	10.040	88.906	79.894	50.440	-38.625	-10.359	.373
5700	10.060	89.083	80.054	51.445	-38.594	-9.434	.325
5800	10.079	89.259	80.215	52.451	-38.563	-8.509	.278
5900	10.099	89.431	80.371	53.457	-38.532	-7.584	.231
6000	10.119	89.601	80.522	54.472	-38.501	-6.659	.186

Dec. 31, 1961 June 30, 1967

Ground State Configuration 1s²

S_{298.15} = 61.704 gibbs/mol

ΔH_f⁰ = -29.2 ± 0.5 kcal/mol

ΔH_f⁰_{298.15} = -30.0 ± 0.5 kcal/mol

Electronic Levels and Quantum Weights

$$\frac{E_i, \text{cm}^{-1}}{0} \quad \frac{g_i}{1}$$

$\omega_e = 186.287 \pm 0.04 \text{ cm}^{-1}$ $\omega_e x_e = 0.8725 \pm 0.006 \text{ cm}^{-1}$ $\sigma = 1$

$B_e = 0.06072 \text{ cm}^{-1}$ $a_e = 0.000267 \text{ cm}^{-1}$ $r_e = 3.0478 \text{ Å}$

Heat of Formation

The heat of formation is derived from the sublimation and vaporization data analyzed below. Many investigators have determined the total pressures of KI(g) and KI₂(g) over KI(s) or KI(l) by static methods or "apparent" pressures by Knudsen effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see K₂I₂(g) table] which are consistent with the dimer-monomer equilibrium data of Batz (3). Second and third law analyses of the monomer pressures show reasonable agreement. The selected value of ΔH_f⁰₂₉₈ = -30.0 ± 0.5 kcal/mol is also in good agreement with -30.23 ± 1.15 and -30.46 kcal/mol derived from D₀⁰ = 3.32 ± 0.05 and 3.33 eV reported by Gaydon (12) and Herzberg (11), respectively.

Investigator	Reaction**	Temperature, °K	No. of Points	ΔH _f ⁰ ₂₉₈ , kcal/mol	Drift, kcal/mol	ΔH _f ⁰ ₂₉₈ , kcal/mol
1. Wartenberg-Albrecht	(B)	1336.2-1606.2	9	47.79±0.38	44.76	-2.110.2
2. Ruff-Mugdan	(B)	1319.2-1590.2	12	49.38±1.03	44.59	-3.3±0.7
3. Flock-Rodhush	(B)	1116.1-1275.7	8	45.43±0.03	44.75	-0.6±0.1
4. Greiner-Jellinek	(B)	1453.2	1	-	45.24	-29.53
5. Niwa	(A)	803.2-873.2	8	46.11±0.35	48.30	2.6±0.4
6. Zimm-Mayer	(A)	618.4-892.9	10	48.66±0.25	48.47	-0.4±0.3
7. Cogan-Kimball	(A)	721.5-897.7	29	48.52±0.40	47.73	-1.1±0.5
8. Bridgers	(A)	597.5-891.7	25	48.48±0.22	47.72	-1.1±0.3

*Based on the third law ΔH_f⁰₂₉₈ value.

** (A) KI(c) = KI(g); (B) KI(l) = KI(g)

Heat Capacity and Entropy

The ground state configuration is obtained from Herzberg (11). The adopted values of ω_e , $\omega_e x_e$, B_e , a_e , and r_e were determined using millimeter wave molecular beam spectroscopy by Rusk and Gordy (12), and corrected to the average isotopic species. Similar values were reported by Honig et al. (13) from microwave spectra, except ω_e which was given as 193.74 cm⁻¹. The value of ω_e was derived to be 200 and 173 cm⁻¹ by Barrow and Caunt (14) and Rice and Klemperer (15). The moment of inertia is 4.5979 x 10⁻³⁸ g cm².

References

1. H. von Wartenberg and P. Albrecht, Z. Elektrochem. 22, 182 (1921).
2. O. Ruff and S. Mugdan, Z. Anorg. Chem. 112, 147 (1921).
3. E. F. Flock and W. H. Rodhush, J. Am. Chem. Soc. 48, 2522 (1926).
4. B. Greiner and K. Jellinek, Z. Physik. Chem. (Leipzig) 165, 97 (1933).
5. K. Niwa, J. Fac. Sci. Hokkaido Imperial Univ., Ser. III, 2, 201 (1938).
6. B. H. Zimm and J. E. Mayer, J. Chem. Phys. 12, 362 (1944).
7. G. E. Cogan and G. E. Kimball, J. Chem. Phys. 16, 1035 (1948).
8. H. E. Bridgers, Ph.D. Thesis, The Ohio State University, 1953.
9. S. Batz, ORNL-2933, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1960.
10. A. G. Gaydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.
11. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.
12. J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).
13. A. Honig, M. L. Storch and C. H. Townes, Phys. Rev. 36, 629 (1954).
14. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) A213, 120 (1953).
15. S. A. Rice and W. Klemperer, J. Chem. Phys. 22, 573 (1957).

IK

Lithium Iodide (LiI)

(Crystal) GFW = 133.8434

T, °K	Cp	$\frac{\text{gibbs/mol}}{S^\circ}$	$\frac{-(G^\circ - H^\circ_{298})/T}{\text{kcal/mol}}$	$\frac{\Delta H^\circ}{\text{kcal/mol}}$	ΔG°	Log Kp
0						
100						
200						
298	11.970	20.500	20.500	0.000	-64.451	47.244
300	11.995	20.574	20.400	-0.022	-64.450	46.952
400	12.770	24.110	20.677	1.253	-66.527	39.154
500	13.372	27.025	21.904	2.561	-72.599	27.640
600	14.020	28.517	22.669	3.939	-72.192	22.372
700	14.800	31.472	24.066	5.572	-71.896	18.023
800	15.615	33.787	25.221	7.568	-71.628	14.560
900	16.415	35.697	26.221	8.528	-71.028	11.941
1000	17.200	37.480	27.259	10.221	-70.478	10.347
1100	17.975	39.137	28.264	11.960	-69.880	9.429
1200	18.619	40.619	29.236	13.724	-69.252	8.345
1300	19.235	41.952	30.173	15.533	-68.600	7.129
1400	19.815	43.152	31.073	17.330	-67.934	6.760
1500	18.210	44.706	31.940	19.148	-67.255	6.906
1600	18.210	45.681	32.775	20.969	-66.572	6.296
1700	18.210	46.026	33.575	22.670	-65.895	5.875
1800	18.210	46.026	34.333	24.431	-65.215	5.473
1900	18.210	49.010	35.099	26.432	-64.531	4.938
2000	18.210	49.944	35.818	28.253	-63.846	4.438
2100	18.210	50.833	36.512	30.074	-63.161	3.961
2200	18.210	51.680	37.185	31.895	-62.472	3.506
2300	18.210	52.490	37.830	33.716	-61.786	3.073
2400	18.210	53.265	38.457	35.537	-61.100	2.666
2500	18.210	54.008	39.065	37.358	-60.404	2.286

LITHIUM IODIDE (LiI)

(CRYSTAL)

GFW = 133.8434

ILI

 $\Delta H^\circ_f = \text{Unknown}$ $\Delta H^\circ_{298.15} = -64.55 \pm 0.1 \text{ kcal/mol}$ $\Delta H^\circ_m = 3.50 \text{ kcal/mol}$ $S^\circ_{298.15} = [20.5] \text{ gibbs/mol}$ $T_m = 742^\circ \text{K}$

Heat of Formation.

The heat of formation, $\Delta H^\circ_{298}(\text{LiI}, c) = -64.55 \text{ kcal/mol}$, was calculated from the heat of solution of lithium iodide (c) at infinite dilution and the ionic heats of formation of $\text{Li}^+(\text{COOH}_2\text{O})$ and $\text{I}^-(\text{COOH}_2\text{O})$.

V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," NSRDS-NBS 2, Apr. 1, 1965, reviewed the literature heat of solution data and gave the "best" value, $\Delta H^\circ_{298}(\text{Li}^+\text{COOH}_2\text{O}) = -15.130 \pm 75 \text{ cal/mol}$ for $\text{LiI}(c) \rightarrow \text{LiI}(\text{COOH}_2\text{O})$ at 298.15°K . The ionic heat of formation, $\Delta H^\circ_{298}(\text{I}^+\text{COOH}_2\text{O}) = -66.49 \text{ kcal/mol}$, was calculated from $\Delta H^\circ_{298}(\text{LiOH}\cdot\text{COOH}_2\text{O}) = -121.46 \text{ kcal/mol}$ (see JANAF $\text{LiOH}(c)$ Table, Mar. 31, 1966) with $\Delta H^\circ_{298}(\text{OH}^-\text{COOH}_2\text{O}) = -54.97 \text{ kcal/mol}$ from NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Oct. 1, 1965. The value $\Delta H^\circ_{298}(\text{I}^-\text{COOH}_2\text{O}) = -13.19 \text{ kcal/mol}$ was also obtained from NBS Technical Note 270-1. Combination of the ionic heats of formation of $\text{Li}^+(\text{COOH}_2\text{O})$ and $\text{I}^-(\text{COOH}_2\text{O})$ gives the heat of formation of $\text{LiI}(\text{COOH}_2\text{O})$, $\Delta H^\circ_{298} = -79.68 \text{ kcal/mol}$.

Heat Capacity and Entropy.

A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1964, has measured the enthalpy changes by the drop method ($642\text{--}802^\circ \text{K}$), yielding ($H^\circ_{42} - H^\circ_{298}$) = 6.0 kcal/mol for the crystal at the melting point. Heat capacities derived from his data were $C_p 692^\circ = 14.8$ and $C_p 772 = 15.1 \text{ cal/deg-mol}$ for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of $\text{LiCl}(c)$, $\text{NaCl}(c)$ and $\text{NaI}(c)$.

The entropy, $S^\circ_{298.15} = 20.5 \text{ eu}$, was estimated by adding the entropy difference between $\text{NaI}(c)$ and $\text{NaCl}(c)$ to the entropy of lithium chloride (c) at 298.15°K . Comparisons with other alkali halides give results within $\pm 0.5 \text{ eu}$ of this value.

K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960), 592 (1961), has estimated the heat capacities ($C_p = 12.30 + 2.44 \times 10^{-3} T \text{ gibbs/mol}$) and the entropy ($S^\circ_{298} = 17.50 \text{ eu}$).

Melting Data.

The selected heat of fusion ($\Delta H^\circ_{298} = 3.50 \text{ kcal/mol}$) was obtained from enthalpy measurements in a drop calorimeter by A. S. Dworin and M. A. Bredig, J. Phys. Chem. 64, 269 (1960).

(Liquid) GFW = 133.8434

T, °K	Cp*	$\frac{S^\circ}{T}$	$-(C^\circ - H^\circ_{\text{mol}})/T$	$H^\circ - H^\circ_{\text{mol}}$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	15.100	23.568	23.568	+0.00	- 61.749	- 62.564	45.861
300	15.100	23.601	23.568	+0.28	- 61.744	- 62.570	45.562
400	15.100	26.456	25.199	+3.048	- 60.111	- 62.121	27.133
500	15.100	31.375	25.179	+3.048	- 60.111	- 62.121	27.133
600	15.100	34.128	26.531	+4.568	- 60.762	- 60.756	22.130
700	15.100	36.456	27.767	+6.068	- 60.402	- 59.451	16.561
800	15.100	38.472	29.000	+7.578	- 60.034	- 58.197	13.898
900	15.100	40.183	30.233	+9.098	- 59.666	- 56.943	11.235
1000	15.100	41.681	31.466	+10.598	- 59.298	- 55.682	12.200
1100	15.100	43.281	32.699	+12.098	- 58.931	- 54.429	10.866
1200	15.100	44.881	33.932	+13.598	- 58.564	- 53.176	9.761
1300	15.100	46.481	35.165	+15.098	- 58.194	- 51.923	8.831
1400	15.100	48.081	36.398	+16.598	- 57.826	- 50.670	8.061
1500	15.100	49.681	37.631	+18.098	- 57.459	- 49.417	7.355
1600	15.100	48.938	36.652	+19.598	- 55.083	- 49.495	6.761
1700	15.100	49.854	37.402	+21.468	- 52.758	- 47.206	6.069
1800	15.100	50.717	38.118	+22.678	- 50.403	- 44.129	5.358
1900	15.100	51.538	38.800	+23.878	- 48.028	- 41.052	4.647
2000	15.100	52.308	39.459	+25.098	- 45.653	- 38.071	4.160
2100	15.100	53.045	40.088	+27.208	- 43.278	- 35.084	3.651
2200	15.100	53.747	40.693	+28.718	- 40.903	- 32.121	3.191
2300	15.100	54.418	41.276	+30.228	- 38.528	- 29.154	2.762
2400	15.100	55.061	41.841	+31.738	- 36.153	- 26.187	2.369
2500	15.100	55.677	42.378	+33.248	- 33.778	- 23.220	2.004

Sept. 30, 1961; June 30, 1968

LITHIUM IODIDE (LiI)

(LIQUID)

GFW = 133.8434

 $\Delta H^\circ_{298.15} = [23.568]$ gibbs/mol $\Delta H^\circ_{298.15} = -61.749$ kcal/mol $\Delta H^\circ_{\text{m}} = 3.50$ kcal/mol ΔH° (to equilibrium mixture) = 23.3 kcal/mol ΔH° (to monomer only) = [32.6] kcal/mol $T_m = 742^\circ\text{K}$ T_b (to equilibrium mixture) = 1449°K T_b (to monomer only) = [1497]°K

Heat of Formation.

The heat of formation was calculated from that of the crystal by adding the heat of fusion and the difference between $H^\circ_{742} - H^\circ_{298}$ for crystal and liquid.

Heat Capacity and Entropy.

A. S. Dworin, private communication, Oak Ridge National Laboratory, Dec. 1964, has derived the heat capacity, $C_p = 15.1$ gibbs/mol, from enthalpy measurements, $742 - 802^\circ\text{K}$, by the drop method. The liquid heat capacity was assumed to be a constant, 15.1 gibbs/mol. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See LiI(c) table for detail.

Vaporization Data.

T_b (to monomer only) is determined as the temperature at which the Gibbs energy change (ΔG°) for the reaction $\text{LiI(l)} = \text{LiI(g)}$ approaches zero. The corresponding enthalpy change (ΔH°) at boiling point is the heat of vaporization ΔH°_v (to monomer only).

T_b (to equilibrium mixture) is the temperature at which the sum of the calculated partial vapor pressures of LiI(g) and $\text{Li}_2\text{I}_2(\text{g})$ reaches one atmosphere (trimer and higher polymer have been neglected in calculation). This value is in good agreement with the boiling point of 1444°K from the least squares fit of the total vapor pressure data measured by O. Ruff and S. Mugdan, Z. anorg. Chem. **117**, 147 (1921). ΔH°_v (to equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 30.44 mole percent of dimer. For detailed information see LiI(g) and $\text{Li}_2\text{I}_2(\text{g})$ tables.

Lithium Iodide (LiI)

(Ideal Gas) GFW = 133.8434

OPW = 133.8434 [Li]

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-2.222	-21.290	-21.290	INFINITE
100	7.045	62.451	-	-1.526	-21.077	-24.892	54.401
200	7.742	52.280	-	-0.788	-21.068	-28.606	31.260
298	8.263	55.478	-	0.000	-21.750	-32.079	23.515
300	8.270	55.529	55.478	0.015	-21.758	-32.144	23.417
400	8.556	57.951	55.406	0.858	-24.122	-35.472	19.381
500	8.720	59.880	56.435	1.472	-30.437	-37.700	16.479
600	8.824	61.480	57.146	2.400	-30.721	-38.126	14.252
700	8.896	62.840	57.865	3.486	-30.984	-40.566	12.252
800	8.950	64.037	58.564	4.736	-31.234	-41.849	11.433
900	8.993	65.094	59.232	5.276	-31.480	-43.162	10.481
1000	9.029	66.043	59.866	6.177	-31.721	-44.446	9.714
1100	9.060	66.905	60.467	7.082	-31.958	-45.707	9.091
1200	9.087	67.695	61.037	7.986	-32.186	-46.947	8.580
1300	9.113	68.423	61.578	8.880	-32.424	-48.167	8.098
1400	9.136	69.099	62.091	9.811	-32.653	-49.369	7.707
1500	9.159	69.730	62.580	10.736	-32.877	-50.556	7.368
1600	9.180	70.322	63.045	11.643	-33.098	-51.726	7.065
1700	9.201	70.872	63.482	12.542	-33.308	-52.880	6.790
1800	9.221	71.406	63.915	13.463	-33.509	-54.015	6.530
1900	9.240	71.905	64.323	14.406	-33.692	-55.132	6.282
2000	9.260	72.379	64.714	15.331	-33.865	-56.233	6.040
2100	9.278	72.832	65.090	16.249	-34.028	-57.317	5.807
2200	9.297	73.264	65.445	17.148	-34.181	-58.385	5.580
2300	9.315	73.677	65.800	18.117	-34.325	-59.437	5.358
2400	9.334	74.074	66.137	19.050	-34.459	-60.473	5.140
2500	9.352	74.456	66.462	19.984	-34.584	-61.494	4.926
2600	9.370	74.823	66.776	20.920	-34.700	-62.500	4.716
2700	9.387	75.177	67.076	21.859	-34.808	-63.492	4.510
2800	9.403	75.518	67.376	22.792	-34.908	-64.470	4.308
2900	9.423	75.849	67.663	23.739	-35.000	-65.435	4.108
3000	9.440	76.168	67.941	24.682	-35.085	-66.386	3.910
3100	9.458	76.478	68.211	25.627	-35.166	-67.323	3.714
3200	9.475	76.777	68.471	26.572	-35.242	-68.246	3.520
3300	9.493	77.071	68.731	27.522	-35.313	-69.156	3.328
3400	9.510	77.354	68.980	28.473	-35.380	-70.053	3.138
3500	9.527	77.630	69.223	29.424	-35.443	-70.938	2.949
3600	9.545	77.899	69.461	30.378	-35.502	-71.811	2.762
3700	9.563	78.166	69.691	31.329	-35.557	-72.672	2.576
3800	9.579	78.416	69.918	32.280	-35.608	-73.521	2.392
3900	9.597	78.665	70.140	33.249	-35.656	-74.358	2.209
4000	9.614	78.908	70.356	34.210	-35.700	-75.183	2.028
4100	9.631	79.146	70.567	35.172	-35.740	-75.996	1.848
4200	9.647	79.377	70.777	36.130	-35.776	-76.797	1.669
4300	9.665	79.605	70.977	37.102	-35.809	-77.586	1.491
4400	9.682	79.828	71.176	38.069	-35.839	-78.363	1.314
4500	9.699	80.045	71.370	39.038	-35.866	-79.128	1.138
4600	9.717	80.250	71.561	40.009	-35.890	-79.881	0.963
4700	9.734	80.469	71.750	40.983	-35.911	-80.621	0.788
4800	9.751	80.673	71.932	41.956	-35.929	-81.348	0.613
4900	9.768	80.874	72.113	42.931	-35.945	-82.062	0.438
5000	9.785	81.072	72.290	43.909	-35.959	-82.763	0.263
5100	9.802	81.266	72.464	44.888	-35.970	-83.451	0.088
5200	9.819	81.456	72.635	45.869	-35.979	-84.126	-0.087
5300	9.836	81.643	72.803	46.852	-35.986	-84.789	-0.262
5400	9.853	81.827	72.969	47.837	-35.991	-85.440	-0.437
5500	9.870	82.008	73.131	48.823	-35.994	-86.078	-0.612
5600	9.887	82.186	73.292	49.811	-35.996	-86.704	-0.787
5700	9.904	82.363	73.450	50.800	-35.997	-87.318	-0.962
5800	9.921	82.534	73.604	51.791	-35.998	-87.920	-1.137
5900	9.938	82.704	73.757	52.784	-35.999	-88.511	-1.312
6000	9.955	82.871	73.908	53.776	-35.999	-89.091	-1.487

Sept. 30, 1961, June 30, 1966

LITHIUM IODIDE (LiI)

(IDEAL GAS)

Ground State Configuration 1Σ

ΔH₀⁰ = -21.3 ± 2 kcal/molΔH_{298.15}⁰ = -21.75 ± 2 kcal/molS_{298.15}⁰ = 55.478 gibbs/mol

Electronic Levels and Quantum Weights

$$\frac{\epsilon, \text{ cm}^{-1}}{g_i}$$

$$\frac{g_i}{0}$$
ω_e = 498.16 cm⁻¹

σ = 1

ω_ex_e = 3.39 cm⁻¹r_e = 2.3919 ÅQ_e = 0.00416 cm⁻¹

Heat of Formation.

The heat of formation (ΔH_{f298} (LiI, g) = -21.75 ± 2 kcal/mol) was calculated from the selected heat of sublimation and the heat of formation for lithium iodide (c). The heat of sublimation has been determined mass-spectrometrically from the ion intensity measurement (2nd law method) by L. N. Gorokhov, Dokl. Akad. Nauk SSSR 142, 113 (1962), as ΔH_s⁰ (to monomer) = 42.9 ± 0.6 and ΔH_s⁰ (to dimer) = 43.2 ± 0.4 kcal/mol in the temperature range from 626-722°K. Gorokhov also reported the partial vapor pressure of monomeric lithium iodide (P_{monomer} = 3 X 10⁻³ mm Hg) and the ratio of dimer to monomer (P_{dimer}/P_{monomer} = 6) which have been used for third law calculation. Using the same technique, L. Friedman, J. Chem. Phys. 23, 477 (1955), reported the heats of sublimation as ΔH_s⁰ (to monomer) = 41.9 ± 0.5 and ΔH_s⁰ (to dimer) = 40.8 ± 0.5 kcal/mol in the temperature range from 630° to 730°K. J. Berkowitz, H. A. Tammann and W. A. Chupka, J. Chem. Phys. 36, 2170 (1962) have also studied the lithium iodide vapor in the mass spectrometer and reported the second law and third law values of the heat of dimerization at 800°K as 37.9 and 40.4 kcal/mol, respectively. Using the JANAF thermodynamic functions, all the heats of sublimation and dimerization at different temperatures have been reduced to 298°K and summarized in the following table. The total vapor pressure over the liquid has been measured by a boiling point method in the temperature range 1223° to 1413°K by O. Ruff and S. Muggen, Z. anorg. Chem. 117, 147 (1921). (Their data have been quoted by H. von Wartenberg and H. Schulz, Z. Elektrochem. 27, 568 (1921).) In order to have good agreement between the calculated vapor pressure and the observed total vapor pressure, the heats of sublimation have been so chosen as ΔH_s⁰ (to monomer) = 42.8 kcal/mol and ΔH_s⁰ (to dimer) = 42.6 kcal/mol and the heat of dissociation of dimer, ΔH_d⁰ = 43.0 kcal/mol. The calculated boiling point (to equilibrium mixture) is 1449°K which agrees with 1443°K reported by Wartenberg and Schulz, and also 1462°K by Ruff and Muggen.

Chemical Reaction	Investigator	ΔH _{f298} kcal/mol	
		2nd law	3rd law
LiI(c) → LiI(g)	Gorokhov	44.7	42.2
	Friedman	43.9	—
2LiI(c) → Li ₂ I ₂ (g)	Gorokhov	46.0	41.3
	Friedman	44.1	—
Li ₂ I ₂ (g) → 2LiI(g)	Berkowitz et al.	38.8	41.3
	Friedman	43.7	—
	Gorokhov	43.2	43.1

Heat Capacity and Entropy.

The bond distance and the rotational constants (B_e and α_e), corrected to the isotopic abundance of 7.4% Li⁶ and 92.6% Li⁷, were obtained from the microwave studies by A. Honig, M. Mandel, M. L. Stiche and C. H. Townes, Phys. Rev. 96, 629 (1954). The vibrational constants (ω_e and ω_ex_e) were determined from the infrared spectrum by W. Klemperer, W. G. Norris, A. Buchler and A. O. Emalle, J. Chem. Phys. 33, 1534 (1960).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by R. L. Wilkins, J. Chem. Eng. Data 5, 337 (1960), who used slightly different molecular constants.

[Li]

(Ideal Gas)

GFW = 156.9105

NITROSYL IODIDE (NOI)

(IDEAL GAS)

OPW = 156.9105

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	9.131	56.417	77.041	27.557	27.557	27.557	INFINITE
200	10.543	63.234	68.988	27.330	26.396	26.396	- 27.688
298	11.199	67.561	67.981	26.800	25.581	25.581	- 27.953
300	11.208	67.650	68.026	26.796	24.906	24.906	- 18.144
400	11.607	70.932	68.078	24.647	24.377	24.377	- 13.319
500	11.938	73.559	68.078	19.347	24.813	24.813	- 10.846
600	12.232	75.762	69.847	19.373	25.804	25.804	- 9.436
700	12.492	77.599	70.493	19.407	26.891	26.891	- 8.427
800	12.732	79.059	71.059	19.436	27.978	27.978	- 7.678
900	12.952	80.256	71.571	19.461	29.146	29.146	- 7.078
1000	13.156	81.220	72.040	19.482	30.218	30.218	- 6.604
1100	13.347	82.068	72.462	19.499	31.284	31.284	- 6.216
1200	13.526	82.806	72.842	19.512	32.346	32.346	- 5.891
1300	13.694	83.446	73.177	19.522	33.406	33.406	- 5.623
1400	13.852	84.000	73.471	19.529	34.464	34.464	- 5.380
1500	13.997	84.470	73.732	19.533	35.518	35.518	- 5.175
1600	14.133	84.866	73.966	19.536	36.571	36.571	- 4.995
1700	14.260	85.190	74.177	19.537	37.620	37.620	- 4.836
1800	14.379	85.452	74.366	19.538	38.666	38.666	- 4.696
1900	14.490	85.666	74.534	19.539	39.714	39.714	- 4.568
2000	14.594	85.834	74.683	19.540	40.757	40.757	- 4.454
2100	14.692	85.960	74.816	19.541	41.801	41.801	- 4.350
2200	14.784	86.055	74.936	19.542	42.844	42.844	- 4.256
2300	14.871	86.121	75.045	19.543	43.886	43.886	- 4.171
2400	14.954	86.169	75.145	19.544	44.929	44.929	- 4.091
2500	15.033	86.200	75.237	19.545	45.969	45.969	- 4.019
2600	15.108	86.225	75.322	19.546	47.010	47.010	- 3.952
2700	15.179	86.244	75.400	19.547	48.051	48.051	- 3.889
2800	15.246	86.258	75.472	19.548	49.091	49.091	- 3.829
2900	15.310	86.268	75.538	19.549	50.134	50.134	- 3.778
3000	15.371	86.274	75.600	19.550	51.174	51.174	- 3.728
3100	15.429	86.277	75.657	19.551	52.216	52.216	- 3.681
3200	15.484	86.277	75.710	19.552	53.259	53.259	- 3.637
3300	15.537	86.274	75.759	19.553	54.302	54.302	- 3.597
3400	15.588	86.268	75.804	19.554	55.343	55.343	- 3.557
3500	15.637	86.259	75.845	19.555	56.383	56.383	- 3.521
3600	15.683	86.247	75.882	19.556	57.429	57.429	- 3.486
3700	15.727	86.232	75.916	19.557	58.472	58.472	- 3.452
3800	15.769	86.215	75.946	19.558	59.518	59.518	- 3.423
3900	15.809	86.196	75.973	19.559	60.565	60.565	- 3.394
4000	15.847	86.175	75.997	19.560	61.611	61.611	- 3.366
4100	15.882	86.152	76.019	19.561	62.661	62.661	- 3.340
4200	15.915	86.127	76.038	19.562	63.709	63.709	- 3.315
4300	15.946	86.100	76.054	19.563	64.758	64.758	- 3.291
4400	15.975	86.071	76.068	19.564	65.808	65.808	- 3.269
4500	15.999	86.040	76.079	19.565	66.863	66.863	- 3.247
4600	16.019	86.008	76.088	19.566	67.916	67.916	- 3.227
4700	16.036	85.974	76.095	19.567	68.968	68.968	- 3.207
4800	16.051	85.939	76.100	19.568	69.998	69.998	- 3.188
4900	16.064	85.902	76.104	19.569	71.080	71.080	- 3.170
5000	16.075	85.864	76.107	19.570	72.139	72.139	- 3.153
5100	16.084	85.825	76.109	19.571	73.194	73.194	- 3.137
5200	16.091	85.785	76.110	19.572	74.254	74.254	- 3.121
5300	16.096	85.744	76.111	19.573	75.318	75.318	- 3.106
5400	16.100	85.702	76.112	19.574	76.378	76.378	- 3.090
5500	16.103	85.659	76.113	19.575	77.443	77.443	- 3.077
5600	16.105	85.616	76.114	19.576	78.503	78.503	- 3.064
5700	16.106	85.572	76.115	19.577	79.567	79.567	- 3.051
5800	16.107	85.528	76.116	19.578	80.636	80.636	- 3.039
5900	16.108	85.483	76.117	19.579	81.704	81.704	- 3.026
6000	16.108	85.438	76.118	19.580	82.776	82.776	- 3.015

Mar. 31, 1962; Dec. 31, 1966

Point Group C_s
 $S_{298.15}^{\circ} = [67.56] \text{ gibbs/mol}$
 $\Delta H_f^{\circ} = [27.6 \pm 5] \text{ kcal/mol}$
 $\Delta H_f^{\circ} = [26.8 \pm 5] \text{ kcal/mol}$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	
[1780] (1)	
[440] (1)	
[200] (1)	

Bond Distance: O-N = [1.15] Å

N-I = [2.3] Å

Bond Angle: O-N-I = [120]°

Product of the Moment of Inertia: $I_A I_B I_C = [7.742 \times 10^{-115}] \text{ g}^3 \text{ cm}^6$

Heat of Formation.

The heat of formation (ΔH_f°) for INO (g) is estimated by comparison with those for FNO(g), ClNO(g), BrNO(g), and the related cyanogen halides.

Heat Capacity and Entropy.

The molecular structure and bond angle are estimated by comparison with those for ClNO(g) and BrNO(g). The N-O bond distance is assumed to be the same as that in NO(g). The N-I bond distance (r_{N-I}) is calculated based on an assumption that $r_{ON-Cl} - r_{ON-I} = r_{Cl-I} - r_{I-I}$. The vibrational frequencies are estimated by comparison with those for FNO(g), ClNO(g) and BrNO(g). The three principal moments of inertia are: $I_A = 8.834 \times 10^{-40}$, $I_B = 2.916 \times 10^{-38}$ and $I_C = 3.005 \times 10^{-36} \text{ g cm}^2$.

Sodium Iodide (NaI)

(Crystal) Mol. Wt. = 149.901

T. °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	-0.000	0.000	INFINITE	-	2.933	-68.615	-68.615	INFINITE
100	10.285	10.899	34.195	-2.330	-68.697	-68.488	-68.488	149.676
200	11.915	18.667	24.667	-1.200	-68.743	-68.261	-68.261	74.589
298	12.482	23.542	23.542	-0.000	-68.800	-68.014	-68.014	49.853
300	12.490	23.610	23.542	-0.023	-68.801	-68.009	-68.009	49.542
400	12.860	27.265	24.037	1.293	-76.463	-66.614	-66.614	36.921
500	13.150	30.167	24.082	2.592	-76.664	-66.158	-66.158	28.916
600	13.440	32.591	26.034	3.922	-76.504	-64.071	-64.071	23.337
800	13.910	34.693	28.141	5.280	-76.302	-62.016	-62.016	19.361
900	14.246	36.191	29.221	6.076	-75.793	-57.897	-57.897	14.083
1000	14.508	37.708	30.195	9.513	-75.498	-56.035	-56.035	12.246
1100	14.766	41.103	31.124	10.977	-75.184	-54.105	-54.105	10.749
1200	15.020	42.399	32.010	12.466	-74.866	-52.146	-52.146	9.424
1300	15.272	43.621	32.851	13.971	-74.543	-50.159	-50.159	8.053
1400	15.528	44.782	33.659	15.491	-74.215	-48.143	-48.143	6.735
1500	15.778	45.832	34.441	17.087	-73.877	-46.107	-46.107	5.480
1600	16.027	46.858	35.185	18.677	-73.529	-44.051	-44.051	4.299
1700	16.273	47.837	35.901	20.292	-73.172	-41.977	-41.977	3.177
1800	16.518	48.774	36.580	21.930	-72.806	-39.886	-39.886	2.107
1900	16.760	49.674	37.225	23.595	-72.431	-37.775	-37.775	1.082
2000	17.000	50.540	37.898	25.283	-72.048	-35.648	-35.648	0.000

SODIUM IODIDE (NaI)

(CRYSTAL)

MOL. WT. = 149.901

$$\Delta H_f^o = -68.6 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = -68.15 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_m = 5.64 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = 23.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 933^\circ \text{K.}$$

Heat of Formation.

The heat of formation was obtained as follows:

- (1) $\text{HI} \cdot 100\text{H}_2\text{O} + \text{NaOH} \cdot 100\text{H}_2\text{O} \rightarrow \text{NaI} \cdot 20\text{H}_2\text{O}$
T. W. Richards, A. W. Rowe, J. Am. Chem. Soc. **44**, 684 (1922).
 $\Delta H_{298}^o (\text{kcal. mole}^{-1})$
-13.51 ± 0.02
 - (2) $\text{Na(c)} + 100\text{H}_2\text{O(l)} \rightarrow \text{NaOH} \cdot 100\text{H}_2\text{O} + 1/2\text{H}_2(\text{g})$
S. R. Dunn, L. G. Green, J. Am. Chem. Soc. **80**, 4782 (1958).
-44.069 ± 0.006
 - (3) $\text{NaOH} \cdot 100\text{H}_2\text{O} \rightarrow \text{NaOH} \cdot 100\text{H}_2\text{O} + 900\text{H}_2\text{O(l)}$
National Bureau of Standards Circular 500.
+0.031 ± 0.004
 - (4) $1/2\text{H}_2(\text{g}) + 1/2\text{I}_2(\text{s}) \rightarrow \text{HI(g)}$
JANAF Tables.
+6.30 ± 0.05
 - (5) $\text{HI(g)} + 100\text{H}_2\text{O(l)} \rightarrow \text{HI} \cdot 100\text{H}_2\text{O}$
W. A. Roth, Z. Elektrochem. **50**, 107 (1944).
-19.30 ± 0.05
 - (6) $\text{NaI} \cdot 20\text{H}_2\text{O} \rightarrow \text{NaI(c)} + 20\text{H}_2\text{O(l)}$
J. Wust, E. Lange, Z. physik. Chem. **116**, 161 (1925).
E. Lange, A. L. Robinson, Chem. Revs. **9**, 89 (1931).
Askew, Bullock, Smith, Tinkler, Gatty, Wolfenden, J. Chem. Soc., **1934**, 1368.
+1.75 ± 0.06
- $$(1) + (2) + (3) + (4) + (5) + (6) \text{ gives Na(c)} + 1/2\text{I}_2(\text{s}) \rightarrow \text{NaI(c)}$$
- $$-68.80 \pm 0.2$$

Heat Capacity and Entropy.

Smoothed heat capacities between 3° and 270°K. have been presented by M. T. Berg and J. A. Morrison, Proc. Roy. Soc. (London) **242A**, 467 (1957). Above 270°K. the heat capacity was obtained by comparing with KI(c) on a reduced temperature plot of C_p/T versus T. The values so obtained were increased by 1.4% to bring them into line with the low temperature data.

Melting Data.

A. Dworkin and M. Bredig, J. Phys. Chem. **64**, 269 (1960) have measured both T_m and ΔH_m .

Sodium Iodide (NaI)

(Liquid) Mol. Wt. = 149.901

SODIUM IODIDE (NaI)

(LIQUID)

MOL. WT. = 149.901

INa

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H _{298°)/T}	H°-H _{298°} kcal. mole ⁻¹	ΔH _f ^o kcal. mole ⁻¹	ΔF _f ^o kcal. mole ⁻¹	Log K _f
0						
100	12.482	28.862	28.862	.000	- 63.695	- 64.496
200	28.639	28.862	.029	- 63.696	- 64.500	47.274
300	32.595	29.337	1.291	- 66.358	- 66.637	46.986
400	35.487	30.302	2.592	- 71.559	- 63.715	35.314
500	37.010	31.374	3.922	- 71.399	- 62.158	27.848
600	37.910	32.483	5.472	- 71.005	- 60.650	22.640
700	40.300	33.562	7.022	- 70.600	- 59.198	18.935
800	42.370	34.611	8.571	- 70.192	- 57.797	16.171
900	44.195	35.651	10.122	- 69.785	- 56.441	14.034
1000	45.828	36.695	11.672	- 69.384	- 55.128	12.335
1100	47.304	37.636	13.222	- 68.984	- 53.892	10.932
1200	48.634	38.532	14.772	- 68.584	- 52.724	9.724
1300	49.895	39.385	16.322	- 68.184	- 51.592	8.636
1400	51.044	40.198	17.872	- 67.784	- 50.491	7.639
1500	52.113	40.975	19.422	- 67.384	- 49.425	6.734
1600	53.113	41.717	20.972	- 66.984	- 48.394	5.924
1700	54.053	42.427	22.522	- 66.584	- 47.394	5.210
1800	54.939	43.107	24.072	- 66.184	- 46.424	4.594
1900	55.777	43.761	25.622	- 65.784	- 45.494	4.054
2000	56.572	44.389	27.172	- 65.384	- 44.604	3.510
2100	57.328	44.994	28.722	- 64.984	- 43.744	2.964
2200	58.059	45.577	30.272	- 64.584	- 42.914	2.410
2300	58.738	46.139	31.822	- 64.184	- 42.114	1.854
2400	59.398	46.682	33.372	- 63.784	- 41.344	1.294
2500	60.031	47.207	34.922	- 63.384	- 40.604	.984
2600	60.639	47.715	36.472	- 62.984	- 39.894	.724
2700	61.224	48.208	38.022	- 62.584	- 39.214	.484
2800	61.787	48.686	39.572	- 62.184	- 38.564	.264
2900	62.331	49.149	41.122	- 61.784	- 37.944	.054
3000	62.857					

Sept. 30, 1963

S_{298.15} = 28.862 cal. deg.⁻¹ mole⁻¹
 T_m = 933°K.
 T_b = 1577°K. (equilibrium mixture)

ΔH_f^o 298.15 = -63.695 kcal. mole⁻¹ΔH_m = 5.64 kcal. mole⁻¹

Heat of Formation.

ΔH_f^o 298.15 was calculated from the heat of formation of the crystal plus the heat of melting and the difference between H₉₃₃-H₂₉₈ for crystal and liquid.

Heat Capacity and Entropy.

C_p was estimated assuming each atom contributed 7/5 cal. deg.⁻¹ mole⁻¹. S_{298.15} was calculated in a manner similar to ΔH_f^o 298.15.

Melting Data.

See table for crystal.

Vaporization Data.

The boiling point is that given by K. K. Kelley, U. S. Bureau of Mines Bulletin 363, 1955 from examination of the high temperature vapor pressure.

INa

Lead Moniodide (PbI)

(Ideal Gas) Mol. Wt. = 334.12

INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.262	57.411	26.451	26.451	26.451	INFINITE
200	8.752	63.334	26.410	26.410	26.410	-48.688
300	8.870	66.855	26.076	26.076	26.076	-19.967
400	8.871	66.910	25.692	25.692	25.692	-10.528
500	8.920	69.470	25.344	25.344	25.344	-5.920
600	8.966	73.096	24.961	24.961	24.961	-3.602
700	8.993	75.680	24.586	24.586	24.586	-2.313
800	9.005	76.740	24.226	24.226	24.226	-1.605
900	9.017	77.689	23.882	23.882	23.882	-1.094
1000	9.029	78.549	23.554	23.554	23.554	-0.759
1100	9.039	79.329	23.244	23.244	23.244	-0.588
1200	9.046	80.040	22.951	22.951	22.951	-0.478
1300	9.050	80.693	22.674	22.674	22.674	-0.405
1400	9.052	81.300	22.412	22.412	22.412	-0.363
1500	9.053	81.861	22.164	22.164	22.164	-0.334
1600	9.054	82.386	21.930	21.930	21.930	-0.312
1700	9.054	82.874	21.709	21.709	21.709	-0.294
1800	9.054	83.325	21.500	21.500	21.500	-0.280
1900	9.054	83.747	21.302	21.302	21.302	-0.269
2000	9.054	84.139	21.115	21.115	21.115	-0.260
2100	9.054	84.499	20.938	20.938	20.938	-0.253
2200	9.054	84.827	20.771	20.771	20.771	-0.248
2300	9.054	85.123	20.614	20.614	20.614	-0.244
2400	9.054	85.387	20.466	20.466	20.466	-0.241
2500	9.054	85.619	20.327	20.327	20.327	-0.239
2600	9.054	85.818	20.196	20.196	20.196	-0.237
2700	9.054	85.984	20.073	20.073	20.073	-0.236
2800	9.054	86.117	19.957	19.957	19.957	-0.235
2900	9.054	86.216	19.848	19.848	19.848	-0.234
3000	9.054	86.281	19.745	19.745	19.745	-0.233
3100	9.054	86.313	19.647	19.647	19.647	-0.232
3200	9.054	86.322	19.554	19.554	19.554	-0.231
3300	9.054	86.318	19.466	19.466	19.466	-0.230
3400	9.054	86.301	19.383	19.383	19.383	-0.229
3500	9.054	86.271	19.305	19.305	19.305	-0.228
3600	9.054	86.228	19.232	19.232	19.232	-0.227
3700	9.054	86.172	19.164	19.164	19.164	-0.226
3800	9.054	86.103	19.101	19.101	19.101	-0.225
3900	9.054	86.021	19.042	19.042	19.042	-0.224
4000	9.054	85.927	18.987	18.987	18.987	-0.223
4100	9.054	85.822	18.936	18.936	18.936	-0.222
4200	9.054	85.707	18.888	18.888	18.888	-0.221
4300	9.054	85.582	18.843	18.843	18.843	-0.220
4400	9.054	85.447	18.801	18.801	18.801	-0.219
4500	9.054	85.302	18.762	18.762	18.762	-0.218
4600	9.054	85.147	18.726	18.726	18.726	-0.217
4700	9.054	84.982	18.693	18.693	18.693	-0.216
4800	9.054	84.807	18.662	18.662	18.662	-0.215
4900	9.054	84.622	18.633	18.633	18.633	-0.214
5000	9.054	84.427	18.606	18.606	18.606	-0.213
5100	9.054	84.222	18.581	18.581	18.581	-0.212
5200	9.054	84.007	18.557	18.557	18.557	-0.211
5300	9.054	83.782	18.534	18.534	18.534	-0.210
5400	9.054	83.547	18.512	18.512	18.512	-0.209
5500	9.054	83.302	18.491	18.491	18.491	-0.208
5600	9.054	83.047	18.471	18.471	18.471	-0.207
5700	9.054	82.782	18.452	18.452	18.452	-0.206
5800	9.054	82.507	18.434	18.434	18.434	-0.205
5900	9.054	82.222	18.417	18.417	18.417	-0.204
6000	9.054	81.927	18.401	18.401	18.401	-0.203

June 30, 1952

Lead Moniodide (PbI)

Mol. Wt. = 334.12

ΔH_f⁰ 298.15 = 25.7 ± 9.2 kcal. mole⁻¹

S_{298.15} = 66.855 cal. deg.⁻¹ mole⁻¹

Ground State Configuration ²Π_{1/2}

Electronic Levels and Multiplicities

E, cm. ⁻¹	g _i
0	2
[8000]	2

ω_e = 160.5 cm.⁻¹

ω_ex_e = 0.25 cm.⁻¹

B_e = [0.02940] cm.⁻¹

α_e = [0.00000] cm.⁻¹

σ = 1

Heat of Formation. ΔH_f⁰ 298.15 was calculated from the dissociation energy of PbI(g) reported by A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1953.

Heat Capacity and Entropy. Ground state configuration, ω_e and ω_ex_e were obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950. B_e and α_e were estimated by comparison with the corresponding values for the other diatomic halide molecules. Electronic levels and multiplicities were estimated from those for PbF(g).

Titanium Moniodide (TiI)
(Ideal Gas) GFW = 174.8044

TITANIUM MONIODIDE (TiI)

GFW = 174.8044

Ground State Configuration [⁴F]

(IDEAL GAS)

$$\Delta H_f^\circ = [65.8 \pm 10.0] \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = [65.5 \pm 10.0] \text{ kcal/mol}$$

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
0	[4]
[1000]	[4]
[2000]	[4]
[4000]	[4]
[6000]	[4]
[8000]	[4]
[10000]	[4]

$$\omega_e = [240] \text{ cm}^{-1} \quad \omega_e x_e = [1.67] \text{ cm}^{-1} \quad \sigma = 1$$

$$B_e = [0.062] \text{ cm}^{-1} \quad \alpha_e = [0.00043] \text{ cm}^{-1} \quad r_e = [2.8] \text{ \AA}$$

Heat of Formation

The heat of formation, ΔH_f° , of TiI (g) is calculated from the dissociation energy, D_0° , which is estimated as 73 kcal/mol. This estimate is obtained from the relation $D(\text{TiI}_2) < D(\text{TiI}) < D(\text{TiI}_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF₂(g) by Zmbov and Margrave (1).

Heat Capacity and Entropy

The vibrational frequency, ω_e , and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenheimer's relation (2). B_e is calculated from r_e . The ground state term and electronic levels are estimated from the ground state multiplet of Ti⁺ (3). α_e is estimated from the Morse potential function.

References

1. K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
2. K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
3. C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

T, °K	Cp°	S°	-(G°-H° ₃₀₀)/T	H°-H° ₃₀₀	ΔH°	ΔG°	Log Kp
0	7.900	54.980	INFINITE	-2.983	65.866	65.866	INFINITE
100	7.786	54.942	77.005	-1.764	61.456	61.456	134.315
200	6.647	60.666	65.048	-	65.608	56.957	62.240
298	6.192	64.225	64.224	-	65.500	52.673	36.611
300	6.201	64.281	64.225	-0.17	65.494	52.594	36.315
400	6.015	64.193	64.193	1.987	65.712	57.612	16.768
500	6.039	64.239	64.239	2.961	65.712	42.715	15.559
600	6.039	64.239	64.239	3.952	65.712	40.284	12.559
700	6.039	64.239	64.239	4.943	65.712	37.769	10.313
800	6.039	64.239	64.239	5.934	65.712	35.260	8.067
900	6.039	64.239	64.239	6.925	65.712	32.751	5.819
1000	6.039	64.239	64.239	7.916	65.712	30.242	3.571
1100	6.032	64.232	64.232	8.907	65.712	27.733	1.323
1200	6.032	64.232	64.232	9.898	65.712	25.224	-0.925
1300	6.032	64.232	64.232	10.889	65.712	22.715	-3.173
1400	6.032	64.232	64.232	11.880	65.712	20.206	-5.421
1500	6.032	64.232	64.232	12.871	65.712	17.697	-7.669
1600	6.032	64.232	64.232	13.862	65.712	15.188	-9.917
1700	6.032	64.232	64.232	14.853	65.712	12.679	-12.165
1800	6.032	64.232	64.232	15.844	65.712	10.170	-14.413
1900	6.032	64.232	64.232	16.835	65.712	7.661	-16.661
2000	6.032	64.232	64.232	17.826	65.712	5.152	-18.909
2100	6.032	64.232	64.232	18.817	65.712	2.643	-21.157
2200	6.032	64.232	64.232	19.808	65.712	0.134	-23.405
2300	6.032	64.232	64.232	20.799	65.712	-2.375	-25.653
2400	6.032	64.232	64.232	21.790	65.712	-4.884	-27.901
2500	6.032	64.232	64.232	22.781	65.712	-7.393	-30.149
2600	6.032	64.232	64.232	23.772	65.712	-9.902	-32.397
2700	6.032	64.232	64.232	24.763	65.712	-12.411	-34.645
2800	6.032	64.232	64.232	25.754	65.712	-14.920	-36.893
2900	6.032	64.232	64.232	26.745	65.712	-17.429	-39.141
3000	6.032	64.232	64.232	27.736	65.712	-19.938	-41.389
3100	6.032	64.232	64.232	28.727	65.712	-22.447	-43.637
3200	6.032	64.232	64.232	29.718	65.712	-24.956	-45.885
3300	6.032	64.232	64.232	30.709	65.712	-27.465	-48.133
3400	6.032	64.232	64.232	31.700	65.712	-29.974	-50.381
3500	6.032	64.232	64.232	32.691	65.712	-32.483	-52.629
3600	6.032	64.232	64.232	33.682	65.712	-34.992	-54.877
3700	6.032	64.232	64.232	34.673	65.712	-37.501	-57.125
3800	6.032	64.232	64.232	35.664	65.712	-40.010	-59.373
3900	6.032	64.232	64.232	36.655	65.712	-42.519	-61.621
4000	6.032	64.232	64.232	37.646	65.712	-45.028	-63.869
4100	6.032	64.232	64.232	38.637	65.712	-47.537	-66.117
4200	6.032	64.232	64.232	39.628	65.712	-50.046	-68.365
4300	6.032	64.232	64.232	40.619	65.712	-52.555	-70.613
4400	6.032	64.232	64.232	41.610	65.712	-55.064	-72.861
4500	6.032	64.232	64.232	42.601	65.712	-57.573	-75.109
4600	6.032	64.232	64.232	43.592	65.712	-60.082	-77.357
4700	6.032	64.232	64.232	44.583	65.712	-62.591	-79.605
4800	6.032	64.232	64.232	45.574	65.712	-65.100	-81.853
4900	6.032	64.232	64.232	46.565	65.712	-67.609	-84.101
5000	6.032	64.232	64.232	47.556	65.712	-70.118	-86.349
5100	6.032	64.232	64.232	48.547	65.712	-72.627	-88.597
5200	6.032	64.232	64.232	49.538	65.712	-75.136	-90.845
5300	6.032	64.232	64.232	50.529	65.712	-77.645	-93.093
5400	6.032	64.232	64.232	51.520	65.712	-80.154	-95.341
5500	6.032	64.232	64.232	52.511	65.712	-82.663	-97.589
5600	6.032	64.232	64.232	53.502	65.712	-85.172	-99.837
5700	6.032	64.232	64.232	54.493	65.712	-87.681	-102.085
5800	6.032	64.232	64.232	55.484	65.712	-90.190	-104.333
5900	6.032	64.232	64.232	56.475	65.712	-92.699	-106.581
6000	6.032	64.232	64.232	57.466	65.712	-95.208	-108.829

June 30, 1964; Sept. 30, 1964; June 30, 1968; Dec. 31, 1968

Zirconium Moniodide (ZrI)

(Ideal Gas) Mol. Wt. = 218.13

ZIRCONIUM MONIODIDE (ZrI)

(IDEAL GAS)

MOL. WT. = 218.13

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔG _f ^o	Log K _p
0	0.000	INFINITE	2.411	141.763	141.763	INFINITE
100	7.664	96.651	73.535	141.926	137.330	-300.120
200	8.681	86.668	66.668	141.988	132.111	-185.144
298	9.093	83.068	63.068	141.990	128.575	-94.244
300	8.625	85.923	65.868	141.293	128.497	-93.605
400	8.924	68.477	66.216	138.760	124.358	-67.943
500	8.983	70.475	66.875	133.423	121.239	-52.991
600	9.025	72.116	67.616	133.171	118.825	-43.240
700	9.059	73.510	68.381	132.901	116.555	-36.397
800	9.089	74.722	69.082	132.620	114.124	-31.176
900	9.116	75.794	69.769	132.333	111.630	-27.155
1000	9.142	76.756	70.421	132.040	109.568	-23.945
1100	9.166	77.629	71.037	131.732	107.335	-21.325
1200	9.190	78.427	71.620	131.457	105.179	-19.155
1300	9.214	79.163	72.172	131.169	103.085	-17.359
1400	9.237	79.847	72.696	130.833	101.014	-15.768
1500	9.259	80.485	73.194	129.513	98.767	-14.419
1600	9.282	81.083	73.669	129.188	96.944	-13.241
1700	9.304	81.647	74.122	128.857	94.936	-12.204
1800	9.327	82.179	74.555	128.521	92.952	-11.285
1900	9.349	82.684	74.969	128.179	90.985	-10.465
2000	9.371	83.164	75.367	127.831	89.034	-9.729
2100	9.393	83.622	75.750	127.479	87.103	-9.045
2200	9.415	84.059	76.117	127.122	85.355	-8.479
2300	9.437	84.478	76.472	126.761	83.688	-7.952
2400	9.459	84.880	76.814	126.390	82.038	-7.470
2500	9.481	85.267	77.144	126.017	80.400	-7.028
2600	9.503	85.639	77.464	125.649	78.779	-6.622
2700	9.524	85.995	77.773	125.287	77.172	-6.266
2800	9.546	86.335	78.073	124.924	75.576	-5.969
2900	9.568	86.660	78.364	124.561	74.000	-5.577
3000	9.590	86.975	78.647	124.197	72.429	-5.276
3100	9.612	87.280	78.922	123.830	70.870	-4.994
3200	9.633	87.576	79.189	123.457	69.324	-4.734
3300	9.655	87.862	79.449	123.076	67.794	-4.490
3400	9.677	88.131	79.703	122.688	66.270	-4.260
3500	9.698	88.392	79.950	122.296	64.756	-4.043
3600	9.720	88.645	80.191	121.897	63.252	-3.840
3700	9.742	89.037	80.426	121.494	61.756	-3.648
3800	9.764	89.292	80.656	121.087	60.276	-3.466
3900	9.785	89.546	80.881	120.673	58.802	-3.295
4000	9.807	89.794	81.101	120.253	57.334	-3.132
4100	9.829	90.036	81.316	119.826	55.880	-2.979
4200	9.850	90.273	81.526	119.394	54.433	-2.832
4300	9.872	90.505	81.732	118.957	52.991	-2.693
4400	9.894	90.733	81.934	118.513	51.552	-2.560
4500	9.915	90.955	82.132	118.060	50.131	-2.435
4600	9.937	91.173	82.326	117.606	48.715	-2.314
4700	9.959	91.387	82.517	117.151	47.303	-2.199
4800	9.980	91.597	82.704	116.694	45.899	-2.083
4900	10.002	91.803	82.887	116.233	44.500	-1.961
5000	10.024	92.005	83.068	115.768	43.107	-1.838
5100	10.045	92.204	83.245	115.306	41.719	-1.713
5200	10.067	92.399	83.419	114.840	40.334	-1.588
5300	10.088	92.591	83.590	114.369	38.954	-1.463
5400	10.110	92.780	83.759	113.894	37.579	-1.338
5500	10.132	92.966	83.925	113.415	36.207	-1.213
5600	10.154	93.149	84.086	112.932	34.834	-1.088
5700	10.175	93.329	84.248	112.445	33.461	-0.963
5800	10.197	93.506	84.406	111.954	32.088	-0.838
5900	10.219	93.680	84.562	111.459	30.715	-0.713
6000	10.240	93.852	84.715	110.960	29.342	-0.588

Sept. 30, 1964

$$\Delta H_f^o = [141.8 \pm 10.0] \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = [65.67] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^o = [141.5 \pm 10.0] \text{ kcal. mole}^{-1}$$

Electronic Levels and Multiplicities

E , cm. ⁻¹	g_i
0	4

$$\omega_e x_e = [1.2] \text{ cm.}^{-1}$$

$$\omega_e = [0.03789] \text{ cm.}^{-1}$$

$$\omega_e = [0.00020] \text{ cm.}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

$$\omega_e = [2.9] \text{ Å}^{-1}$$

Heat of Formation

The dissociation energy was estimated from a correlation of the JANAP values for TiCl(g), TiI(g), and ZrCl(g). The resulting value, 29.7 kcal. mole⁻¹, was employed with auxiliary JANAP heats of formation for Zr(g) and I(g) in calculating ΔH_f^o 298.15°

Heat Capacity and Entropy

The vibrational frequency was estimated from those of TiI(g), TiCl(g), and the alkali halides. The ground state configuration was assumed to be analogous to the ground term of TiCl(g) as given by E. A. Shenoy, et al., Optics and Spectroscopy, 12, 359 (1962). The internuclear distance was estimated from those of TiBr(g), TiI(g) and ZrI(g).

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° _T	Log K _P
0	0.000	INFINITE	0.000	0.000	0.000
100	10.911	16.581	2.424	0.000	0.000
200	12.325	22.696	1.247	0.000	0.000
298	13.011	27.786	0.000	0.000	0.000
300	13.026	27.839	0.000	0.000	0.000
400	13.251	28.632	0.000	0.000	0.000
500	13.488	29.438	0.000	0.000	0.000
600	13.736	30.252	0.000	0.000	0.000
700	14.005	31.074	0.000	0.000	0.000
800	14.294	31.903	0.000	0.000	0.000
900	14.601	32.738	0.000	0.000	0.000
1000	14.927	33.580	0.000	0.000	0.000
1100	15.272	34.429	0.000	0.000	0.000
1200	15.636	35.285	0.000	0.000	0.000
1300	16.018	36.148	0.000	0.000	0.000
1400	16.418	37.018	0.000	0.000	0.000
1500	16.835	37.894	0.000	0.000	0.000
1600	17.268	38.776	0.000	0.000	0.000
1700	17.716	39.664	0.000	0.000	0.000
1800	18.179	40.557	0.000	0.000	0.000
1900	18.656	41.456	0.000	0.000	0.000
2000	19.147	42.361	0.000	0.000	0.000
2100	19.651	43.272	0.000	0.000	0.000
2200	20.168	44.189	0.000	0.000	0.000
2300	20.697	45.112	0.000	0.000	0.000
2400	21.238	46.041	0.000	0.000	0.000
2500	21.791	46.976	0.000	0.000	0.000
2600	22.355	47.917	0.000	0.000	0.000
2700	22.930	48.864	0.000	0.000	0.000
2800	23.515	49.817	0.000	0.000	0.000
2900	24.110	50.776	0.000	0.000	0.000
3000	24.715	51.741	0.000	0.000	0.000
3100	25.330	52.712	0.000	0.000	0.000
3200	25.954	53.689	0.000	0.000	0.000
3300	26.587	54.672	0.000	0.000	0.000
3400	27.229	55.661	0.000	0.000	0.000
3500	27.879	56.656	0.000	0.000	0.000
3600	28.537	57.657	0.000	0.000	0.000
3700	29.202	58.664	0.000	0.000	0.000
3800	29.874	59.677	0.000	0.000	0.000
3900	30.553	60.696	0.000	0.000	0.000
4000	31.239	61.721	0.000	0.000	0.000
4100	31.931	62.752	0.000	0.000	0.000
4200	32.629	63.789	0.000	0.000	0.000
4300	33.333	64.832	0.000	0.000	0.000
4400	34.042	65.881	0.000	0.000	0.000
4500	34.756	66.936	0.000	0.000	0.000
4600	35.475	67.997	0.000	0.000	0.000
4700	36.198	69.064	0.000	0.000	0.000
4800	36.925	70.137	0.000	0.000	0.000
4900	37.656	71.216	0.000	0.000	0.000
5000	38.391	72.301	0.000	0.000	0.000
5100	39.129	73.392	0.000	0.000	0.000
5200	39.871	74.489	0.000	0.000	0.000
5300	40.617	75.592	0.000	0.000	0.000
5400	41.367	76.699	0.000	0.000	0.000
5500	42.120	77.812	0.000	0.000	0.000
5600	42.876	78.930	0.000	0.000	0.000
5700	43.635	80.054	0.000	0.000	0.000
5800	44.397	81.183	0.000	0.000	0.000
5900	45.161	82.318	0.000	0.000	0.000
6000	45.928	83.459	0.000	0.000	0.000

September 30, 1961

IODINE (I₂)

(REFERENCE STATE)

MOL. WT. = 253.82

0°K to 366.75°K Crystal
366.75°K to 458.59°K Liquid
458.59°K to 8000°K Ideal Diatomic Gas

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal.

The recent measurements of D. A. Shirley and W. P. Giauque [J. Am. Chem. Soc. 81, 4778 (1959)] over the temperature range 13° to 327°K are adopted, no weight being given to the earlier work of E. Lange [Z. Physik. Chem. 110, 343 (1924)], which deviate by 1% or more. L. G. Carpenter and T. F. Harle [Phil. Mag. 23, 193 (1937)] measured the heat capacity of crystalline and liquid iodine by an adiabatic method. Their data are in poor agreement with Shirley and Giauque in the range 275° to 330°K and are given no weight. K. J. Frederick and J. H. Hildebrand [J. Am. Chem. Soc. 80, 1436 (1958)] measured the enthalpy of crystalline and liquid iodine relative to 298°K by the method of mixtures. For calibration they used a slug of copper. The enthalpy of copper which they used now appears to be too high [K. K. Kelley, U. S. Bur. Mines Bull. 594 (1960)]. The results of Frederick and Hildebrand were corrected by a factor which varied linearly from zero at 300°K to 0.995 at 400°K and 0.990 at 500°K. These corrected enthalpies and the heat capacities of Shirley and Giauque above 298°K were used to derive the equations for crystalline iodine:

$$H_p - H_{298} = -12.1048 T + 0.029505 T^2 - 6.686 \times 10^{-5} T^3 + 3228.65$$

$$C_p = -12.1048 + 0.059012 T + 6.686 \times 10^{-5} T^2$$

Heat Capacity of Liquid, Melting Point, and Heat of Melting.

For the liquid, the corrected results of Frederick and Hildebrand give:

$$H_p - H_{298} = 19.281 T - 2516.5$$

$$C_p = 19.281$$

The melting point given by Frederick and Hildebrand is 113.6°C. The difference in the heat content equations at the melting point gives the heat of melting as 3708.7 cal. mole⁻¹.

Heat of Sublimation, Ideal Gas Functions.

See tables for ideal gases for details.

Iodine (I₂)
(Liquid) Mol. Wt. = 253.82

IODINE (I₂) (LIQUID) MOL. WT. = 253.82

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0						
100	14.281	35.936	.000	3.232	.794	.582
200	14.281	36.055	.036	3.236	.779	.567
300	14.281	36.175	.071	3.240	.764	.552
400	14.281	36.295	.106	3.244	.749	.537
500	14.281	36.415	.141	3.248	.734	.522
600	14.281	36.535	.176	3.252	.719	.507
700	14.281	36.655	.211	3.256	.704	.492
800	14.281	36.775	.246	3.260	.689	.477
900	14.281	36.895	.281	3.264	.674	.462
1000	14.281	37.015	.316	3.268	.659	.447

$$\Delta H_f^\circ 298 = +3.232 \text{ kcal. mole}^{-1}$$

$$S^\circ 298 = 35.936 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

$$\Delta H_m = 3708.7 \text{ cal. mole}^{-1}$$

$$\Delta H_v = 10025.5 \text{ cal. mole}^{-1}$$

$$T_m = 386.75^\circ\text{K}$$

$$T_b = 458.39^\circ\text{K}$$

Heat of Formation.

Obtained as the heat of fusion calculated to 298.15°K by adding H_{386.75}-H_{298.15} for solid and subtracting H_{386.75}-H_{298.15} for liquid.

Heat Capacity.

The liquid heat capacity of 19.281 cal. mole⁻¹ deg.⁻¹ derived from the data of Frederick and Hildebrand (see Reference State) was extrapolated back to 298.15°K and up to 1000°K.

Entropy.

The value at 400°K calculated for the reference state was back calculated to 298.15°K by means of the constant heat capacity of 19.281 cal. mole⁻¹ deg.⁻¹

Vaporization.

See ideal gas tables for details.

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	.000	INFINITE	2.41H	15.660	15.660	INFINITE
100	7.920	53.037	60.958	15.657	11.811	25.812
200	8.619	58.797	63.083	15.654	8.094	8.884
300	8.814	62.261	62.281	14.924	4.631	3.394
400	8.817	62.336	62.281	14.916	4.567	3.327
500	8.901	62.605	62.628	10.631	1.317	.720
		62.677	62.628	10.631	1.317	.720
600	9.040	68.511	68.025	.000	.000	.000
700	9.225	71.101	65.485	.000	.000	.000
800	9.404	72.165	53.364	.000	.000	.000
900	9.577	73.119	46.818	.000	.000	.000
1000	9.747	73.983	42.308	.000	.000	.000
1100	9.907	74.762	39.599	.000	.000	.000
1200	10.057	75.462	37.427	.000	.000	.000
1300	10.197	76.097	35.657	.000	.000	.000
1400	10.327	76.667	34.257	.000	.000	.000
1500	10.447	77.177	33.177	.000	.000	.000
1600	10.557	77.627	32.367	.000	.000	.000
1700	10.657	78.017	31.787	.000	.000	.000
1800	10.747	78.347	31.387	.000	.000	.000
1900	10.827	78.617	31.107	.000	.000	.000
2000	10.897	78.827	30.927	.000	.000	.000
2100	10.957	78.977	30.827	.000	.000	.000
2200	11.007	79.067	30.787	.000	.000	.000
2300	11.047	79.107	30.787	.000	.000	.000
2400	11.077	79.127	30.807	.000	.000	.000
2500	11.107	79.137	30.827	.000	.000	.000
2600	11.127	79.147	30.847	.000	.000	.000
2700	11.147	79.157	30.857	.000	.000	.000
2800	11.167	79.167	30.867	.000	.000	.000
2900	11.177	79.177	30.877	.000	.000	.000
3000	11.187	79.187	30.887	.000	.000	.000
3100	11.197	79.197	30.897	.000	.000	.000
3200	11.207	79.207	30.907	.000	.000	.000
3300	11.217	79.217	30.917	.000	.000	.000
3400	11.227	79.227	30.927	.000	.000	.000
3500	11.237	79.237	30.937	.000	.000	.000
3600	11.247	79.247	30.947	.000	.000	.000
3700	11.257	79.257	30.957	.000	.000	.000
3800	11.267	79.267	30.967	.000	.000	.000
3900	11.277	79.277	30.977	.000	.000	.000
4000	11.287	79.287	30.987	.000	.000	.000
4100	11.297	79.297	30.997	.000	.000	.000
4200	11.307	79.307	31.007	.000	.000	.000
4300	11.317	79.317	31.017	.000	.000	.000
4400	11.327	79.327	31.027	.000	.000	.000
4500	11.337	79.337	31.037	.000	.000	.000
4600	11.347	79.347	31.047	.000	.000	.000
4700	11.357	79.357	31.057	.000	.000	.000
4800	11.367	79.367	31.067	.000	.000	.000
4900	11.377	79.377	31.077	.000	.000	.000
5000	11.387	79.387	31.087	.000	.000	.000
5100	11.397	79.397	31.097	.000	.000	.000
5200	11.407	79.407	31.107	.000	.000	.000
5300	11.417	79.417	31.117	.000	.000	.000
5400	11.427	79.427	31.127	.000	.000	.000
5500	11.437	79.437	31.137	.000	.000	.000
5600	11.447	79.447	31.147	.000	.000	.000
5700	11.457	79.457	31.157	.000	.000	.000
5800	11.467	79.467	31.167	.000	.000	.000
5900	11.477	79.477	31.177	.000	.000	.000
6000	11.487	79.487	31.187	.000	.000	.000

September 30, 1961

IODINE, DIATOMIC (I₂)

MOL. WT. = 253.82

$$\Delta H_{f, 298}^{\circ} = 15.66 \pm .01 \text{ kcal. mole}^{-1}$$

(IDEAL GAS)

$$\Delta H_{f, 298}^{\circ} = 14.924 \text{ kcal. mole}^{-1}$$

$$\text{Ground State} = \sum$$

$$S_{298}^{\circ} = 62.281 \text{ cal. mole}^{-1} \text{ deg}^{-1}$$

$$\omega_e = 214.52 \text{ cm}^{-1}$$

$$\omega_e x_e = 0.6133 \text{ cm}^{-1}$$

$$B_e = 0.037584 \text{ cm}^{-1}$$

$$D_e = 0.455 \times 10^{-8} \text{ cm}^{-1}$$

$$\alpha_e = 0.0001206 \text{ cm}^{-1}$$

$$\sigma = 2$$

Thermodynamic Functions.

The molecular constants are from the work of D. H. Rank and W. M. Baldwin [J. Chem. Phys. **19**, 1210 (1951)] with a revised value of $\omega_e = 214.52$ as given by R. D. Verma [J. Chem. Phys. **32**, 738 (1960)]. The value of $\omega_e x_e$ has been adjusted to allow for the dropping of higher order corrections not used in the computer program. The calculated thermodynamic functions are in good agreement with those of W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards **55**, 147 (1955)], who used very slightly different constants. L. Mathieson and A. L. O. Rees [J. Chem. Phys. **25**, 753 (1956)] give further refinements to the spectroscopic data which are negligible for our purpose. Their ω_e is also slightly low since it is based on Rank and Baldwin.

Heat of Formation.

The heat of sublimation of iodine was calculated from published vapor pressure data as follows, using thermodynamic functions of condensed and gaseous phases described above.

	$\Delta H_{f, 298}^{\circ}$, kcal. mole ⁻¹
Baxter, Hickey, and Holmes ¹ (273° to 328°K)	15.657 ± .004
Baxter and Grose ² (323° to 358°K)	15.657 ± .002
Ramsay and Young ³ (solid) (331° to 386°K)	15.671 ± .018
Ramsay and Young ³ (liquid) (386° to 454°K)	15.676 ± .007
Haber and Kerschbaum ⁴ (225° to 283°K)	15.765 ± .012
Gillespie and Fraser ⁵ (303° to 333°K)	15.655 ± .005
Sklyarenko, Markin, and Belyaeva ⁶ (283° to 303°K)	15.813
Naumann ⁷ (as given by Haber and Kerschbaum) (232° to 292°K)	15.699 ± .034
Wiedemann ⁸ (333° to 453°K)	15.635 ± .008
Braune and Strassman ⁹ (305° to 358°K)	15.658 ± .012
Arctowski ¹⁰ (286° to 345°K)	15.623 ± .080
Wright ¹¹ (352° to 372°K)	15.659 ± .003
Dewar ¹² (273° to 303°K)	15.821 ± .103
Richter ¹³ (358° to 383°K)	15.639 ± .043

The uncertainties given are the average deviation from the mean. The data of Braune and Strassman are as recalculated by Gerry and Gillespie¹⁴. The data of Haber and Kerschbaum appear systematically too high. The results of Sklyarenko, et al., Naumann, Arctowski, Dewar, and Richter are scattered and are not given any weight. A weighted average of the remaining data yield $\Delta H_{f, 298}^{\circ} = 15.66 \pm 0.01$ kcal. mole⁻¹, which calculates to $\Delta H_{f, 298}^{\circ} = 14.924$ cal. mole⁻¹.

References to Vapor Pressure Data

- (1) G. P. Baxter, C. H. Hickey, and W. C. Holmes, J. Am. Chem. Soc. **29**, 127 (1907).
- (2) G. P. Baxter and M. R. Grose, J. Am. Chem. Soc. **37**, 1061 (1915).
- (3) W. Ramsay and S. Young, J. Chem. Soc. **49**, 453 (1886).
- (4) P. Haber and F. Kerschbaum, Z. Elektrochem. **20**, 286 (1914).
- (5) L. J. Gillespie and C. H. D. Fraser, J. Am. Chem. Soc. **58**, 2260 (1936).
- (6) S. I. Sklyarenko, B. I. Markin, and L. B. Belyaeva, Zhur. Fiz. Khim. **32**, 1916 (1958).
- (7) R. Naumann, Dissertation, Berlin (1907).
- (8) E. Wiedemann, Ber. deut. physikal. Ges. **3**, 159 (1905).
- (9) H. Braune and F. Strassman, Z. physikal. Chem. **143A**, 225 (1929).
- (10) H. Arctowski, Z. anorg. Chem. **12**, 427 (1896).
- (11) R. Wright, J. Chem. Soc. **107**, 1527 (1917).
- (12) J. Dewar, Proc. Chem. Soc. **13**, 241 (1899).
- (13) V. Richter, Ber. **19**, 1057 (1886).
- (14) H. T. Gerry and L. J. Gillespie, Phys. Rev. **40**, 269 (1932).

Potassium Iodide, Dimeric (K_2I_2)
(Ideal Gas) GFW = 332.0128

I_2K_2

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	-0.000	-0.000	INFINITE	-	-	-	INFINITE
100	14.157	73.647	111.819	5.181	-99.541	-99.541	227.158
200	19.406	86.752	96.351	3.817	-103.639	-103.639	117.964
298	19.660	94.556	94.556	0.000	-100.255	-100.255	81.605
300	19.662	94.680	94.559	0.036	-100.914	-111.665	81.348
400	19.753	100.351	95.331	2.008	-106.742	-114.776	62.711
500	19.796	104.764	96.793	3.985	-117.774	-115.727	50.584
600	19.819	108.375	98.431	5.966	-118.182	-115.282	41.991
700	19.833	111.431	100.076	7.949	-118.490	-114.777	35.835
800	19.842	114.080	101.664	9.933	-118.831	-114.224	31.205
900	19.848	116.418	103.176	11.917	-119.175	-113.628	27.593
1000	19.853	118.509	104.607	13.902	-119.537	-112.993	24.695
1100	19.856	120.401	105.958	15.884	-119.732	-112.272	21.000
1200	19.858	122.129	107.235	17.873	-119.740	-111.450	17.000
1300	19.860	123.719	108.462	19.859	-119.567	-101.658	13.518
1400	19.862	125.191	109.587	21.846	-119.486	-97.354	10.198
1500	19.863	126.554	110.673	23.832	-119.407	-93.066	7.015
1600	19.864	127.883	111.707	25.818	-119.329	-88.777	4.016
1700	19.865	129.087	112.692	27.805	-119.254	-84.494	1.216
1800	19.866	130.183	113.632	29.791	-119.181	-80.220	0.740
1900	19.866	131.257	114.532	31.774	-119.113	-75.947	0.436
2000	19.867	132.276	115.394	33.764	-119.047	-71.677	0.232
2100	19.867	133.245	116.221	35.751	-118.985	-67.407	0.015
2200	19.868	134.166	117.016	37.725	-118.931	-63.137	0.000
2300	19.868	135.053	117.781	39.725	-118.882	-58.864	0.000
2400	19.868	135.898	118.518	41.711	-118.841	-54.592	0.000
2500	19.869	136.709	119.230	43.698	-118.811	-50.326	0.000
2600	19.869	137.489	119.917	45.685	-118.788	-46.066	0.000
2700	19.869	138.238	120.572	47.672	-118.779	-41.806	0.000
2800	19.869	138.961	121.226	49.659	-118.785	-37.546	0.000
2900	19.869	139.658	121.869	51.644	-118.804	-33.286	0.000
3000	19.870	140.332	122.484	53.633	-118.839	-29.026	0.000
3100	19.870	140.983	123.081	55.620	-118.895	-24.766	0.000
3200	19.870	141.614	123.662	57.607	-118.970	-20.506	0.000
3300	19.870	142.226	124.227	59.594	-119.069	-16.246	0.000
3400	19.870	142.819	124.707	61.581	-119.195	-11.986	0.000
3500	19.870	143.395	125.233	63.568	-119.348	-7.726	0.000
3600	19.870	143.955	125.745	65.555	-119.535	-3.466	0.000
3700	19.870	144.499	126.244	67.542	-119.757	0.804	0.000
3800	19.870	145.029	126.732	69.529	-119.920	5.091	0.000
3900	19.870	145.545	127.208	71.516	-119.927	9.389	0.000
4000	19.870	146.048	127.687	73.503	-119.683	13.693	0.000
4100	19.871	146.539	128.157	75.490	-119.093	18.010	0.000
4200	19.871	147.018	128.611	77.477	-118.567	22.326	0.000
4300	19.871	147.485	129.005	79.464	-118.103	26.642	0.000
4400	19.871	147.942	129.430	81.451	-117.715	30.958	0.000
4500	19.871	148.388	129.887	83.438	-117.404	35.274	0.000
4600	19.871	148.825	130.355	85.425	-117.178	39.590	0.000
4700	19.871	149.253	130.824	87.412	-117.043	43.906	0.000
4800	19.871	149.671	131.294	89.399	-116.908	48.222	0.000
4900	19.871	150.081	131.764	91.387	-116.773	52.538	0.000
5000	19.871	150.482	132.234	93.374	-116.649	56.854	0.000
5100	19.871	150.876	132.707	95.361	-116.539	61.170	0.000
5200	19.871	151.261	133.177	97.348	-116.450	65.486	0.000
5300	19.871	151.641	133.648	99.335	-116.381	69.802	0.000
5400	19.871	152.011	134.124	101.322	-116.328	74.118	0.000
5500	19.871	152.376	134.601	103.309	-116.292	78.434	0.000
5600	19.871	152.738	135.081	105.296	-116.266	82.750	0.000
5700	19.871	153.086	135.654	107.285	-116.250	87.066	0.000
5800	19.871	153.431	136.224	109.270	-116.242	91.382	0.000
5900	19.871	153.771	136.791	111.258	-116.240	95.698	0.000
6000	19.871	154.105	137.351	113.245	-116.242	100.014	0.000

Dec. 31, 1961 June 30, 1967

POTASSIUM IODIDE, DIMERIC (K_2I_2)
(IDEAL GAS)

Point Group [D_{2h}]

$S_{298.15}^\circ = [94.61 \text{ gbbbs/mol}]$

Ground State Quantum Weight = [1]

GFW = 332.0128

$\Delta H_f^\circ = -99.5 \pm 1 \text{ kcal/mol}$

$\Delta H_{298.15}^\circ = -100.9 \pm 1 \text{ kcal/mol}$

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[90] (1)	[80] (1)
[60] (1)	[105] (1)
[110] (1)	[120] (1)

Bond Distance: K-I = [3.29] Å

Bond Angles: K-I-K = [75°] I-K-I = [105°]

Product of the Moments of Inertia: $I_A I_B I_C = [5.041 \times 10^{-11}] \text{ g cm}^6$

$\sigma = [4]$

Heat of Formation

The chemical equilibrium for the reaction $K_2I_2(g) = 2KI(g)$ has been studied by S. Datz, ORNL-2933, Oak Ridge, Tenn., 1960, and S. Datz, W. T. Smith, Jr. and E. H. Taylor, J. Chem. Phys. 34, 588 (1961). They measured the temperature dependence of the molecular weight of $KI(g)$ which was determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. Based on the reported P-V-T measurements, the enthalpy change of the reaction at 298°K is evaluated by the second and third law methods. The results are given in the table below.

R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956), determined the molecular composition of KI vapor by measurement of the velocity distribution of the molecules in the beam produced as the vapor effused through a small slit in a source. The analysis was based on an assumption that the velocity distribution within the oven is Maxwellian and that the vapor effuses through the ideal slit of kinetic theory. The velocity distributions of potassium and thallium atomic beams were found to be in excellent agreement with the theoretical distributions, so the determination of the molecular composition of KI beams was tried. Using the derived equilibrium constants, we calculate the enthalpy change of the dissociation reaction by the second and third law methods. The results are presented in the following table.

The value of $\Delta H_{298}^\circ(K_2I_2, g)$ is adopted as $-100.9 \pm 1 \text{ kcal/mol}$.

Investigator	Temperature, °K	No. of Points	$\Delta H_{298}^\circ, \text{kcal/mol}$	Drift, au	$\Delta H_{298}^\circ, \text{kcal/mol}$
Datz	1228-1395	10	40.0940.82	40.56	-100.86
		6	41.3711.91	41.01	-101.01
Miller-Kusch	816-921	10	54.6222.46	36.28	-21.442.8

Heat Capacity

The molecular structure and bond distance and angles were estimated by J. Berkowitz, J. Chem. Phys. 29, 1386 (1958). The vibrational frequencies are estimated by comparison with those calculated by J. Berkowitz, J. Chem. Phys. 32, 1519 (1960), and adjusted to give good agreement between second and third law evaluations of the equilibrium data. The three principal moments of inertia are: $I_A = 5.194 \times 10^{-38}$, $I_B = 2.866 \times 10^{-37}$, $I_C = 3.366 \times 10^{-37} \text{ g cm}^2$.

I_2K_2

Point Group D_{2h}
S_{298.15} = [79.0] gibbs/mol
Ground State Quantum Weight = 1
ΔHf° = -85.3 ± 4 kcal/mol
ΔHf°_{298.15} = -86.5 ± 4 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[166](1)	[310](1)
[160](1)	248 (1)
[383](1)	375 (1)

Bond Distance: Li-I = 2.54 Å
Bond Angle: I-Li-I = 116° ± 4°
Product of the Moments of Inertia: I_AI_BI_C = 1.63429 X 10⁻¹¹² g³ cm⁶
σ = 4

Heat of Formation

This was obtained from the heat of formation of the crystal and the heat of sublimation of the dimer, which derivation has been given in the LiI(g) table.

Heat Capacity and Entropy

J. Berkowitz, J. Chem. Phys. 29, 1366 (1958), 32, 1519 (1960), has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by A. Büchler, J. L. Stauffer and W. Klemperer, J. Am. Chem. Soc. 86, 4544 (1964). The selected bond distances and angle were obtained from the electron diffraction studies of monomer-dimer vapor by P. A. Akishin and N. G. Rambidi, Z. Physik Chem. 213, 111 (1960). The bond distances (r_{Li-I} = 2.72 Å and r_{I-I} = 4.520 Å) calculated by Berkowitz are in good agreement with those from Akishin and Rambidi. The three principal moments of inertia are I_A = 4.2152 X 10⁻³⁹, I_B = 194.8074 X 10⁻³⁹ and I_C = 199.0226 X 10⁻³⁹ g cm².

S. H. Bauer, T. Ito and R. F. Porter, J. Chem. Phys. 33, 685 (1960), have estimated six vibrational frequencies (501, 501, 148, 200, 298, 360 cm⁻¹) for Li₂I₂(g) in the electron diffraction studies of the Li₂Cl₂(g). W. Klemperer and M. O. Norris, J. Chem. Phys. 35, 1071 (1961), have observed two fundamental vibrational frequencies (248 and 375 cm⁻¹) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes; these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from J. Berkowitz, loc. cit., because his model and derivation are self-consistent.

Sept. 30, 1961; June 30, 1966

T, °K	Cp°	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	∞	∞	∞	∞	85.263	85.263	INFINITE
100	12.245	61.676	93.907	3.193	85.296	85.484	196.004
200	12.553	61.676	93.907	3.193	85.296	85.484	196.004
298	18.175	78.097	78.097	0.000	86.500	87.630	711.563
300	18.193	79.108	78.097	0.34	86.512	87.699	711.174
400	18.877	86.449	79.720	1.891	91.069	101.188	55.287
500	19.219	88.702	81.106	3.788	103.521	102.518	44.811
600	19.412	92.225	82.674	5.730	103.912	102.281	37.256
700	19.531	95.227	84.258	7.678	104.263	101.982	31.680
800	19.610	97.840	85.786	9.635	104.591	101.633	27.765
900	19.664	100.153	87.265	11.599	104.913	101.244	24.586
1000	19.703	102.227	88.659	13.568	105.228	100.819	22.034
1100	19.732	104.106	89.980	15.539	105.541	100.363	19.940
1200	19.754	105.824	91.229	17.514	105.851	99.880	18.191
1300	19.771	107.406	92.414	19.490	106.156	99.370	16.706
1400	19.785	108.872	93.538	21.468	106.460	98.836	15.479
1500	19.796	110.237	94.606	23.447	106.760	98.282	14.320
1600	19.805	111.515	95.623	25.427	107.056	97.704	13.246
1700	19.813	112.716	96.594	27.408	107.345	97.105	12.243
1800	19.819	113.849	97.521	29.390	107.628	96.484	11.306
1900	19.825	114.920	98.409	31.372	107.905	95.849	10.426
2000	19.829	115.937	99.260	33.354	108.179	95.207	9.597
2100	19.833	116.905	100.078	35.338	108.445	94.559	8.821
2200	19.836	117.828	100.864	37.321	108.705	93.900	8.093
2300	19.839	118.709	101.620	39.305	108.960	93.236	7.416
2400	19.842	119.554	102.350	41.289	109.211	92.569	6.789
2500	19.844	120.364	103.055	43.273	109.458	91.900	6.212
2600	19.846	121.142	103.735	45.258	109.700	91.230	5.685
2700	19.848	121.891	104.394	47.243	109.938	90.560	5.207
2800	19.850	122.613	105.032	49.227	110.173	89.890	4.776
2900	19.851	123.310	105.650	51.212	110.405	89.220	4.390
3000	19.853	123.983	106.250	53.198	110.635	88.550	4.047
3100	19.854	124.634	106.833	55.183	110.863	87.880	3.746
3200	19.855	125.264	107.399	57.168	111.089	87.210	3.484
3300	19.856	125.874	107.950	59.154	111.313	86.540	3.260
3400	19.857	126.468	108.486	61.140	111.534	85.870	3.074
3500	19.858	127.044	109.008	63.125	111.753	85.200	2.926
3600	19.858	127.603	109.516	65.111	111.969	84.530	2.814
3700	19.859	128.147	110.013	67.097	112.182	83.860	2.730
3800	19.860	128.677	110.497	69.083	112.392	83.190	2.674
3900	19.860	129.193	110.970	71.069	112.600	82.520	2.636
4000	19.861	129.695	111.432	73.055	112.806	81.850	2.604
4100	19.862	130.186	111.883	75.041	113.011	81.180	2.577
4200	19.862	130.664	112.325	77.027	113.215	80.510	2.554
4300	19.862	131.132	112.757	79.014	113.419	79.840	2.534
4400	19.863	131.588	113.179	81.000	113.623	79.170	2.517
4500	19.863	132.035	113.593	82.986	113.827	78.500	2.502
4600	19.864	132.471	114.009	84.973	114.031	77.830	2.489
4700	19.864	132.899	114.417	86.959	114.235	77.160	2.477
4800	19.864	133.317	114.817	88.945	114.439	76.490	2.466
4900	19.865	133.726	115.216	90.932	114.643	75.820	2.456
5000	19.865	134.128	115.614	92.918	114.847	75.150	2.447
5100	19.865	134.521	115.912	94.905	115.051	74.480	2.439
5200	19.865	134.907	116.274	96.891	115.255	73.810	2.432
5300	19.866	135.285	116.679	98.878	115.459	73.140	2.426
5400	19.866	135.657	117.078	100.864	115.663	72.470	2.421
5500	19.866	136.021	117.472	102.851	115.867	71.800	2.417
5600	19.866	136.379	117.868	104.838	116.071	71.130	2.414
5700	19.866	136.731	118.264	106.824	116.275	70.460	2.411
5800	19.867	137.076	118.611	108.811	116.479	69.790	2.409
5900	19.867	137.416	118.957	110.798	116.683	69.120	2.407
6000	19.867	137.750	119.292	112.784	116.887	68.450	2.406

Lead Diiodide (PbI₂)

(Crystal) Mol. Wt. = 461.03

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	0.000	INFINITE	-	41.765	-	INFINITE
100	19.840	22.394	3.688	41.778	-	6.0386
200	19.050	34.495	1.616	41.806	-	45.425
298	19.918	41.869	0.000	41.855	-	30.379
300	19.935	41.886	0.035	41.856	-	30.190
400	19.450	45.061	1.655	41.868	-	22.056
500	20.290	51.984	4.063	55.950	-	17.070
600	20.620	55.729	45.703	55.482	-	13.010
700	21.290	58.974	47.372	56.146	-	10.076
800	21.760	61.848	48.006	55.615	-	7.894
900	22.270	64.388	50.095	55.334	-	6.215
1000	22.700	66.804	52.095	54.398	-	4.886
1100	23.170	68.990	53.523	53.711	-	3.812
1200	23.640	71.026	54.998	52.970	-	2.928
1300	24.110	72.937	56.213	52.178	-	2.191
1400	24.580	74.691	57.284	51.360	-	1.570
1500	25.050	76.353	58.681	50.456	-	1.040
1600	25.520	77.944	59.883	49.528	-	.584
1700	25.990	79.466	60.862	48.558	-	.190
1800	26.460	80.944	61.642	47.546	-	.153
1900	26.930	82.384	62.344	46.496	-	.133
2000	27.400	83.981	64.096	45.400	-	.118
2100	27.870	85.329	65.075	44.533	-	1.113
2200	28.300	86.534	65.344	43.488	-	1.520
2300	28.810	87.807	66.950	48.201	-	1.886
2400	29.260	89.143	68.106	41.156	-	2.217
2500	29.750	90.347	69.723	42.838	-	2.516
				61.439	-	28.783

Lead Diiodide (PbI₂)

(crystal)

Mol. Wt. = 461.03

ΔH°_f 298.15 = -41.86 ± 0.06 kcal. mole⁻¹S°_{298.15} = 41.869 cal. deg.⁻¹ mole⁻¹ΔH°_f 298.15 = 41.70 ± 0.10 kcal. mole⁻¹T_m = 680°K.ΔH°_m = 3.87 kcal. mole⁻¹

Heat of Formation. Calculated from the data reported by H. Braune and F. Kref, Z. anorg. Chem. 87, 175 (1914) and R. H. Gerike, J. Am. Chem. Soc. 44, 1684 (1922).

Heat Capacity, Entropy, and Melting Data. C_p (10° to 298.15°K.) obtained from Edgar F. Westrum, Jr., University of Michigan, Ann Arbor, Michigan, private communication, May, 1961. Above 298.15°K., C_p given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation. T_m and ΔH°_m reported by M. Blanc and G. Petit, Compt. rend., 248, 1305 (1959).

Heat of Sublimation. Calculated from vapor pressure data of K. Jellinek and A. Rudat, Z. Physik. Chem., A143, 55 (1929) and B. Ordiner and K. Jellinek, Z. Physik. Chem., A165, 97 (1933).

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0									
100									
200									
298	16.920	42.786	42.786	.000	-	40.637	-	40.501	29.667
300									
350	19.915	42.003	42.786	.015	-	40.638	-	40.500	29.503
400	21.410	40.450	43.518	1.965	-	40.532	-	40.312	22.024
500	32.400	54.064	45.035	4.525	-	44.168	-	36.323	16.750
600	32.400	59.991	47.051	7.765	-	52.515	-	35.310	12.463
700	32.400	64.966	49.265	11.005	-	56.944	-	36.681	10.108
800	32.400	69.335	51.701	17.685	-	66.808	-	27.166	6.401
900	32.400	73.159	53.701	27.725	-	87.175	-	24.871	5.435
1000	32.400	76.542	55.818	20.725	-	87.175	-	24.871	5.435
1100	32.400	79.610	57.864	23.965	-	85.581	-	22.720	4.514
1200	32.400	82.449	59.779	27.205	-	83.293	-	19.857	3.169
1300	32.400	85.084	61.564	30.685	-	80.613	-	17.113	2.071
1400	32.400	87.684	63.384	34.925	-	76.970	-	15.491	2.257
1500	32.400	89.679	65.063	36.925	-	76.970	-	15.491	2.257
1600	32.400	91.770	66.667	40.164	-	77.331	-	13.978	1.909
1700	32.400	93.725	68.292	43.845	-	76.069	-	11.257	1.367
1800	32.400	95.483	69.843	47.985	-	74.444	-	10.034	1.154
1900	32.400	97.338	71.083	49.895	-	72.438	-	8.898	.972
2000	32.400	99.000	72.438	53.125	-	71.666	-	6.287	.654
2100	32.400	100.581	73.741	56.365	-	69.595	-	3.212	.021
2200	32.400	102.098	74.995	59.605	-	66.641	-	2.708	-.247
2300	32.400	103.553	76.125	62.845	-	65.013	-	5.562	-.466
2400	32.400	104.907	77.132	66.085	-	63.407	-	8.354	-.702
2500	32.400	106.230	78.500	69.325	-	61.923	-	11.084	-.974
2600	32.400	107.501	79.591	72.565	-	59.720	-	16.373	-1.234
2700	32.400	108.723	80.668	75.805	-	57.198	-	18.936	-1.379
2800	32.400	109.901	81.651	79.045	-	54.525	-		
2900	32.400	111.039	82.665	82.285	-		-		
3000	32.400	112.137	83.659	85.525	-		-		

March 31, 1952

Lead Diiodide (PbI₂) (Liquid)

Mol. Wt. = 461.03

 $\Delta H_f^\circ 298.15 = [-40.657] \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = [42.786] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $T_m = 680^\circ \text{K.}$ $\Delta H_m^\circ = 3.67 \text{ kcal. mole}^{-1}$ $T_b = 1135^\circ \text{K.}$ $\Delta H_v^\circ = 26.99 \pm 0.10 \text{ kcal. mole}^{-1}$

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p obtained from K.K. Kelley, U. S. Bur. Mines Bull. 584 (1950). T_m and ΔH_m° re-

ported by M. Blanc and G. Petit, Compt. rend. 248, 1305-6 (1959).

A glass transition temperature of 454°K. is assumed.Vaporization Phenomena. T_b and ΔH_v° calculated from $\Delta H_f^\circ 298.15$

and free energy functions for condensed and gaseous states.

Lead Diiodide (PbI₂)

(Ideal Gas) Mol. Wt. = 461.03 **INTERIM TABLE**

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	13.900	104.005	23.493	11.124	17.901	21.693	6.349	
100	13.902	105.915	93.737	12.514	18.111	22.285	4.051	
200	13.903	107.326	94.632	13.204	18.316	22.581	3.796	
300	13.904	108.253	95.125	13.725	18.475	22.825	3.635	
400	13.905	108.317	97.194	16.465	18.729	23.207	3.361	
500	13.906	109.215	97.918	18.075	18.940	23.498	3.209	
600	13.906	110.058	98.607	19.466	19.154	23.776	3.056	
700	13.907	110.853	99.266	20.657	19.374	24.043	2.919	
800	13.907	111.603	99.897	21.661	19.599	24.295	2.795	
900	13.908	112.318	100.499	23.638	19.833	24.539	2.681	
1000	13.908	112.997	101.076	25.029	20.075	24.760	2.576	
1100	13.908	113.644	101.635	26.820	20.321	24.961	2.476	
1200	13.908	114.262	102.170	27.811	20.567	25.145	2.381	
1300	13.908	114.854	102.681	28.999	20.814	25.314	2.291	
1400	13.909	115.422	103.185	30.592	21.061	25.469	2.206	
1500	13.909	115.967	103.666	31.983	21.308	25.610	2.126	
1600	13.909	116.492	104.131	33.374	21.554	25.740	2.051	
1700	13.909	116.998	104.581	34.764	21.801	25.860	1.981	
1800	13.909	117.485	105.018	36.154	22.048	25.970	1.916	
1900	13.909	117.958	105.442	37.547	22.295	26.071	1.856	
2000	13.910	118.414	105.853	38.938	22.542	26.163	1.799	
2100	13.910	118.855	106.252	40.329	22.789	26.246	1.744	
2200	13.910	119.283	106.641	41.720	23.036	26.321	1.691	
2300	13.910	119.698	107.018	43.111	23.283	26.388	1.639	
2400	13.910	120.102	107.387	44.502	23.530	26.447	1.588	
2500	13.910	120.494	107.746	45.893	23.777	26.498	1.538	
2600	13.910	120.875	108.095	47.284	24.024	26.541	1.489	
2700	13.910	121.246	108.437	48.675	24.271	26.576	1.441	
2800	13.910	121.606	108.770	50.066	24.518	26.603	1.394	
2900	13.910	121.956	109.095	51.457	24.765	26.621	1.348	
3000	13.910	122.303	109.413	52.848	25.012	26.631	1.303	
3100	13.910	122.638	109.724	54.239	25.259	26.634	1.259	
3200	13.910	122.965	110.028	55.630	25.506	26.631	1.216	
3300	13.910	123.285	110.326	57.021	25.753	26.621	1.174	
3400	13.910	123.598	110.617	58.412	26.000	26.603	1.133	
3500	13.910	123.903	110.903	59.803	26.247	26.576	1.092	
3600	13.910	124.202	111.182	61.194	26.494	26.541	1.051	
3700	13.910	124.494	111.457	62.585	26.741	26.498	1.011	
3800	13.910	124.782	111.726	63.976	27.000	26.447	0.971	
3900	13.910	125.063	111.990	65.367	27.247	26.388	0.931	
4000	13.910	125.339	112.249	66.758	27.500	26.321	0.891	
4100	13.910	125.603	112.503	68.149	27.747	26.246	0.851	
4200	13.910	125.863	112.753	69.540	28.000	26.163	0.811	
4300	13.910	126.118	113.000	70.931	28.247	26.071	0.771	
4400	13.910	126.369	113.239	72.322	28.500	25.970	0.731	
4500	13.910	126.610	113.476	73.713	28.747	25.860	0.691	
4600	13.910	126.846	113.710	75.104	29.000	25.740	0.651	
4700	13.910	127.076	113.939	76.495	29.247	25.610	0.611	
4800	13.910	127.301	114.163	77.886	29.500	25.469	0.571	
4900	13.910	127.519	114.386	79.277	29.747	25.314	0.531	
5000	13.910	127.729	114.603	80.668	30.000	25.145	0.491	
5100	13.910	127.933	114.816	82.059	30.247	24.961	0.451	
5200	13.910	128.132	115.024	83.450	30.500	24.760	0.411	
5300	13.910	128.326	115.228	84.841	30.747	24.539	0.371	
5400	13.910	128.516	115.428	86.232	31.000	24.295	0.331	
5500	13.910	128.701	115.624	87.623	31.247	24.043	0.291	
5600	13.910	128.882	115.816	89.014	31.500	23.776	0.251	
5700	13.910	129.059	116.004	90.405	31.747	23.498	0.211	
5800	13.910	129.232	116.188	91.796	32.000	23.199	0.171	
5900	13.910	129.401	116.368	93.187	32.247	22.880	0.131	
6000	13.910	129.566	116.543	94.578	32.500	22.542	0.091	

March 31, 1962

Lead Diiodide (PbI₂) (Ideal Gas)

Mol. Wt. = 461.03
 ΔH_f^0 298.15 = -0.16 ± 0.12 kcal. mole⁻¹
 $S_{298.15}^0$ = [85.911] cal. deg.⁻¹ mole⁻¹
 Point group C_{2v}

Vibrational Levels and Multiplicities

ω, cm. ⁻¹
[100] (1)
[40] (1)
[160] (1)

Pb-I distance = 2.79 ± 0.02 Å IPBI angle = 85° σ = 2
 I_A = 67.294 X 10⁻³⁹ g. cm.² I_B = 178.298 X 10⁻³⁹ g. cm.²
 I_C = I_A + I_B = 245.592 X 10⁻³⁹

Heat of Formation. Calculated from ΔH_f^0 298.15 and ΔH_f^0 298.15 for PbI₂(c).

Heat Capacity and Entropy. Molecular dimensions obtained from L. E. Sutton (ed.), "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958. Vibrational frequencies estimated by comparison with the corresponding values for HgI₂(E).

TITANIUM DIODIDE (TiI₂) (CRYSTAL)

GFW = 301.7088

Titanium Diiodide (TiI₂)

GFW = 301.7088

 $\Delta H_f^\circ = \text{unknown}$ $\Delta H_f^\circ_{298.15} = -63.6 \pm 3.0 \text{ kcal/mol}$ $\Delta H_s^\circ = [51.80] \text{ kcal/mol}$ $S^\circ_{298.15} = [29.3 \pm 3.0] \text{ gibbs/mol}$ $T_m = [1358.2]^\circ\text{K}$

Heat of Formation

The heat of formation of TiI₂(c) is calculated from the heat of reaction for the process $2\text{TiI}_2(\text{c}) = \text{Ti}(\text{c}) + \text{TiI}_4(\text{g})$, and the heat of formation of TiI₄(c). Vapor pressure data for this reaction were reported by Herczog and Pidgeon (1) over the temperature range 750° to 902°K. Second and third law analyses of these data give values for ΔH°_{298} of 60.5 ± 0.8 and 60.85 kcal/mol respectively, the third law drift being $0.4 \pm 1.0 \text{ au}$. The third law ΔH°_{298} is used to obtain the adopted value of ΔH°_{298} .

Heat Capacity and Entropy

The estimated heat capacity is that reported by Kelley (2). The value of $S^\circ_{298.15}$ is estimated from that of TiCl₂(c) and the difference between ionic entropy contributions of Cl⁻ and I⁻.

Heat of Sublimation

The heat of sublimation of TiI₂(c) is taken as the difference in the heats of formation of TiI₂(c) and TiI₂(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta G_s^\circ = 0$ for the reaction $\text{TiI}_2(\text{c}) = \text{TiI}_2(\text{g})$.

References

1. A. Herczog and L. M. Pidgeon, Can. J. Chem., **34**, 1687 (1956).
2. K. K. Kelley, U. S. Bur. Mines Bull. 584, 1961.

T, °K	Cp*	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
100							
200							
298	20.609	29.300	29.300	.000	- 63.600	- 61.876	45.356
300	20.612	29.428	29.300	.038	- 63.597	- 61.865	45.068
400	20.766	35.361	30.111	2.108	- 67.317	- 61.173	33.423
500	20.960	40.038	31.687	4.195	- 77.399	- 59.690	25.653
600	21.134	43.875	33.375	6.300	- 76.857	- 55.001	20.034
700	21.288	47.164	36.000	8.600	- 75.800	- 47.480	13.079
800	21.482	50.002	38.411	10.562	- 75.750	- 47.470	13.079
900	21.656	52.543	38.411	12.719	- 75.274	- 44.518	10.766
1000	21.830	54.633	39.940	15.893	- 74.769	- 41.016	8.964
1100	22.004	56.922	41.391	17.085	- 74.273	- 37.664	7.483
1200	22.178	58.852	44.072	18.520	- 74.122	- 34.308	6.308
1300	22.352	60.626	45.315	21.520	- 73.516	- 30.978	5.208
1400	22.526	62.289	45.315	23.768	- 73.516	- 27.683	4.321
1500	22.700	63.849	46.499	26.025	- 72.516	- 24.430	3.559
1600	22.874	65.370	47.630	28.304	- 72.114	- 21.214	2.898
1700	23.048	66.852	48.712	30.580	- 71.712	- 18.000	2.308
1800	23.222	68.034	49.746	32.910	- 71.129	- 14.900	1.809
1900	23.396	69.294	50.744	35.245	- 70.540	- 11.793	1.356
2000	23.570	70.499	51.702	37.593	- 74.410	- 8.563	.936

GTW = 301.7088

(IDEAL GAS)

TITANIUM DIIODIDE (TiI₂)Titanium Diiodide (TiI₂)

GTW = 301.7088

(Ideal Gas)

Point Group [D_{2h}]

(IDEAL GAS)

 $\Delta H_f^\circ = [-4.1 \pm 8.0] \text{ kcal/mol}$ $S_{298.15}^\circ = [77.3 \pm 4] \text{ gibbs/mol}$ $\Delta H_f^\circ = [-4.7 \pm 8.0] \text{ kcal/mol}$

Ground State Quantum Weight = [3]

 $\Delta H_f^\circ = [-4.7 \pm 8.0] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	g
[134] (1)	
[92] (2)	
[290] (1)	

Bond Distance: Ti-I = [2.7] Å

Bond Angle: I-Ti-I = [180°]

Rotational Constant: $B_0 = [0.0081] \text{ cm}^{-1}$ $\sigma = 2$

Heat of Formation

The heat of formation of $\text{TiI}_2(\text{g})$ is calculated from that of $\text{TiI}_2(\text{c})$ and the heat of vaporization. Vapor pressure data over the temperature range 750°K to 902°K have been reported by Herzog and Pidgeon (1). Second and third law analyses of these data give values for ΔH_{298}° of 51.9 and 58.9 kcal/mol, respectively. The third law drift for these data is 8.3 ± 1.1 eu, with one point rejected due to failure of a statistical test. The adopted value of ΔH_{298}° is calculated from the third law heat of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $\text{TiCl}_2(\text{g})$, $\text{TiCl}_4(\text{g})$, $\text{TiBr}_2(\text{g})$, $\text{TiBr}_4(\text{g})$ and $\text{TiI}_4(\text{g})$. The vibrational frequencies are estimated from a valence force field model. The force constant K is estimated as 1.0 millidynes/Å and the constant K_0/l^2 is assumed to be 0.05 millidynes/Å.

The electronic levels are assumed to be the same as $\text{TiCl}_2(\text{g})$. The levels of TiCl_2 are estimated by assuming they correspond to the inverted states of $\text{NiCl}_2(\text{g})$ (2). The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear (3, 4, 5, 6).

References

1. A. Herzog and L. M. Pidgeon, Can. J. Chem., **34**, 1887 (1956).
2. C. W. DeKock and D. M. Gruen, J. Chem. Phys., **44**, 4387 (1966).
3. R. A. Berg and O. Sinanoglu, J. Chem. Phys., **32**, 1082 (1960).
4. J. T. Houghen, G. E. Leroy and T. C. James, J. Chem. Phys., **34**, 1670 (1961).
5. G. E. Leroy, T. C. James, J. T. Houghen, and W. Klemperer, J. Chem. Phys., **36**, 2879 (1962).
6. A. Buchlar, J. L. Stauffer and W. Klemperer, J. Chem. Phys., **40**, 3471 (1964).

T, °K	Cp°	$-\frac{\text{gibbs/mol}}{S^\circ}$	$-\frac{\text{kcal/mol}}{H^\circ - H_{298}^\circ}$	ΔG°	Log Kp
0	∞	∞	∞	∞	∞
100	12.418	62.404	3.708	4.102	INFINITE
200	14.027	71.635	2.743	4.000	18.764
298	14.476	77.335	1.603	4.294	14.282
300	14.481	77.425	1.603	4.294	12.679
400	14.659	81.618	1.485	4.708	12.656
500	14.745	84.600	2.956	19.738	23.461
600	14.793	87.593	4.433	19.824	8.814
700	14.822	89.875	5.911	19.924	7.780
800	14.843	91.656	7.397	20.056	7.000
900	14.861	93.605	8.882	20.211	6.369
1000	14.880	95.172	10.369	20.393	5.896
1100	14.905	96.591	11.858	20.600	5.480
1200	14.939	97.889	13.344	20.836	5.119
1300	14.983	99.087	14.846	21.104	4.813
1400	15.037	100.199	16.344	21.404	4.557
1500	15.102	101.239	17.854	21.736	4.340
1600	15.177	102.216	19.368	22.100	4.157
1700	15.262	103.133	20.879	22.496	3.997
1800	15.348	104.013	22.390	22.924	3.856
1900	15.440	104.845	23.909	23.384	3.732
2000	15.535	105.640	25.434	23.876	3.623
2100	15.631	106.400	26.964	24.392	3.526
2200	15.728	107.128	28.498	24.932	3.440
2300	15.818	107.830	30.036	25.496	3.364
2400	15.907	108.505	31.578	26.084	3.296
2500	15.992	109.156	33.124	26.696	3.234
2600	16.074	109.785	34.674	27.332	3.176
2700	16.152	110.392	36.226	27.992	3.122
2800	16.223	110.982	37.782	28.676	3.071
2900	16.291	111.553	39.342	29.384	3.022
3000	16.355	112.106	40.906	30.116	2.974
3100	16.415	112.643	42.474	30.872	2.928
3200	16.472	113.163	44.046	31.652	2.883
3300	16.526	113.667	45.622	32.456	2.839
3400	16.574	114.167	47.202	33.284	2.796
3500	16.621	114.668	48.786	34.136	2.754
3600	16.666	115.117	50.374	35.012	2.713
3700	16.709	115.616	51.966	35.912	2.673
3800	16.750	116.020	53.562	36.836	2.634
3900	16.788	116.456	55.162	37.784	2.595
4000	16.826	116.881	56.766	38.756	2.557
4100	16.862	117.297	58.374	39.752	2.520
4200	16.892	117.704	59.986	40.772	2.483
4300	16.918	118.102	61.602	41.816	2.447
4400	16.941	118.492	63.222	42.884	2.411
4500	16.966	118.873	64.846	43.976	2.375
4600	16.992	119.247	66.474	45.092	2.340
4700	17.016	119.616	68.106	46.232	2.305
4800	17.040	119.979	69.742	47.396	2.270
4900	17.113	120.326	71.374	48.584	2.235
5000	17.140	120.672	73.006	49.796	2.200
5100	17.166	121.011	74.642	51.032	2.165
5200	17.191	121.345	76.282	52.292	2.130
5300	17.215	121.672	77.926	53.576	2.095
5400	17.237	121.994	79.574	54.884	2.060
5500	17.259	122.311	81.226	56.216	2.025
5600	17.279	122.622	82.882	57.572	1.990
5700	17.298	122.928	84.542	58.952	1.955
5800	17.315	123.229	86.206	60.356	1.920
5900	17.332	123.525	87.874	61.784	1.885
6000	17.347	123.817	89.546	63.236	1.850

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

Zirconium Dioxide (ZrI_2)
(Crystal) Mol. Wt. = 345.04

INTERIM TABLE

T, °K.	C_p	S° cal. mole ⁻¹ deg. ⁻¹	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f kcal. mole ⁻¹	ΔF°_f	Log K _r
0							
100	22.500	35.900	35.900	.000	- 62.000	- 61.652	45.190
200	22.550	36.039	35.900	.042	- 61.993	- 61.649	44.909
300	22.710	36.668	34.802	2.346	- 65.496	- 61.454	33.575
400	22.910	37.757	34.502	4.627	- 75.409	- 59.515	26.013
500	23.000	38.451	34.008	6.998	- 78.700	- 56.403	20.584
600	23.050	38.725	33.315	9.267	- 78.004	- 53.407	15.674
700	23.080	38.887	32.466	11.585	- 73.315	- 50.510	11.768
800	23.100	38.932	31.491	13.951	- 72.598	- 47.703	8.583
900	23.110	38.967	30.410	16.337	- 71.871	- 44.974	5.829
1000	23.120	38.980	29.231	18.731	- 71.134	- 42.321	3.408
1100	23.130	38.985	27.957	21.157	- 70.386	- 39.652	1.232
1200	23.140	38.988	26.590	23.579	- 69.628	- 37.072	0.232
1300	23.150	38.990	25.140	26.031	- 68.858	- 34.519	0.368
1400	23.160	38.991	23.600	28.503	- 68.077	- 32.021	0.665
1500	23.170	38.992	22.000	30.993	- 67.286	- 29.570	1.039
1600	23.180	38.993	20.350	33.502	- 66.486	- 27.164	1.484
1700	23.190	38.994	18.650	36.031	- 65.677	- 24.822	2.014
1800	23.200	38.995	16.900	38.571	- 64.859	- 22.516	2.590
1900	23.210	38.996	15.100	41.125	- 64.032	- 20.255	3.213
2000	23.220	38.997	13.250	43.694	- 63.197	- 18.038	3.884

June 30, 1962

Zirconium Dioxide (ZrI_2) (Crystal)

Mol. Wt. = 345.04

ΔH°_f 298.15 = [-62] kcal. mole⁻¹

$S^\circ_{298.15}$ = [35.8] cal. deg.⁻¹ mole⁻¹

T_m = [700]°K.

ΔH°_m = [6] kcal. mole⁻¹

T_b = [1300]°K.

ΔH°_v = [27] kcal. mole⁻¹

Heat of Formation. Estimated from a consideration of ΔH°_f $ZrI_4(c)$ and of the disproportionation data given by R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley and Sons, Inc., New York, (1961).

Heat Capacity and Entropy. Heat capacity estimated by comparison to the other zirconium halides and titanium halides. Entropy estimated from additive constants.

Melting and Vaporization. ΔH°_m was estimated. T_m , T_b , and ΔH°_v from L. Brewer, National Nuclear Energy Series, Div. IV, 196, paper 7, McGraw-Hill Book Co., Inc., New York, 1950.

I_2Zr

I_2Zr

Zirconium Diiodide (ZrI₂)
(Liquid) Mol. Wt. = 345.04

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f kcal. mole ⁻¹	ΔF _f	Log K _p
0						
100						
200						
298	22,500	44,494	.000	55,985	58,199	42,659
300	22,550	44,633	.042	55,978	58,212	42,406
400	22,710	51,262	2,346	58,481	58,877	32,187
500	22,910	56,351	47,096	68,394	57,797	23,282
600	24,090	60,595	48,998	68,694	55,244	20,231
700	24,290	64,095	50,908	68,015	53,407	16,673
800	25,370	67,320	52,759	67,237	51,370	14,033
900	27,460	70,429	54,551	66,244	49,444	12,006
1000	29,540	73,429	56,299	65,053	47,638	10,411
1100	31,620	76,382	57,981	63,672	45,964	9,132
1200	34,700	79,183	59,630	62,164	44,374	8,081
1300	35,780	81,962	61,241	61,262	42,869	7,210
1400	37,870	84,690	62,819	60,620	41,549	6,486
1500	39,950	87,374	64,367	59,511	40,359	5,880
1600	42,030	90,019	65,887	58,610	39,317	5,370
1700	44,110	92,629	67,384	57,917	38,437	4,941
1800	46,170	95,209	68,858	57,432	37,711	4,579
1900	48,240	97,763	70,312	57,156	37,147	4,273
2000	50,360	100,297	71,748	57,068	36,748	4,015

I₂Zr

Zirconium Diiodide (ZrI₂) (Liquid)

Mol. Wt. = 345.04

ΔH_f^o 298.15 = [-56] kcal. mole⁻¹

S_{298.15}^o = [44.5] cal. deg.⁻¹ mole⁻¹

T_m = [700]°K.

ΔH_m = [6] kcal. mole⁻¹

T_b = [1300]°K.

ΔH_v = [27] kcal. mole⁻¹

Heat of Formation. Based upon the ΔH_f ZrI₂(c) and the estimated functions of both crystal and liquid.

Heat Capacity and Entropy. Entropy based upon the estimated values for C_p(c), ΔH_m, and C_p(l).

Melting and Vaporization. ΔH_m was estimated. T_m, T_b, and ΔH_v from L. Brewer, National Nuclear Energy Series, Div. IV, 19B, paper 7, McGraw-Hill Book Co., Inc., 1950.

I₂Zr

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	12.000	47.000	INFINITE	INFINITE	3.660	15.117	15.117	INFINITE
100	12.023	76.625	81.925	1.332	15.431	24.895	21.203	2.203
200	12.046	82.380	82.380	.000	15.928	29.438	21.577	2.577
300	12.063	82.665	82.380	.025	15.938	29.521	21.505	2.505
400	12.071	82.616	82.319	1.399	20.371	33.829	15.882	1.882
500	12.077	82.627	82.337	2.760	31.104	38.161	15.005	1.005
600	12.082	82.620	82.380	4.164	31.401	37.137	13.526	0.526
700	12.086	82.615	82.380	5.550	31.639	38.074	11.687	0.687
800	12.087	82.609	82.338	6.937	31.891	38.976	10.647	0.647
900	12.085	82.604	82.334	8.325	32.152	39.846	9.675	0.675
1000	12.080	82.597	82.333	9.714	32.422	40.685	8.691	0.691
1100	12.073	82.591	82.338	11.103	32.710	41.499	8.245	0.245
1200	12.066	82.584	82.333	12.493	33.007	42.287	7.692	0.692
1300	12.058	82.577	82.333	13.882	33.261	42.914	7.218	0.218
1400	12.050	82.570	82.333	15.272	33.485	43.389	6.801	0.801
1500	12.041	82.562	82.333	16.662	33.676	43.762	6.440	0.440
1600	12.033	82.554	82.333	18.052	33.839	44.030	6.121	0.121
1700	12.025	82.546	82.333	19.442	33.973	44.203	5.837	0.837
1800	12.017	82.538	82.333	20.832	34.083	44.293	5.582	0.582
1900	12.009	82.530	82.333	22.222	34.164	44.303	5.352	0.352
2000	12.000	82.522	82.333	23.612	34.224	44.234	5.143	0.143
2100	12.000	82.514	82.333	25.002	34.265	44.103	4.951	0.951
2200	12.000	82.506	82.333	26.392	34.286	43.913	4.760	0.760
2300	12.000	82.498	82.333	27.782	34.287	43.663	4.576	0.576
2400	12.000	82.490	82.333	29.172	34.268	43.363	4.407	0.407
2500	12.000	82.482	82.333	30.562	34.229	42.913	4.250	0.250
2600	12.000	82.474	82.333	31.952	34.160	42.313	4.104	0.104
2700	12.000	82.466	82.333	33.342	34.061	41.563	3.967	0.967
2800	12.000	82.458	82.333	34.732	33.932	40.673	3.839	0.839
2900	12.000	82.450	82.333	36.122	33.783	39.643	3.718	0.718
3000	12.000	82.442	82.333	37.512	33.614	38.473	3.605	0.605
3100	12.000	82.434	82.333	38.902	33.425	37.163	3.498	0.498
3200	12.000	82.426	82.333	40.292	33.216	35.713	3.397	0.397
3300	12.000	82.418	82.333	41.682	32.987	34.123	3.301	0.301
3400	12.000	82.410	82.333	43.072	32.738	32.393	3.210	0.210
3500	12.000	82.402	82.333	44.462	32.469	30.523	3.124	0.124
3600	12.000	82.394	82.333	45.852	32.180	28.513	3.042	0.042
3700	12.000	82.386	82.333	47.242	31.871	26.363	2.963	0.963
3800	12.000	82.378	82.333	48.632	31.542	24.083	2.888	0.888
3900	12.000	82.370	82.333	50.022	31.193	21.673	2.816	0.816
4000	12.000	82.362	82.333	51.412	30.824	19.133	2.746	0.746
4100	12.000	82.354	82.333	52.802	30.435	16.463	2.681	0.681
4200	12.000	82.346	82.333	54.192	30.026	13.673	2.618	0.618
4300	12.000	82.338	82.333	55.582	29.597	10.763	2.557	0.557
4400	12.000	82.330	82.333	56.972	29.148	7.733	2.499	0.499
4500	12.000	82.322	82.333	58.362	28.679	4.583	2.442	0.442
4600	12.000	82.314	82.333	59.752	28.190	1.313	2.388	0.388
4700	12.000	82.306	82.333	61.142	27.681	-1.957	2.335	0.335
4800	12.000	82.298	82.333	62.532	27.152	-5.207	2.282	0.282
4900	12.000	82.290	82.333	63.922	26.603	-8.427	2.230	0.230
5000	12.000	82.282	82.333	65.312	26.034	-11.607	2.178	0.178
5100	12.000	82.274	82.333	66.702	25.445	-14.747	2.126	0.126
5200	12.000	82.266	82.333	68.092	24.836	-17.847	2.074	0.074
5300	12.000	82.258	82.333	69.482	24.207	-20.907	2.022	0.022
5400	12.000	82.250	82.333	70.872	23.558	-23.927	1.970	0.970
5500	12.000	82.242	82.333	72.262	22.889	-26.907	1.918	0.918
5600	12.000	82.234	82.333	73.652	22.200	-29.847	1.866	0.866
5700	12.000	82.226	82.333	75.042	21.491	-32.747	1.814	0.814
5800	12.000	82.218	82.333	76.432	20.762	-35.607	1.762	0.762
5900	12.000	82.210	82.333	77.822	20.013	-38.427	1.710	0.710
6000	12.000	82.202	82.333	79.212	19.244	-41.207	1.658	0.658

June 30, 1962

Zirconium Dioxide (ZrI₂)

(Ideal Gas)

Mol. Wt. = 345.04

ΔH_f⁰ 239.15 = [-16] kcal. mole⁻¹S_{298.15}⁰ = [82.4] cal. deg⁻¹ mole⁻¹Point group C_{2v}

Vibrational Levels and Multiplicities

ω, cm⁻¹

[60] (1)

[120] (1)

[240] (1)

rZr-I = [2.66 Å]

Δ I-Zr-I = 120°

σ = 2

Product of Moments of Inertia I_AI_BI_C = 1.0716 X 10⁻¹¹¹ g.³ cm.⁶Heat of Formation. Based upon the estimated value of the ΔH_f⁰ for the crystal and the appropriate crystal and gas functions.

Heat Capacity and Entropy. Molecular constants were all estimated by comparison to similar molecules of zirconium and titanium.

TITANIUM TRIIODIDE (TiI₃) (CRYSTAL) GFW = 428.6132

$\Delta H_f^\circ = \text{unknown}$

$\Delta H_{298.15}^\circ = [-77 \pm 5] \text{ kcal/mol}$

$\Delta H_s^\circ = [35.4] \text{ kcal/mol}$

$S_{298.15}^\circ = [46.0 \pm 2.0] \text{ gibbs/mol}$

$T_s = [1000]^\circ\text{K}$

Heat of Formation

The heat of formation of TiI₃(c) is calculated from the free energy of formation at 823°K combined with the increment $\Delta G_{823}^\circ - \Delta G_{298.15}^\circ$ of TiI₂(c), TiI₃(c) and TiI₄(g). The free energy of formation, $\Delta G_{298.15}^\circ$, is estimated such that $\Delta G_{298.15}^\circ = 0$ for the process $2\text{TiI}_3(\text{c}) = \text{TiI}_2(\text{c}) + \text{TiI}_4(\text{g})$. This assumption is based on the observations of Herczog and Pidgeon (1) and Fast (2).

Heat Capacity and Entropy

The heat capacities of TiI₃(c) and the value of $S_{298.15}^\circ$ estimated by Kelley (3) have been adopted.

Heat of Sublimation

The heat of sublimation of TiI₃(c) is taken as the difference in the heats of formation of TiI₃(c) and TiI₃(g) at the sublimation temperature. The sublimation temperature is estimated as the point at which $\Delta G^\circ = 0$ for the process $\text{TiI}_3(\text{c}) = \text{TiI}_3(\text{g})$.

References

1. A. Herczog and L. M. Pidgeon, Can. J. Chem., **34**, 1687 (1956).
2. J. P. Fast, Rec. Trav. Chim., **58**, 174 (1939).
3. K. K. Kelley, U. S. Bur. Mines Bull. **584**, 1960; U. S. Bur. Mines Bull. **592**, 1961.

Titanium Triiodide (TiI₃)

(Crystal) GFW = 428.6132

T, °K	C _p	S ^a	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^b	ΔG ^c	Log K _p
100							
200							
298	27.909	46.000	46.000	0.000	77.000	76.117	55.795
300	27.912	46.173	46.001	-0.052	74.995	74.111	55.487
400	28.086	54.826	47.097	2.052	82.571	75.445	41.331
500	28.260	60.512	49.174	5.669	97.685	72.494	31.687
600	28.434	65.680	51.507	8.504	96.861	67.535	24.600
800	28.608	74.076	53.654	11.356	96.044	62.712	19.579
900	28.696	77.308	54.286	12.830	95.431	58.481	12.846
1000	28.784	80.368	54.851	14.112	94.821	53.998	10.683
1100	28.872	83.152	55.369	15.200	94.216	48.880	8.629
1200	28.960	85.709	55.845	16.145	93.602	44.439	7.291
1400	29.048	90.279	56.834	20.877	92.163	35.637	5.993
1500	30.000	92.343	59.148	34.799	90.430	27.080	3.945

Titanium Triiodide (TiI₃)

(Ideal Gas)

GFW = 428.6132

TITANIUM TRIIODIDE (TiI₃)

(IDEAL GAS)

GFW = 428.6132

Point Group [C_{3v}]

$\Delta H_f^\circ = [-34.5 \pm 8.0]$ kcal/mol

$S_{298.15}^\circ = [81.3 \pm 3]$ gibbs/mol

$\Delta H_f^\circ = [-35.9 \pm 8.0]$ kcal/mol

Ground State Quantum Weight = [2]

$\Delta H_f^\circ = [-35.9 \pm 8.0]$ kcal/mol

T, K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	Log Kp
0	13.000	0.000	INFINITE	4.525	34.542	INFINITE
100	13.986	72.986	107.175	3.419	34.663	66.597
200	17.598	83.901	93.015	1.823	48.250	48.354
298	19.311	91.294	91.294	1.000	35.900	35.567
300	19.322	91.416	91.294	0.916	48.599	35.403
400	20.682	97.062	97.063	2.011	42.312	25.703
500	20.420	101.415	91.337	4.039	58.215	23.418
600	20.569	105.333	95.204	6.089	58.176	19.179
700	20.627	108.528	96.866	8.150	58.150	16.152
800	20.641	111.264	100.518	10.217	58.148	13.683
900	20.635	113.689	103.566	12.284	58.146	11.217
1000	20.625	115.689	101.549	14.340	58.216	10.706
1100	20.612	117.454	102.943	16.402	58.322	9.546
1200	20.599	119.447	104.261	18.463	59.377	8.573
1300	20.586	121.295	105.509	20.522	59.395	7.741
1400	20.573	122.930	106.684	22.581	59.384	7.006
1500	20.562	124.230	107.815	24.637	59.492	6.409
1600	20.551	125.566	108.883	26.692	59.570	5.866
1700	20.541	126.812	109.902	28.747	59.672	5.387
1800	20.530	127.966	110.874	30.801	59.769	4.961
1900	20.520	129.044	111.813	32.854	59.858	4.586
2000	20.512	130.148	112.695	34.905	60.576	4.216
2100	20.503	131.148	113.550	36.956	64.759	3.7278
2200	20.495	132.102	114.372	39.005	64.944	35.967
2300	20.486	133.013	115.163	41.055	65.131	34.645
2400	20.478	133.884	115.924	43.104	65.318	32.992
2500	20.473	134.721	116.660	45.151	65.513	31.978
2600	20.469	135.523	117.370	47.198	65.707	30.633
2700	20.464	136.296	118.057	49.245	65.906	29.280
2800	20.459	137.040	118.722	51.291	66.106	27.918
2900	20.454	137.751	119.366	53.332	66.314	26.548
3000	20.449	138.451	119.991	55.382	66.534	25.178
3100	20.445	139.122	120.597	57.426	66.722	1.677
3200	20.441	139.771	121.186	59.471	66.932	22.409
3300	20.437	140.400	121.759	61.515	67.145	21.011
3400	20.433	141.011	122.316	63.558	67.361	19.604
3500	20.428	141.602	122.859	65.601	67.577	18.202
3600	20.424	142.177	123.387	67.644	67.644	16.527
3700	20.420	142.737	123.903	69.686	69.686	15.003
3800	20.416	143.281	124.406	71.729	71.729	13.481
3900	20.412	143.811	124.896	73.769	73.769	11.961
4000	20.408	144.328	125.378	75.810	75.810	10.447
4100	20.403	144.832	125.844	77.851	77.851	8.931
4200	20.399	145.324	126.302	79.891	79.891	7.415
4300	20.394	145.803	126.750	81.930	81.930	5.900
4400	20.390	146.273	127.189	83.970	83.970	4.385
4500	20.385	146.731	127.618	86.008	86.008	2.870
4600	20.381	147.179	128.038	88.047	88.047	1.355
4700	20.376	147.617	128.450	90.085	90.085	0.840
4800	20.371	148.046	128.854	92.122	92.122	0.325
4900	20.367	148.466	129.250	94.159	94.159	-0.190
5000	20.362	148.877	129.638	96.195	96.195	-0.705
5100	20.357	149.281	130.019	98.231	98.231	-1.220
5200	20.352	149.676	130.394	100.267	100.267	-1.735
5300	20.347	150.063	130.763	102.302	102.302	-2.250
5400	20.342	150.444	131.122	104.336	104.336	-2.765
5500	20.337	150.817	131.477	106.370	106.370	-3.280
5600	20.332	151.183	131.825	108.403	108.403	-3.795
5700	20.327	151.543	132.166	110.438	110.438	-4.310
5800	20.322	151.898	132.501	112.472	112.472	-4.825
5900	20.317	152.248	132.837	114.501	114.501	-5.340
6000	20.312	152.595	133.163	116.532	116.532	-5.855
6100	20.307	152.937	133.484	118.563	118.563	-6.370
6200	20.302	153.274	133.801	120.594	120.594	-6.885
6300	20.297	153.607	134.114	122.625	122.625	-7.400
6400	20.292	153.936	134.423	124.656	124.656	-7.915
6500	20.287	154.261	134.728	126.687	126.687	-8.430
6600	20.282	154.581	135.029	128.718	128.718	-8.945
6700	20.277	154.897	135.326	130.749	130.749	-9.460
6800	20.272	155.209	135.619	132.780	132.780	-9.975
6900	20.267	155.517	135.908	134.811	134.811	-10.490
7000	20.262	155.821	136.193	136.842	136.842	-11.005
7100	20.257	156.122	136.474	138.873	138.873	-11.520
7200	20.252	156.419	136.751	140.904	140.904	-12.035
7300	20.247	156.713	137.024	142.935	142.935	-12.550
7400	20.242	157.004	137.293	144.966	144.966	-13.065
7500	20.237	157.291	137.558	146.997	146.997	-13.580
7600	20.232	157.574	137.819	149.028	149.028	-14.095
7700	20.227	157.854	138.076	151.059	151.059	-14.610
7800	20.222	158.131	138.329	153.090	153.090	-15.125
7900	20.217	158.405	138.578	155.121	155.121	-15.640
8000	20.212	158.676	138.823	157.152	157.152	-16.155
8100	20.207	158.944	139.064	159.183	159.183	-16.670
8200	20.202	159.209	139.301	161.214	161.214	-17.185
8300	20.197	159.471	139.534	163.245	163.245	-17.700
8400	20.192	159.730	139.763	165.276	165.276	-18.215
8500	20.187	160.000	140.000	167.307	167.307	-18.730
8600	20.182	160.261	140.224	169.338	169.338	-19.245
8700	20.177	160.519	140.444	171.369	171.369	-19.760
8800	20.172	160.774	140.661	173.399	173.399	-20.275
8900	20.167	161.026	140.874	175.430	175.430	-20.790
9000	20.162	161.275	141.083	177.461	177.461	-21.305
9100	20.157	161.521	141.288	179.492	179.492	-21.820
9200	20.152	161.764	141.489	181.523	181.523	-22.335
9300	20.147	162.004	141.686	183.554	183.554	-22.850
9400	20.142	162.241	141.879	185.585	185.585	-23.365
9500	20.137	162.475	142.068	187.616	187.616	-23.880
9600	20.132	162.706	142.253	189.647	189.647	-24.395
9700	20.127	162.934	142.434	191.678	191.678	-24.910
9800	20.122	163.159	142.611	193.709	193.709	-25.425
9900	20.117	163.381	142.784	195.740	195.740	-25.940
10000	20.112	163.600	142.953	197.771	197.771	-26.455

June 30, 1964; Dec. 31, 1968

Bond Distance: Ti-I = [2.7] Å

Bond Angle: I-Ti-I = [100°]

$\sigma = 3$

Product of the Moments of Inertia: $I_{A-B-C} = [1.3 \times 10^{-110}] \text{ g cm}^6$

Heat of Formation

The heat of formation, ΔH_f° , of $\text{TiI}_3(\text{g})$ is estimated from the average Ti-I bond energy. The bond energy is estimated from the corresponding quantities for $\text{TiBn}_3(\text{g})$, $\text{TiBn}_3(\text{g})$, and $\text{TiI}_4(\text{g})$.

Heat Capacity and Entropy

The internuclear distance is estimated from those of TiI_4 , TiCl_4 , and TiCl_3 . The pyramidal bond angle is estimated by assuming that $\text{TiI}_3(\text{g})$ is similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 1.9 \times 10^{-37} \text{ g cm}^2$ and $I_C = 3.6 \times 10^{-37} \text{ g cm}^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3} reported by C. E. Moore, U. S. Natl. Bur. Std., Circ. 467, 1949.

Zirconium Triiodide (ZrI_3)
(Crystal) Mol. Wt. = 471.950

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	+0.00	INFINITE	5.822	- 94.774	- 94.774	INFINITE	
100	19.925	24.059	69.939	- 4.288	- 94.846	94.727	207.016
200	23.501	29.282	51.152	- 2.378	- 94.846	94.727	163.382
298	24.832	30.637	48.897	- 0.000	- 94.846	94.727	69.186
300	24.832	49.051	48.897	+0.046	- 95.001	94.384	68.756
400	25.300	56.267	49.878	2.556	- 100.884	93.862	51.336
500	25.400	61.923	51.742	5.091	- 116.305	90.775	39.676
600	25.500	66.564	53.817	7.636	- 115.809	85.717	31.221
700	25.550	70.499	55.944	10.189	- 115.330	80.740	25.207
800	25.600	73.914	57.981	12.746	- 114.862	75.830	20.715
900	25.650	76.932	59.922	15.309	- 114.400	70.979	17.235
1000	25.680	79.636	61.761	17.875	- 113.945	66.178	14.462
1100	25.700	82.085	63.499	20.444	- 113.507	61.424	12.203
1200	25.720	84.322	65.142	23.015	- 113.037	56.660	10.310
1300	25.740	86.381	66.668	25.588	- 112.602	51.896	8.724
1400	25.750	88.289	68.173	28.163	- 112.177	47.166	7.363
1500	25.760	90.066	69.574	30.738	- 111.759	42.467	6.187
1600	25.770	91.729	70.907	33.315	- 111.340	37.790	5.182
1700	25.780	93.291	72.178	35.892	- 110.948	33.144	4.261
1800	25.790	94.765	73.493	38.471	- 110.554	28.520	3.463
1900	25.800	96.160	74.754	41.050	- 110.169	23.917	2.751
2000	25.810	97.484	75.968	43.631	- 110.793	19.339	2.113

June 30, 1962; June 30, 1964

ZIRCONIUM TRIIODIDE (ZrI_3) (CRYSTAL) MOL. WT. = 471.950

$S^\circ_{298.15} = [48.90] \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $T_g = [970]^\circ\text{K.}$
 $T_d = [1000]^\circ\text{K.}$
 $\Delta H^\circ_f 0 = [-95] \text{ kcal. mole}^{-1}$
 $\Delta H^\circ_f 298.15 = [-95] \text{ kcal. mole}^{-1}$
 $\Delta H^\circ_g 298.15 = [42] \text{ kcal. mole}^{-1}$

Heat of Formation.

E. M. Larson and J. J. Leddy, *J. Am. Chem. Soc.* 78, 5985 (1956), studied the reaction $Zr(c) + 3ZrI_3(g) = 4ZrI_3(c)$ in the temperature range 475 to 975°K. and pressure range 5 to 15 atm. They present a plot of the fractional reaction, at a number of temperatures, as a function of reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The free energy function change for this reaction was calculated at 100° intervals from 500 to 1100°K. At each temperature the equilibrium constant was assumed to be 1, and ΔH°_{298} accordingly calculated. These values and the heat of formation of $ZrI_4(g)$ [see ZrI_4 table] were used to compute a series of values for the heat of formation of $ZrI_3(c)$ at 298.15°K. The following table gives representative values at four temperatures.

T (°K.)	K_p	ΔH°_{298}	$\Delta H^\circ_{298.15} [ZrI_3(c)]$
500	1	-86.0 kcal. mole ⁻¹	-80.2 kcal. mole ⁻¹
700	1	-80.3 kcal. mole ⁻¹	-86.2 kcal. mole ⁻¹
900	1	-113.5 kcal. mole ⁻¹	-92.1 kcal. mole ⁻¹
1100	1	-135.9 kcal. mole ⁻¹	-97.7 kcal. mole ⁻¹

If one assumes an initial pressure of from 5 to 10 atm. for ZrI_4 and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of ZrI_4 to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larson and Leddy indicate that the reaction proceeds to the extent of 89% at 975°K. From this it was assumed that at around 1000°K. the equilibrium constant attains a value of 1 giving -95 kcal. mole⁻¹ for the heat of formation of ZrI_3 at 298.15°K.

Their data was subjected to a second law calculation but the results are of doubtful value in view of the uncertainty in the attainment of thermodynamic equilibrium at the lower temperatures. The limits of error assigned to the heat of formation are $\pm 15 \text{ kcal. mole}^{-1}$ corresponding to a temperature spread of $\pm 500^\circ$ in the above table.

Heat Capacity and Entropy.

The heat capacity was estimated in the same manner as for $ZrBr_3(c)$ [see $ZrBr_3(c)$ table]. The values $\theta_D = 60^\circ\text{K.}$ and $\theta_E = 115^\circ\text{K.}$ were taken to be the same as those estimated for $ZrI_4(c)$. The internal contribution was obtained from the estimated ZrI_3 vibrational frequencies and the anharmonicity factor, " a ", was taken to be 2.5×10^{-3} . The specific heat above 300°K. was obtained by graphical extrapolation.

For the above estimation, it was assumed that the crystalline lattice is made up of ZrI_3 molecules. However, E. Holze [see R. F. Rolsten, "Iodide Metals and Metal Iodides", John Wiley & Sons, Inc., New York, 1961, page 46] came to the conclusion that crystalline ZrI_3 is composed of a chain lattice of $(ZrI_3)_n$ units. The results of an analysis for a crystalline lattice composed of Zr_2I_6 units would probably not differ significantly from that for a crystalline lattice composed of ZrI_3 units since both are approaching the classical harmonic heat capacity of 12R calories per formula weight of ZrI_3 at relatively low temperatures.

Until more quantitative information becomes available, it is felt that the above analysis gives a fair approximation to the heat capacity of ZrI_3 .

Temperature of Disproportionation.

As described in the "Heat of Formation" section, this was assumed to be $1000^\circ \pm 500^\circ\text{K.}$

Liquid Phase.

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data.

The heat of sublimation at 298.15°K. was obtained from the difference in the heats of formation of the gas and solid at 298.15°K. The sublimation point was obtained from the free energy crossover between gas and solid.

Zirconium Triiodide (ZrI₃)

(Ideal Gas)

Mol. Wt. = 471.950

ZIRCONIUM TRIIODIDE (ZrI₃)

(IDEAL GAS)

MOL. WT. = 471.950

T, K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	16.291	51.828	4.876	51.828	51.828	INFINITE
200	18.704	111.712	3.651	51.800	124.359	124.359
298	19.517	95.047	0.000	51.800	61.709	67.429
300	19.524	95.166	0.036	53.011	66.148	48.486
400	19.557	100.762	1.981	59.459	70.534	38.427
500	19.669	105.139	3.943	75.452	71.531	31.264
600	19.730	108.731	5.914	75.531	70.740	25.766
700	19.768	111.776	7.889	75.530	69.531	21.766
800	19.792	114.417	9.867	75.741	69.112	18.880
900	19.806	116.749	11.847	75.862	68.277	16.579
1000	19.821	118.837	13.828	75.992	67.426	14.735
1100	19.830	120.727	15.811	76.140	66.564	13.224
1200	19.837	122.452	17.794	77.258	65.638	11.954
1300	19.842	124.040	19.778	77.412	64.663	10.870
1400	19.846	125.511	21.763	77.577	63.677	9.940
1500	19.850	126.880	23.747	77.750	62.679	9.132
1600	19.852	128.161	25.733	77.931	61.664	8.423
1700	19.855	129.365	27.718	78.122	60.634	7.797
1800	19.857	130.500	29.703	78.322	59.610	7.237
1900	19.858	131.574	31.689	78.530	58.564	6.736
2000	19.860	132.592	33.675	78.748	57.512	6.284
2100	19.861	133.561	35.661	78.974	56.442	5.874
2200	19.862	134.485	37.647	80.117	55.359	5.491
2300	19.863	135.368	39.634	81.262	54.279	5.119
2400	19.864	136.213	41.620	82.413	53.207	4.785
2500	19.864	137.024	43.606	83.567	52.147	4.476
2600	19.865	137.803	45.593	84.723	51.095	4.191
2700	19.866	138.553	47.579	85.879	50.056	3.928
2800	19.866	139.276	49.566	87.041	49.022	3.678
2900	19.866	139.973	51.552	88.203	47.990	3.447
3000	19.867	140.646	53.539	89.367	46.954	3.231
3100	19.867	141.298	55.526	90.533	45.920	3.028
3200	19.868	141.928	57.513	91.700	44.887	2.836
3300	19.868	142.540	59.499	92.868	43.853	2.658
3400	19.868	143.133	61.486	94.036	42.819	2.488
3500	19.868	143.709	63.473	95.200	41.784	2.327
3600	19.869	144.269	65.460	96.364	40.749	2.176
3700	19.869	144.813	67.447	97.528	39.714	2.032
3800	19.869	145.343	69.434	98.690	38.679	1.894
3900	19.869	145.859	71.420	99.853	37.643	1.764
4000	19.869	146.362	73.407	101.016	36.607	1.640
4100	19.870	146.853	75.394	102.179	35.571	1.521
4200	19.870	147.331	77.381	103.342	34.535	1.407
4300	19.870	147.794	79.368	104.505	33.498	1.299
4400	19.870	148.256	81.355	105.668	32.461	1.195
4500	19.870	148.702	83.342	106.830	31.424	1.095
4600	19.870	149.139	85.329	107.993	30.387	1.000
4700	19.870	149.566	87.316	109.156	29.350	0.908
4800	19.870	149.985	89.303	110.319	28.313	0.819
4900	19.870	150.394	91.290	111.482	27.276	0.733
5000	19.871	150.796	93.277	112.645	26.239	0.650
5100	19.871	151.189	95.264	113.808	25.202	0.568
5200	19.871	151.575	97.252	114.971	24.165	0.489
5300	19.871	151.956	99.239	116.134	23.128	0.413
5400	19.871	152.325	101.226	117.297	22.091	0.339
5500	19.871	152.690	103.213	118.460	21.054	0.267
5600	19.871	153.048	105.200	119.623	20.017	0.197
5700	19.871	153.400	107.187	120.786	18.980	0.130
5800	19.871	153.745	109.174	121.949	17.943	0.065
5900	19.871	154.085	111.161	123.112	16.906	0.001
6000	19.871	154.419	113.148	124.275	15.869	-0.064

June 30, 1964

Point Group = [C_{3v}]S_{298.15} = [95.05] cal. mole⁻¹ deg.⁻¹

Ground State Quantum Weight = [2]

ΔH_f⁰ = [-52] kcal. mole⁻¹ΔH_f⁰ 298.15 = [-53] kcal. mole⁻¹

Vibrational Frequencies and Degeneracies

ω, cm.⁻¹

[198] (1)

[88] (1)

[220] (2)

[65] (2)

σ = [3]

Bond Distances Zr-I = [2.59] Å

Bond Angle: I-Zr-I = [101]°

Product of the Moments of Inertia: I_AI_BI_C = [1.1545 X 10⁻¹¹⁰] gm.³ cm.⁶

Heat of Formation.

The heats of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium-halide bond energy, taken as 1/4 of this heat of formation, was found to be linear with internuclear separation. From gaseous titanium tri- and tetrachloride, it was found that the bond energy of the trichloride was around 7 kcal. mole⁻¹ greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium triiodide, the heat of formation from the gaseous atoms was -275 kcal. mole⁻¹ and from the elements in their standard state, -55 kcal. mole⁻¹.

Heat Capacity and Entropy.

The measured internuclear distances for the triiodides of phosphorus, arsenic, and antimony were plotted as a function of the atomic weight of these elements and a smooth curve was drawn through the points. The bond distance in ZrI₃ was taken from this plot. The bond angle was assumed to be 101°. The individual moments of inertia are: I_A = I_B = 1.8520 X 10⁻⁵⁷ gm. cm.², I_C = 3.3661 X 10⁻⁵⁷ gm. cm.².

Force constants for ZrI₃ were estimated from those of the triiodides of phosphorus and arsenic. These were used in a valence force field calculation giving ω₁ = 185, ω₂ = 88, ω₃ = 181, and ω₄ = 65 cm.⁻¹. For the fluorides and chlorides of P, As, and Sb, ω₁ is greater than ω₃ but there appears to be a reversal as one goes to the bromides and iodides with ω₃ becoming greater than ω₁. An empirical correlation procedure for ZrI₃ gave ω₁ = 195, ω₂ = 90, ω₃ = 220, and ω₄ = 65 cm.⁻¹ in which ω₃ > ω₁. Since ω₃ > ω₁ for PI₃ and AsI₃, the correlation value for ω₃ was used to represent this frequency in ZrI₃.

Lead Tetraiodide (PbI₄)
(Ideal Gas) Mol. Wt. = 714.85 INTERIM TABLE

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	22.757	84.703	133.594	6.603	.949	.949	INFINITE
200	24.923	101.355	113.728	2.475	.782	3.892	8.505
298	25.419	111.416	111.416	.000	.400	12.450	9.126
300	25.4415	111.573	111.416	.047	.413	12.524	9.123
400	25.596	118.913	112.416	2.599	.857	16.181	8.840
500	25.681	124.634	114.308	5.163	30.012	16.003	6.995
600	25.727	130.321	116.431	7.734	29.025	15.210	4.812
700	25.756	135.749	118.485	10.285	30.965	14.273	1.987
800	25.776	140.924	120.624	12.885	30.905	4.316	1.048
900	25.787	145.766	122.585	15.463	30.846	1.364	.298
1000	25.796	149.484	124.442	18.042	30.779	1.580	.314
1100	25.802	152.993	126.195	20.622	30.709	1.753	.325
1200	25.808	156.314	127.853	23.193	30.631	1.883	.332
1300	25.812	159.459	129.420	25.763	30.548	1.973	.337
1400	25.815	162.431	130.906	28.335	30.458	2.037	.340
1500	25.817	165.248	132.317	30.946	30.367	2.078	.342
1600	25.819	167.914	133.659	33.528	30.270	2.107	.343
1700	25.821	170.437	134.934	36.083	30.168	2.126	.344
1800	25.823	172.819	136.160	38.622	30.061	2.136	.345
1900	25.824	175.052	137.328	41.147	30.259	2.146	.346
2000	25.825	177.146	138.448	43.657	30.219	2.156	.347
2100	25.826	179.103	139.522	46.140	30.172	2.165	.348
2200	25.827	180.928	140.552	48.597	30.120	2.173	.349
2300	25.827	182.624	141.549	51.035	30.063	2.180	.350
2400	25.828	184.285	142.507	53.454	29.999	2.187	.351
2500	25.828	185.913	143.431	55.857	29.930	2.193	.352
2600	25.829	187.512	144.324	58.246	29.856	2.199	.353
2700	25.829	189.083	145.187	60.619	29.777	2.205	.354
2800	25.830	190.626	146.024	62.978	29.693	2.211	.355
2900	25.830	192.143	146.834	65.324	29.604	2.217	.356
3000	25.830	193.628	147.620	67.658	29.511	2.223	.357
3100	25.831	195.083	148.393	70.000	29.414	2.229	.358
3200	25.831	196.509	149.146	72.268	29.313	2.235	.359
3300	25.831	197.907	149.885	74.534	29.208	2.241	.360
3400	25.831	199.278	150.607	76.798	29.100	2.247	.361
3500	25.831	174.830	151.230	82.600	29.000	2.253	.362
3600	25.832	175.558	151.896	85.184	28.900	2.259	.363
3700	25.832	176.255	152.545	87.766	28.800	2.265	.364
3800	25.832	176.925	153.178	90.344	28.700	2.271	.365
3900	25.832	177.576	153.797	92.933	28.600	2.277	.366
4000	25.832	178.200	154.400	95.516	28.500	2.283	.367
4100	25.832	178.817	154.991	98.100	28.400	2.289	.368
4200	25.832	179.418	155.566	100.683	28.300	2.295	.369
4300	25.832	180.000	156.132	103.266	28.200	2.301	.370
4400	25.833	180.742	156.685	105.849	28.100	2.307	.371
4500	25.833	181.322	157.226	108.432	28.000	2.313	.372
4600	25.833	181.890	157.756	111.016	27.900	2.319	.373
4700	25.833	182.439	158.276	113.600	27.800	2.325	.374
4800	25.833	182.989	158.785	116.182	27.700	2.331	.375
4900	25.833	183.522	159.284	118.766	27.600	2.337	.376
5000	25.833	184.044	159.774	121.348	27.500	2.343	.377
5100	25.833	184.556	160.255	123.932	27.400	2.349	.378
5200	25.833	185.059	160.726	126.516	27.300	2.355	.379
5300	25.833	185.549	161.191	129.099	27.200	2.361	.380
5400	25.833	186.032	161.647	131.682	27.100	2.367	.381
5500	25.833	186.506	162.094	134.265	27.000	2.373	.382
5600	25.833	186.971	162.534	136.849	26.900	2.379	.383
5700	25.833	187.428	162.963	139.432	26.800	2.385	.384
5800	25.833	187.878	163.389	142.015	26.700	2.391	.385
5900	25.833	188.320	163.811	144.599	26.600	2.397	.386
6000	25.834	188.754	164.224	147.182	26.500	2.403	.387

June 30, 1962

I₄Pb

Lead Tetraiodide (PbI₄) (Ideal Gas)

Mol. Wt. = 714.85

ΔH_f⁰ 298.15 = [-0.4] kcal. mole⁻¹

S_{298.15} = 111.4 cal. deg.⁻¹ mole⁻¹

Point Group T_d

Vibrational Levels and Multiplicities

ω, cm.⁻¹

137 (1)
37 (2)
168 (3)
46 (3)

Pb-I distance = 2.77 Å I-Pb-I angle = 109° 28'

I_AB₂C = 8.0044 X 10⁻¹¹⁰ g.³ cm.⁶ σ = 12

Heat of Formation. ΔH_f⁰ 298.15 was estimated by comparison with the value of ΔH_f⁰ 298.15 for PbI₂(g).

Heat Capacity and Entropy. Vibrational frequencies and molecular constants were obtained from O. Nagarsajan, Bull. Soc. Chim. Belg., 71, 119 (1962).

I₄Pb

Titanium Tetraiodide (TiI₄)
(Crystal) GFW = 555.5176

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 6.948	- 89.305	- 89.305	INFINITE
100	24.081	28.695	84.359	- 5.566	- 89.498	- 89.245	195.066
200	28.525	47.130	61.536	- 2.881	- 89.627	- 88.961	97.212
298	30.026	58.831	58.831	.000	- 89.600	- 88.605	64.949
300	30.102	59.017	58.832	.056	- 89.603	- 88.507	64.843
400	35.400	74.583	60.393	5.176	- 89.145	- 88.061	8.103
500	35.400	82.482	64.050	9.216	- 115.297	- 88.372	36.879
600	35.400	88.937	67.676	12.756	- 114.217	- 78.291	28.517
700	35.400	94.394	71.113	16.296	- 113.161	- 72.387	22.400
800	35.400	99.074	74.327	19.836	- 112.133	- 66.631	18.203
900	35.400	103.280	77.277	23.376	- 111.124	- 61.016	14.514
1000	35.400	107.020	80.104	26.916	- 110.171	- 55.466	12.126
1100	35.400	110.394	82.706	30.456	- 109.234	- 50.062	9.946
1200	35.400	113.474	85.144	33.996	- 109.264	- 44.666	8.138
1300	35.400	116.276	87.484	37.536	- 109.256	- 39.345	6.674
1400	35.400	118.931	89.891	41.076	- 109.256	- 34.024	5.472
1500	35.400	121.373	91.629	44.616	- 106.300	- 28.600	4.209

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

TITANIUM TETRAIODIDE (TiI₄)

(CRYSTAL)

GFW = 555.5176

$$\Delta H_f^\circ = -89.3 \pm 2.0 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = -89.8 \pm 2.0 \text{ kcal/mol}$$

$$\Delta H^\circ = 2.37 \pm 0.15 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 4.74 \pm 0.15 \text{ kcal/mol}$$

$$S^\circ_{298.15} = 88.8 \pm 1.6 \text{ gibbs/mol}$$

$$T_f = 379^\circ\text{K}$$

$$T_m = 428^\circ\text{K}$$

Heat of Formation

The heat of formation of TiI₄(c) was measured by Johnson et al. (1), based on the heats of hydrolysis of TiBr₄(c) and TiI₄(c) in sulfuric acid. These data result in a heat of reaction of -57.88 kcal/mol for the process TiI₄(c) + 2Br₂(l) = TiBr₄(c) + 2I₂(c), when recalculated with revised values of ΔHf° for HBr(aq) and HI(aq) (2). Combination of ΔHf°₂₉₈ with auxiliary JANAF data gives the adopted value of ΔHf°₂₉₈.

Heat Capacity and Entropy

King et al. (3) reported the heat capacity and enthalpy of TiI₄(c) over the temperature range 51° to 428°K. The value of S°₂₉₈ is calculated from these data based on S°₅₁ = 14.62 eu. The value of H°₅₁ - H°₀ is calculated to be 0.358 kcal/mol from a Debye-Einstein extrapolation of the measured heat capacities.

Transition Data

A first order transition was observed by King et al. (2) at 379°K. They reported the measured value of 2.37 kcal/mol, noting that this value had an uncertainty of 0.15 kcal/mol due to hysteresis in the transition.

Melting Data

The melting temperature and heat of melting were reported by King et al. (2). The large uncertainty on ΔHm° is due to the uncertainty and close proximity of the transition at 379°K.

References

1. W. H. Johnson, A. A. Gilliland, and E. J. Prosen, J. Res. Natl. Bur. Std., **63A**, 161 (1959).
2. U. S. Natl. Bur. Std. Tech. Note 270-3, 1968.
3. E. G. King, W. W. Waller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

Titanium Tetraiodide (TiI₄)

(Liquid) GFW = 555.5176

TITANIUM TETRAIODIDE (TiI₄)

(LIQUID)

GFW = 555.5176

 $\Delta H_f^\circ = \text{unknown}$ $\Delta H_f^\circ_{298.15} = -83.25 \text{ kcal/mol}$ $\Delta H_m^\circ = 4.74 \pm 0.15 \text{ kcal/mol}$ $\Delta H_v^\circ = 13.50 \pm 0.5 \text{ kcal/mol}$ $S^\circ_{298.15} = 74.532 \text{ gibbs/mol}$ $T_m = 428^\circ\text{K}$ $T_b = 652.6^\circ\text{K}$

Heat of Formation

The heat of formation of $\text{TiI}_4(l)$ is calculated from the heat of melting, ΔH_m° , the heat of formation of $\text{TiI}_4(c)$, and the values of $H_{428}^\circ - H_{298.15}^\circ$ for both crystal and liquid.

Heat Capacity and Entropy

King et al. (1) reported the enthalpy of $\text{TiI}_4(l)$ above the melting temperature. The heat capacity derived from these data is constant. The entropy, S°_{298} , of $\text{TiI}_4(l)$ is calculated from ΔS_m° and the values of $S_{428}^\circ - S_{298.15}^\circ$ of both crystal and liquid.

Melting Data

The melting temperature and heat of melting were reported by King et al. (1).

Vaporization Data

The boiling temperature, T_b , is taken as the point at which $K_p = 1$ for the reaction $\text{TiI}_4(l) = \text{TiI}_4(g)$. The heat of vaporization is calculated as the difference between ΔH_f° of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $\text{TiI}_4(g)$.

Reference

1. E. G. King, W. Weller, A. U. Christensen, and K. K. Kelley, U. S. Bur. Mines RI 5799, 1961.

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0							
100							
200							
298	37.400	74.532	74.531	0.000	83.250	86.736	63.579
300	37.400	74.763	74.532	0.069	83.240	86.757	63.202
400	37.400	85.522	75.999	3.869	90.462	87.753	57.935
500	37.400	93.888	78.769	7.589	110.414	85.162	37.233
600	37.400	100.687	81.871	11.289	109.134	80.299	29.234
700	37.400	106.652	84.982	15.029	107.878	75.545	23.566
800	37.400	111.446	87.984	18.769	106.650	71.008	19.399
900	37.400	115.051	90.841	22.509	105.454	66.628	16.179
1000	37.400	119.191	93.542	26.249	104.288	62.374	13.632
1100	37.400	123.356	96.093	29.989	103.151	58.238	11.571
1200	37.400	126.610	98.503	33.729	102.081	54.166	9.865
1300	37.400	129.604	100.781	37.469	101.773	50.147	8.430
1400	37.400	132.376	102.940	41.209	100.586	46.220	7.215
1500	37.400	134.956	104.990	44.949	99.417	42.381	6.175

TITANIUM TETRAIODIDE (TiI₄)

GFW = 555.5176

(IDEAL GAS)

Titanium Tetraiodide (TiI₄)

(Ideal Gas) GFW = 555.5176

Point Group T_d

$$\Delta H_f^\circ = -65.0 \pm 2 \text{ kcal/mol}$$

$$\Delta H_{298.15}^\circ = -66.27 \pm 2 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 103.48 \pm 2 \text{ gibbs/mol}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies
 $\frac{\omega_e}{\text{cm}^{-1}}$
[175] (1) [260] (3) [55] (2) [69] (3)

Bond Distance: Ti-I = [2.5] Å

Bond Angle: I-Ti-I = [109°28']

 $\sigma = 12$ Product of the Moments of Inertia: $I_A I_B I_C = [4.33 \times 10^{-110}] \text{ g cm}^6$

Heat of Formation

The heat of formation of TiI₄(g) is calculated from that of TiI₄(l) and the heat of vaporization of the liquid. Blocher and Campbell (1) reported vapor pressure data for TiI₄(l) over the temperature range 473° to 655°K. Second and third law analyses of these data give values for ΔH_f° of 17.2 ± 0.1 and 16.98 kcal/mol, respectively, the third law drift being -0.4 ± 0.2 eu. The adopted value of ΔH_f° is based on the third law heat of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of TiBr₄(c), TiBr₄(g) and TiI₄(c) (2). The tetrahedral model is assumed by analogy with TiCl₄(g) and TiBr₄(g). The principal moments of inertia are: $I_A = I_B = I_C = 3.51 \times 10^{-37} \text{ g cm}^2$. The vibrational frequencies of TiI₄(g) have been estimated by Ushanova et al. (3). The given estimates are based on their predictions and valence force field calculations.

References

1. J. N. Blocher, Jr. and I. E. Campbell, J. Am. Chem. Soc., **65**, 2100 (1947).
2. O. Hasoel and H. Kringstand, Z. Phys. Chem. **133**, 274 (1932).
3. N. I. Ushanova, I. N. Godnev and I. V. Orlova, Opt. Spektrosk., **5**, 567 (1958).

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	+000	INFINITE	INFINITE	6.169	64.979	64.979	INFINITE
100	20.496	78.168	124.839	4.667	69.773	69.773	152.488
200	23.946	93.703	105.734	2.406	65.622	74.271	81.159
298	24.917	103.479	103.479	+000	64.270	78.386	57.459
300	24.928	103.633	103.479	-046	66.283	78.461	57.159
400	25.309	110.864	100.462	2.540	74.731	82.139	44.879
500	25.493	116.533	106.330	5.102	85.881	81.982	35.434
600	25.595	121.191	108.430	7.657	95.786	79.213	28.953
700	25.658	125.142	110.543	10.219	95.708	76.457	23.871
800	25.677	128.599	112.150	12.830	95.622	73.697	19.334
900	25.678	131.599	113.534	15.359	95.534	70.950	15.234
1000	25.747	134.311	114.376	17.932	95.425	68.230	14.612
1100	25.762	136.766	115.122	20.508	95.652	65.480	13.012
1200	25.773	139.008	115.770	23.085	96.645	62.706	11.421
1300	25.786	141.082	116.340	25.662	96.594	59.917	10.067
1400	25.789	142.982	116.810	28.240	96.544	57.107	8.913
1500	25.795	144.761	117.215	30.820	96.546	54.238	7.902
1600	25.799	146.426	117.551	33.400	96.577	51.411	7.02
1700	25.803	147.990	117.826	35.980	96.612	48.589	6.247
1800	25.806	149.461	118.047	38.561	96.647	45.767	5.576
1900	25.809	150.861	118.207	41.151	96.755	42.953	5.000
2000	25.811	152.185	118.323	43.722	101.312	39.947	4.365
2100	25.813	153.444	118.395	46.303	101.423	36.873	3.837
2200	25.815	154.655	118.424	48.885	101.537	33.799	3.358
2300	25.817	155.827	118.410	51.468	101.654	30.725	2.919
2400	25.818	156.961	118.371	54.058	101.772	27.657	2.519
2500	25.819	158.045	118.303	56.630	101.894	24.537	2.145
2600	25.820	159.058	118.184	59.212	102.018	21.481	1.802
2700	25.821	160.022	118.026	61.794	102.146	18.339	1.484
2800	25.822	160.947	117.830	64.376	102.276	15.177	1.193
2900	25.823	161.778	117.608	66.959	102.407	12.017	0.913
3000	25.823	162.653	117.373	69.541	102.533	9.006	0.656
3100	25.824	163.500	117.123	72.123	102.681	5.882	0.415
3200	25.825	164.310	116.874	74.706	102.820	2.762	0.189
3300	25.826	165.085	116.644	77.289	102.960	-0.358	-0.036
3400	25.826	165.885	116.394	79.871	103.109	-3.504	-0.225
3500	25.826	166.634	116.076	82.453	103.257	-6.644	-0.415
3600	25.826	167.361	115.740	85.036	205.034	10.046	0.610
3700	25.827	168.059	115.390	87.619	205.150	16.019	0.946
3800	25.827	168.758	115.029	90.201	205.267	21.992	1.282
3900	25.827	169.429	114.638	92.784	205.437	27.986	1.560
4000	25.828	170.083	114.241	95.367	205.629	33.968	1.856
4100	25.828	170.720	113.830	97.950	205.816	39.969	2.131
4200	25.828	171.340	113.400	100.532	206.020	45.965	2.392
4300	25.829	171.951	112.956	103.115	206.224	51.961	2.646
4400	25.829	172.544	112.500	105.698	206.449	57.955	2.879
4500	25.829	173.125	112.062	108.281	206.714	63.985	3.108
4600	25.829	173.692	111.640	110.864	206.971	70.007	3.326
4700	25.829	174.242	111.219	113.447	207.240	76.024	3.535
4800	25.829	174.782	110.790	116.030	207.507	82.032	3.736
4900	25.830	175.324	110.363	118.613	207.817	88.029	3.929
5000	25.830	175.846	110.000	121.196	208.173	94.136	4.115
5100	25.830	176.358	119.627	123.779	208.437	100.181	4.293
5200	25.830	176.851	119.240	126.362	208.705	106.234	4.465
5300	25.830	177.351	118.840	128.945	208.974	112.281	4.631
5400	25.830	177.834	118.427	131.528	209.246	118.371	4.791
5500	25.830	178.308	117.994	134.111	209.520	124.451	4.945
5600	25.830	178.773	117.544	136.694	210.163	130.510	5.093
5700	25.830	179.228	117.080	139.277	210.811	136.565	5.236
5800	25.831	179.680	116.600	141.860	211.464	142.617	5.375
5900	25.831	180.121	116.110	144.443	212.122	148.670	5.512
6000	25.831	180.556	115.601	147.026	211.687	154.904	5.642

Dec. 31, 1961; June 30, 1964; Dec. 31, 1968

Zirconium Tetraiodide (ZrI₄)
(Crystal) Mol. Wt. = 598.86

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	INFINITE
100	24.645	31.267	86.777	-115.414	-115.414	INFINITE
200	28.446	49.862	64.065	-115.496	-115.370	252.128
250	29.543	61.412	50.55	-115.496	-115.496	125.869
298	29.556	61.413	3.043	-115.800	-114.882	84.707
300	29.556	61.413	0.055	-115.804	-114.875	83.682
400	30.170	70.188	62.580	-114.895	-114.221	62.404
500	30.550	76.966	64.804	-144.574	-109.846	48.011
600	30.810	82.561	67.310	-144.003	-102.956	37.500
700	30.990	87.325	69.838	-143.435	-96.160	30.021
800	31.100	91.471	72.288	-142.870	-89.443	24.434
900	31.180	95.139	74.627	-142.309	-82.800	20.106
1000	31.220	98.426	76.846	-141.753	-76.216	16.656
1100	31.250	101.403	78.945	-141.213	-69.690	13.845
1200	31.260	104.123	80.931	-141.643	-63.163	11.503
1300	31.270	106.625	82.813	-141.109	-56.644	9.522
1400	31.280	108.943	84.598	-140.587	-50.167	7.831
1500	31.290	111.102	86.293	-140.073	-43.729	6.371

ZIRCONIUM TETRAIODOIDE (ZrI₄) (CRYSTAL) MOL. WT. = 598.86

$$\Delta H_f^0 = [-115.4] \pm 1.0 \text{ kcal. mole}^{-1}$$

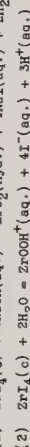
$$\Delta H_f^0 \text{ 298.15} = -115.9 \pm 0.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -115.9 \pm 0.8 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = -115.9 \pm 0.8 \text{ kcal. mole}^{-1}$$

T_g = 704°K.
Heat of Formation.

A. O. Turnbull, J. Phys. Chem. 65, 1652 (1961), measured the heat of reaction for the following reactions:



Turnbull used the same procedure to calculate the heat of formation of zirconium tetraiodide as he did for zirconium tetrabromide [see ZrBr₄ table]. The heat of formation of the solid zirconium tetraiodide from reaction (1) was -115.6 ± 0.8 kcal. mole⁻¹ and from reaction (2) was -116.3 ± 0.8 kcal. mole⁻¹. An average of these was taken as the heat of formation of the tetraiodide.

Heat Capacity and Entropy.

The heat capacity from 0 to 300°K. was calculated in the same manner as for ZrBr₄(c) [see ZrBr₄(c) table]. The values, q_p⁰ = 60°K. and q_p⁰ = 115°K. were used in the analysis. The value, a = 1.5 X 10⁻³, was obtained from a consideration of the sublimation calculations [see below]. The heat capacity above 300°K. represents a graphical extrapolation.

Melting.

T_m = 772°K. was reported by O. Rahlfs and W. Fischer, Z. anorg. allgem. Chem. 211, 349 (1933).

Sublimation Data.

Vapor pressure measurements have been reported by Rahlfs and Fischer (loc. cit.). Four values of "a" were used to compute the thermodynamic functions of the solid. That value of "a" was chosen which gave agreement between 2nd and 3rd law values for the heat of sublimation. The sublimation results for the four values of "a" are given in the following table.

"a"	ΔH _g (298) [3rd law]	ΔH _g (298) [2nd law]
3.0 X 10 ⁻³	29.99 kcal. mole ⁻¹	31.65 kcal. mole ⁻¹
2.5 X 10 ⁻³	30.39 kcal. mole ⁻¹	31.34 kcal. mole ⁻¹
2.0 X 10 ⁻³	30.76 kcal. mole ⁻¹	31.17 kcal. mole ⁻¹
1.5 X 10 ⁻³	31.02 kcal. mole ⁻¹	31.04 kcal. mole ⁻¹

A temperature dependent third law heat of sublimation at 298°K. was obtained for "a" = 3.0 X 10⁻³; this temperature trend decreased for smaller values of "a" and there was essentially no temperature dependence for "a" = 1.5 X 10⁻³. Various high temperature extrapolations were not used since, by experience with ZrBr₄(c), they produced insignificant changes in the heat values. The heat of sublimation was taken to be 31.0 kcal. mole⁻¹ since the entire analysis was conducted to obtain 2nd and 3rd law agreement.

From experience with a number of other compounds, that were found to be amenable to the theoretical treatment used here, the value "a" = 1.5 X 10⁻³ appears to be rather low, but no further analysis was deemed practical since all parameters for the gas and solid are estimated.

The sublimation point obtained from the free energy crossover of solid and gas was 703°K. The value reported by Rahlfs and Fischer (loc. cit.) was 704°K. The sublimation point was taken as 704°K.

Since the sublimation point is lower than the melting point, the liquid phase is thermodynamically unstable under ordinary conditions.

Zirconium Tetraiodide (ZrI₄)
(Ideal Gas) Mol. Wt. = 598.86

T, °K.	C _p cal. mole ⁻¹ deg ⁻¹	S° -(F°-H° ₂₉₈)/T cal. mole ⁻¹	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° _f	Log K _p
0	-0.00	INFINITE	6.330	83.405	INFINITE
100	21.258	80.985	4.743	83.405	13.481
200	24.285	104.900	2.430	84.254	101.602
298	25.090	106.775	0.000	84.254	71.398
300	25.099	106.930	0.046	84.913	71.014
400	25.411	114.200	10.776	91.364	55.342
500	25.560	119.668	10.661	91.364	44.261
600	25.613	124.556	11.750	91.364	35.920
700	25.693	128.513	13.669	91.364	29.925
800	25.776	131.948	15.519	91.364	25.500
900	25.764	134.978	17.396	90.719	22.029
1000	25.765	137.691	19.271	88.090	19.251
1100	25.777	140.198	21.147	85.464	16.979
1200	25.786	142.391	23.027	82.838	14.677
1300	25.793	144.435	24.906	80.212	12.341
1400	25.799	146.367	26.785	77.586	10.076
1500	25.803	148.187	28.665	74.960	7.801
1600	25.807	149.912	30.545	72.334	5.526
1700	25.810	151.577	32.425	69.708	3.251
1800	25.813	153.192	34.305	67.082	0.976
1900	25.815	154.768	36.185	64.456	-1.300
2000	25.817	156.303	38.065	61.830	-3.575
2100	25.819	157.797	40.000	59.204	-5.850
2200	25.820	159.252	41.935	56.578	-8.125
2300	25.821	159.181	43.782	53.952	-10.400
2400	25.822	160.280	45.630	51.326	-12.675
2500	25.823	161.334	47.477	48.700	-14.950
2600	25.824	162.347	49.325	46.074	-17.225
2700	25.825	163.321	51.172	43.448	-19.500
2800	25.826	164.260	53.020	40.822	-21.775
2900	25.826	165.167	54.867	38.196	-24.050
3000	25.827	166.042	56.715	35.570	-26.325
3100	25.827	166.889	58.562	32.944	-28.600
3200	25.828	167.709	60.410	30.318	-30.875
3300	25.828	168.504	62.257	27.692	-33.150
3400	25.828	169.275	64.105	25.066	-35.425
3500	25.829	170.024	65.952	22.440	-37.700
3600	25.829	170.751	67.799	19.814	-40.000
3700	25.829	171.459	69.646	17.188	-42.300
3800	25.830	172.148	71.493	14.562	-44.600
3900	25.830	172.819	73.340	11.936	-46.900
4000	25.830	173.473	75.187	9.310	-49.200
4100	25.830	174.110	77.034	6.684	-51.500
4200	25.830	174.733	78.881	4.058	-53.800
4300	25.831	175.341	80.728	1.432	-56.100
4400	25.831	175.935	82.575	-1.194	-58.400
4500	25.831	176.515	84.422	-3.819	-60.700
4600	25.831	177.083	86.269	-6.444	-63.000
4700	25.831	177.638	88.116	-9.069	-65.300
4800	25.831	178.181	89.963	-11.694	-67.600
4900	25.831	178.715	91.810	-14.319	-69.900
5000	25.832	179.237	93.657	-16.944	-72.200
5100	25.832	179.748	95.504	-19.569	-74.500
5200	25.832	180.250	97.351	-22.194	-76.800
5300	25.832	180.742	99.198	-24.819	-79.100
5400	25.832	181.225	101.045	-27.444	-81.400
5500	25.832	181.699	102.892	-30.069	-83.700
5600	25.832	182.164	104.739	-32.694	-86.000
5700	25.832	182.621	106.586	-35.319	-88.300
5800	25.832	183.071	108.433	-37.944	-90.600
5900	25.832	183.512	110.280	-40.569	-92.900
6000	25.832	183.946	112.127	-43.194	-95.200

Mar. 31, 1962, June 30, 1964

ZIRCONIUM TETRAIODIDE (ZrI₄)

(IDEAL GAS)

MOL. WT. = 598.86

$$\Delta H_f^0 = [83.6] \pm 1.7 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298} = -84.9 \pm 1.5 \text{ kcal. mole}^{-1}$$

Point Group = D_{2d}

$$S_{298}^0 = [106.78] \text{ cal. mole}^{-1} \text{ deg}^{-1}$$

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	
[146] (1)	
[45] (2)	
[237] (3)	
[58] (3)	

$$Q = [12]$$

$$\text{Bond Distance: Zr-I} = [2.68] \text{ \AA}$$

$$\text{Bond Angle: I-Zr-I} = [109^\circ 28']$$

$$\text{Product of the Moments of Inertia: } I_A I_B I_C = [6.5718 \times 10^{-11}] \text{ gm}^3 \text{ cm}^6$$

Heat of Formation

Calculated from the heats of formation and sublimation for the crystal at 298.15°K. (see crystal table for details).

Heat Capacity and Entropy

The interatomic distance was obtained from an involved correlation of the interatomic distances and covalent radii of the tetrahalides of Pb, Si, Ti, Ge, and Sn. I. N. Godnev, A. M. Aleksandrovskaya, and I. V. Regina, Optics and Spectroscopy 2, 172 (1959), estimated the interatomic distance and report 2.67 Å as the Zr-I distance. The I-Zr-I angle was taken as the tetrahedral angle. The three principal moments of inertia are: $I_A = I_B = I_C = 4.0355 \times 10^{-37} \text{ gm. cm}^2$.

The fundamental vibrational frequencies are estimated. The product of ω_1 and internuclear distance for the tetrahalides of Pb, Ti, Ge, and Sn was found to be approximately constant. Using the estimated Zr-I internuclear distance a value of 147 cm^{-1} was obtained for ω_1 . Plots of ω_1 and ω_2 versus internuclear distance for these molecules were constructed and smooth curves drawn through the points. Values of ω_1 and ω_2 for ZrI₄ were read off from these plots; they were 146 cm^{-1} and 44 cm^{-1} respectively. Using $\omega_1 = 146 \text{ cm}^{-1}$ and $\omega_2 = 45 \text{ cm}^{-1}$, $\omega_3 = 237 \text{ cm}^{-1}$ and $\omega_4 = 58 \text{ cm}^{-1}$ were obtained from a valence force field calculation. Godnev, Aleksandrovskaya, and Regina (loc. cit.) estimated the vibrational frequencies and reported $\omega_1 = 152 \text{ cm}^{-1}$, $\omega_2 = 44 \text{ cm}^{-1}$, $\omega_3 = 211 \text{ cm}^{-1}$ and $\omega_4 = 55 \text{ cm}^{-1}$.

Potassium (K)

(Reference State) Mol. Wt. = 39.100

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(R°-H ₂₉₈ °)/T cal. mole ⁻¹	H°-H ₂₉₈ ° kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	1.693	.000	.000	.000
100	5.887	8.509	21.296	.000	.000	.000
200	9.878	14.783	46.076	.000	.000	.000
298	15.457	15.457	.000	.000	.000	.000
300	7.468	15.501	15.457	.013	.000	.000
400	7.598	19.332	16.015	1.327	.000	.000
500	7.336	20.990	16.851	2.070	.000	.000
600	7.203	22.315	17.455	2.794	.000	.000
700	7.124	23.419	18.001	3.512	.000	.000
800	7.112	24.369	19.089	4.224	.000	.000
900	7.155	25.208	19.723	4.936	.000	.000
1000	7.256	25.967	20.310	5.657	.000	.000
1100	4.945	26.782	21.788	25.294	.000	.000
1200	4.968	25.721	23.722	25.791	.000	.000
1300	4.969	25.612	23.391	26.248	.000	.000
1400	4.970	25.481	24.849	26.785	.000	.000
1500	4.972	25.324	24.136	27.282	.000	.000
1600	4.975	25.145	20.283	27.779	.000	.000
1700	4.980	24.944	30.513	28.277	.000	.000
1800	4.988	24.731	31.245	28.775	.000	.000
1900	4.999	24.501	32.094	29.275	.000	.000
2000	5.013	24.258	32.870	29.775	.000	.000
2100	5.033	24.003	33.585	30.277	.000	.000
2200	5.057	23.738	34.246	30.782	.000	.000
2300	5.087	23.463	34.859	31.289	.000	.000
2400	5.122	23.178	35.431	31.799	.000	.000
2500	5.164	22.880	35.965	32.314	.000	.000
2600	5.213	22.574	36.466	32.832	.000	.000
2700	5.270	22.251	36.937	33.356	.000	.000
2800	5.334	21.904	37.382	33.887	.000	.000
2900	5.407	21.533	37.802	34.424	.000	.000
3000	5.489	21.137	38.201	34.968	.000	.000
3100	5.582	20.716	38.580	35.522	.000	.000
3200	5.682	20.271	38.941	36.089	.000	.000
3300	5.802	19.804	39.285	36.659	.000	.000
3400	5.932	19.316	39.615	37.246	.000	.000
3500	6.079	18.803	39.930	37.846	.000	.000
3600	6.242	18.267	40.233	38.462	.000	.000
3700	6.422	17.707	40.520	39.094	.000	.000
3800	6.630	17.124	40.794	39.748	.000	.000
3900	6.858	16.519	41.075	40.422	.000	.000
4000	7.111	15.894	41.336	41.120	.000	.000
4100	7.392	15.245	41.580	41.845	.000	.000
4200	7.701	14.577	41.834	42.600	.000	.000
4300	8.041	13.892	42.072	43.386	.000	.000
4400	8.412	13.191	42.304	44.209	.000	.000
4500	8.815	12.474	42.529	45.070	.000	.000
4600	9.250	11.743	42.749	45.973	.000	.000
4700	9.717	10.997	42.964	46.921	.000	.000
4800	10.215	10.235	43.174	47.917	.000	.000
4900	10.741	9.458	43.380	48.965	.000	.000
5000	11.294	8.675	43.582	50.066	.000	.000
5100	11.871	7.885	43.781	51.224	.000	.000
5200	12.467	7.084	43.976	52.441	.000	.000
5300	13.079	6.274	44.169	53.718	.000	.000
5400	13.701	5.454	44.359	55.057	.000	.000
5500	14.337	4.621	44.546	56.459	.000	.000
5600	14.983	3.775	44.732	57.923	.000	.000
5700	15.742	2.914	44.914	59.453	.000	.000
5800	16.618	2.039	45.098	61.037	.000	.000
5900	17.615	1.153	45.279	62.684	.000	.000
6000	17.736	.000	45.458	64.389	.000	.000

December 31, 1961

K

MOL. WT. = 39.100

(REFERENCE STATE)

POTASSIUM (K)

Crystal
Liquid
Ideal Monatomic Gas

0°K. to 336.35°K.

336.35°K. to 1043.7°K.

1043.7°K. to 8000°K.

Heat of Formation.

Zero by definition.

Heat Capacity of Crystal.

Low temperature heat capacity measurements have been reported by I. M. Roberts [Proc. Phys. Soc. (London) 70B, 744-52 (1957)] (1.5°-20°K), by C. A. Krier, R. S. Craig, and W. E. Wallace [J. Phys. Chem. 61, 522 (1957)] (12°-320°K), by T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas [Proc. Roy. Soc. (London), A233, 214 (1955)] (20°-350°K), by F. Simon and M. Zeidler [Z. physikal. Chem. 123, 383 (1926)] (15°-300°K), and by E. D. Eastman and W. H. Rodebush [J. Am. Chem. Soc. 40, 489 (1918)] (70°-230°K). A smooth curve was drawn through a large scale plot of the data, giving the most weight to the first three references. Above 300°K, the heat capacity data were adjusted to join smoothly with the heat content measurements of T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis [J. Am. Chem. Soc. 74, 2472 (1952)].

Heat Capacity of Liquid and Heat of Melting.

The heat of melting and liquid heat capacity are from the heat content measurements of T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis (loc. cit.).

Heat of Sublimation, Ideal Gas Functions.

See tables for K(g) and K₂(g) for details.

K

T, °K.	C_p	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{g^{\circ}}$	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	ΔH_f°	ΔF_f°	Log K _f
0							
100	7.816	17.078	17.078	.000	.546	.063	.066
200	7.528	16.332	17.078	.014	.547	.060	.064
300	7.336	20.690	17.078	.0781	.000	.000	.000
400				1.523	.000	.000	.000
500					.000	.000	.000
600	7.203	22.315	18.566	2.250	.000	.000	.000
700	7.126	23.419	19.182	2.966	.000	.000	.000
800	7.112	24.369	19.772	3.677	.000	.000	.000
900	7.145	25.208	20.331	4.390	.000	.000	.000
1000	7.256	25.967	20.857	5.110	.000	.000	.000
1100	7.417	26.666	21.354	5.843	16.905	1.021	.203
1200	7.620	27.320	21.824	6.594	16.450	2.824	.514
1300	7.840	27.938	22.271	7.364	16.314	4.602	.774
1400	8.040	28.527	22.697	8.163	16.076	6.359	.993
1500	8.260	29.091	23.104	8.980	17.756	8.094	1.179
1600	8.500	29.632	23.495	9.819	17.414	9.806	1.339
1700	8.720	30.154	23.872	10.680	17.051	11.495	1.478
1800	8.940	30.659	24.235	11.563	16.666	13.164	1.598
1900	9.180	31.148	24.586	12.468	16.261	14.810	1.703
2000	9.380	31.623	24.928	13.395	15.834	16.435	1.796

POTASSIUM (K)

(LIQUID)

MOL. WT. = 39.100

$$\Delta H_f^{\circ} 298 = 0.546 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{\circ} = 0.558 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{\circ} = 18.38 \text{ kcal. per formula weight}$$

$$T_m = 336.35^{\circ}\text{K.}$$

$$T_b = 1037^{\circ}\text{K.}$$

Heat of Formation.

Back calculated from the heat of melting and the heat contents of solid and liquid at the melting point.

Heat of Melting and Heat Capacity.

The heat of melting, melting point, and liquid heat capacity were measured by T. B. Douglas, A. P. Ball, D. C. Glinings, and W. D. Davis [J. Am. Chem. Soc. 74, 2472 (1952)]. The heat capacity curve was extrapolated back to 298°K. and up to 2000°K. in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K.

Vaporization.

Potassium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1037°K. The vapor composition at this temperature is 94.5 mole % monatomic and 5.5 mole % diatomic gas. The heat of vaporization of 39.1 grams of liquid potassium to this equilibrium mixture is 18.38 kcal. See also tables for K(g) and K₂(g).

Potassium, Monatomic (K)

(Ideal Gas) Mol. Wt. = 39.100

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	INFINITE	21.522	21.522	INFINITE
100	4.868	32.869	42.714	21.605	19.169	41.491
200	4.968	36.313	38.761	21.461	16.766	18.331
298	4.968	38.297	.000	21.310	14.500	10.029
300	4.968	38.327	38.297	.000	14.458	10.032
400	4.948	39.757	38.492	1.506	20.489	6.731
500	4.968	40.865	38.860	1.003	20.243	4.504
600	4.948	41.771	39.272	1.500	20.018	3.038
700	4.968	42.537	39.685	1.996	19.794	2.002
800	4.968	43.200	40.084	2.493	19.579	1.233
900	4.968	43.786	40.463	2.990	19.364	.642
1000	4.968	44.309	40.822	3.487	19.140	.174
1100	4.948	44.782	41.161	3.984	.000	.000
1200	4.968	45.215	41.481	4.481	.000	.000
1300	4.968	45.612	41.784	4.977	.000	.000
1400	4.970	45.981	42.070	5.474	.000	.000
1500	4.972	46.324	42.343	5.971	.000	.000
1600	4.975	46.645	42.602	6.469	.000	.000
1700	4.980	46.946	42.846	6.966	.000	.000
1800	4.988	47.231	43.084	7.465	.000	.000
1900	4.999	47.501	43.310	7.964	.000	.000
2000	5.013	47.758	43.526	8.465	.000	.000
2100	5.033	48.003	43.733	8.967	.000	.000
2200	5.057	48.238	43.932	9.471	.000	.000
2300	5.087	48.463	44.125	9.974	.000	.000
2400	5.122	48.680	44.310	10.489	.000	.000
2500	5.164	48.890	44.489	11.003	.000	.000
2600	5.213	49.094	44.662	11.522	.000	.000
2700	5.270	49.294	44.830	12.046	.000	.000
2800	5.334	49.484	44.993	12.576	.000	.000
2900	5.407	49.673	45.151	13.113	.000	.000
3000	5.489	49.857	45.305	13.658	.000	.000
3100	5.582	50.039	45.454	14.211	.000	.000
3200	5.685	50.218	45.601	14.775	.000	.000
3300	5.802	50.394	45.743	15.349	.000	.000
3400	5.932	50.569	45.883	15.935	.000	.000
3500	6.079	50.743	46.019	16.536	.000	.000
3600	6.242	50.917	46.153	17.152	.000	.000
3700	6.426	51.090	46.282	17.782	.000	.000
3800	6.630	51.264	46.412	18.438	.000	.000
3900	6.856	51.440	46.539	19.112	.000	.000
4000	7.111	51.616	46.664	19.810	.000	.000
4100	7.392	51.795	46.787	20.535	.000	.000
4200	7.700	51.977	46.908	21.286	.000	.000
4300	8.041	52.162	47.028	22.076	.000	.000
4400	8.415	52.351	47.147	22.899	.000	.000
4500	8.815	52.545	47.265	23.760	.000	.000
4600	9.250	52.743	47.382	24.663	.000	.000
4700	9.717	52.946	47.497	25.607	.000	.000
4800	10.215	53.157	47.614	26.601	.000	.000
4900	10.741	53.373	47.729	27.655	.000	.000
5000	11.294	53.595	47.844	28.756	.000	.000
5100	11.871	53.825	47.959	29.915	.000	.000
5200	12.467	54.061	48.074	31.131	.000	.000
5300	13.079	54.304	48.189	32.409	.000	.000
5400	13.701	54.555	48.305	33.747	.000	.000
5500	14.337	54.812	48.421	35.149	.000	.000
5600	14.953	55.075	48.537	36.613	.000	.000
5700	15.572	55.346	48.654	38.143	.000	.000
5800	16.178	55.622	48.772	39.727	.000	.000
5900	16.765	55.903	48.891	41.374	.000	.000
6000	17.326	56.190	49.010	43.079	.000	.000

POTASSIUM, MONATOMIC (K)

(IDEAL GAS)

MOL. WT. = 39.100

$$\Delta H_f^0 = 21.522 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^0 = 21.522 \text{ kcal. mole}^{-1}$$

$$\text{Ground State} = {}^2S_{1/2}$$

$$\Delta H_f^0 = 21.31 \pm 0.20 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 38.237 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Electronic Levels and Multiplicities

E_1 cm. ⁻¹	E_1 cm. ⁻¹	E_1 cm. ⁻¹	E_1 cm. ⁻¹
0.00	28998.27	2	33185.5
12985.17	29007.71	4	33578.5
13042.88	30185.44	10	33815.6
21026.58	30274.26	2	34059.8
21537.00	30614.08	32	34335.7
21534.70	31072.15	6	34472.3
24701.43	31072.90	12	34568.3
24720.17	31696.00	10	34662.3
27398.14	31785.37	2	34753.8
27397.10	31958.70	54	34859.4
27450.69	32229.20	6	34985.0
28127.85	32691.70	26	

Thermodynamic Functions.

Thermodynamic functions were calculated using electronic levels and multiplicities from P. Risberg [Arkiv. Fysik 10, 585 (1956)] and C. E. Moore [Nat. Bur. Standards Circ. 467 (1949)]. Higher levels were averaged. The results are in excellent agreement with W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards 55, 83 (1955)].

Heat of Formation.

Evans, Munson, and Wagman (loc. cit.) have reviewed the vapor pressure data on potassium. Their calculations were revised slightly for the changes made in the functions for the condensed state. In addition, the recent data of W. M. Hakansi, M. Hadsen, W. A. Selke, and C. F. Bonilla [J. Phys. Chem. 60, 138 (1956)] were considered in selecting the heat of sublimation of 21.31 ± 0.20 kcal. mole⁻¹. A review of the properties of potassium vapor using imperfect gas theory to establish the dimer dissociation energy has recently been published by R. J. Thorn and G. H. Winslow [J. Phys. Chem. 65, 1297 (1961)]. Although the imperfect gas treatment appears to be favored by the experimental data available, this could not be unequivocally established. Unpublished vapor pressure data cited by Thorn and Winslow are in agreement with the values selected here, assuming ideal gas behavior.

Potassium Unipositive Ion (K^+)
(Ideal Gas) At. Wt. = 39.100

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	ΔF _f ⁰	Log K _p
0					
100	4.968	36.919	0.000	115.010	- 84.301
200	4.968	36.919	0.000	115.010	- 84.301
298	4.968	36.919	0.000	115.010	- 84.301
300	4.968	36.919	0.000	115.010	- 84.301
400	4.968	36.919	0.000	115.010	- 84.301
500	4.968	36.919	0.000	115.010	- 84.301
600	4.968	36.919	0.000	115.010	- 84.301
700	4.968	36.919	0.000	115.010	- 84.301
800	4.968	36.919	0.000	115.010	- 84.301
900	4.968	36.919	0.000	115.010	- 84.301
1000	4.968	36.919	0.000	115.010	- 84.301
1100	4.968	36.919	0.000	115.010	- 84.301
1200	4.968	36.919	0.000	115.010	- 84.301
1300	4.968	36.919	0.000	115.010	- 84.301
1400	4.968	36.919	0.000	115.010	- 84.301
1500	4.968	36.919	0.000	115.010	- 84.301
1600	4.968	36.919	0.000	115.010	- 84.301
1700	4.968	36.919	0.000	115.010	- 84.301
1800	4.968	36.919	0.000	115.010	- 84.301
1900	4.968	36.919	0.000	115.010	- 84.301
2000	4.968	36.919	0.000	115.010	- 84.301
2100	4.968	36.919	0.000	115.010	- 84.301
2200	4.968	36.919	0.000	115.010	- 84.301
2300	4.968	36.919	0.000	115.010	- 84.301
2400	4.968	36.919	0.000	115.010	- 84.301
2500	4.968	36.919	0.000	115.010	- 84.301
2600	4.968	36.919	0.000	115.010	- 84.301
2700	4.968	36.919	0.000	115.010	- 84.301
2800	4.968	36.919	0.000	115.010	- 84.301
2900	4.968	36.919	0.000	115.010	- 84.301
3000	4.968	36.919	0.000	115.010	- 84.301
3100	4.968	36.919	0.000	115.010	- 84.301
3200	4.968	36.919	0.000	115.010	- 84.301
3300	4.968	36.919	0.000	115.010	- 84.301
3400	4.968	36.919	0.000	115.010	- 84.301
3500	4.968	36.919	0.000	115.010	- 84.301
3600	4.968	36.919	0.000	115.010	- 84.301
3700	4.968	36.919	0.000	115.010	- 84.301
3800	4.968	36.919	0.000	115.010	- 84.301
3900	4.968	36.919	0.000	115.010	- 84.301
4000	4.968	36.919	0.000	115.010	- 84.301
4100	4.968	36.919	0.000	115.010	- 84.301
4200	4.968	36.919	0.000	115.010	- 84.301
4300	4.968	36.919	0.000	115.010	- 84.301
4400	4.968	36.919	0.000	115.010	- 84.301
4500	4.968	36.919	0.000	115.010	- 84.301
4600	4.968	36.919	0.000	115.010	- 84.301
4700	4.968	36.919	0.000	115.010	- 84.301
4800	4.968	36.919	0.000	115.010	- 84.301
4900	4.968	36.919	0.000	115.010	- 84.301
5000	4.968	36.919	0.000	115.010	- 84.301
5100	4.968	36.919	0.000	115.010	- 84.301
5200	4.968	36.919	0.000	115.010	- 84.301
5300	4.968	36.919	0.000	115.010	- 84.301
5400	4.968	36.919	0.000	115.010	- 84.301
5500	4.968	36.919	0.000	115.010	- 84.301
5600	4.968	36.919	0.000	115.010	- 84.301
5700	4.968	36.919	0.000	115.010	- 84.301
5800	4.968	36.919	0.000	115.010	- 84.301
5900	4.968	36.919	0.000	115.010	- 84.301
6000	4.968	36.919	0.000	115.010	- 84.301

Mar. 31, 1965

POTASSIUM UNIPosITIVE ION (K^+) (IDEAL GAS) AT. WT. = 39.100

Ground State Configuration $1s^2$
 $\Delta F_f^0 = 121.627$ kcal. mole⁻¹
 $S_{298.15}^0 = 36.919$ cal. deg.⁻¹ mole⁻¹
 $\Delta F_f^0_{298.15} = 122.896$ kcal. mole⁻¹

Electronic Levels and Multiplicities

ϵ , cm. ⁻¹	g_i
0	1
167978	52
187837	36
217452	65

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic potassium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels", Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation $K(\text{ref. state}) = e^-(\text{ref. state}) = K^+(\text{monatomic gas})$, thus K^+ involves the difference in enthalpies of two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore, loc. cit.

K^+

K^+

Potassium Monoxide (KO)

(Ideal Gas)

GFW = 55.1014

T, °K	C _p ^o	S ^o	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	-0.000	INFINITE	-	2.310	17.420	17.420	INFINITE
100	7.309	44.130	44.207	1.404	17.362	15.869	13.808
200	8.205	57.639	57.639	0.827	17.174	13.452	14.919
298	8.500	56.863	56.863	0.000	17.000	11.960	8.767
300	8.468	56.916	56.863	0.015	16.996	11.929	8.600
400	8.171	59.120	57.203	0.887	16.198	10.381	5.722
500	8.596	61.394	57.851	1.771	15.374	8.253	3.913
600	8.966	63.022	58.581	2.665	15.764	7.569	2.757
700	9.318	64.409	59.317	3.564	15.558	6.219	1.942
800	9.560	65.616	60.030	4.464	15.351	4.994	1.338
900	9.725	66.685	60.742	5.365	15.145	3.795	0.845
1000	9.824	67.695	61.356	6.269	14.936	2.735	0.510
1100	9.158	65.516	61.969	7.201	4.226	2.112	0.420
1200	9.186	69.314	62.549	8.114	4.230	2.659	0.490
1300	9.213	70.030	63.098	9.034	4.235	3.265	0.549
1400	9.238	70.661	63.618	9.961	4.240	3.933	0.600
1500	9.264	71.372	64.115	10.884	4.249	4.621	0.644
1600	9.289	71.971	64.587	11.814	4.257	5.329	0.683
1700	9.313	72.535	65.038	12.744	4.266	6.057	0.717
1800	9.338	73.068	65.470	13.674	4.276	6.804	0.748
1900	9.362	73.573	65.883	14.604	4.286	7.569	0.775
2000	9.386	74.054	66.280	15.534	4.291	8.351	0.800
2100	9.409	74.513	66.661	16.468	4.316	9.159	0.822
2200	9.433	74.951	67.028	17.431	4.334	9.994	0.842
2300	9.456	75.371	67.382	18.375	4.355	10.853	0.861
2400	9.478	75.774	67.724	19.322	4.376	11.734	0.878
2500	9.503	76.161	68.053	20.272	4.400	12.635	0.894
2600	9.526	76.534	68.372	21.222	4.442	13.556	0.909
2700	9.549	76.894	68.681	22.176	4.481	14.495	0.923
2800	9.572	77.242	68.980	23.132	4.527	15.454	0.936
2900	9.595	77.578	69.271	24.090	4.560	16.431	0.949
3000	9.618	77.904	69.554	25.051	4.600	17.424	0.960
3100	9.641	78.220	69.828	26.014	4.709	18.437	0.971
3200	9.664	78.526	70.095	26.979	4.788	19.473	0.982
3300	9.687	78.824	70.355	27.947	4.878	20.531	0.991
3400	9.710	79.113	70.606	28.917	4.969	21.611	1.001
3500	9.733	79.395	70.855	29.884	5.095	22.714	1.010
3600	9.756	79.670	71.097	30.853	5.225	23.841	1.019
3700	9.779	79.937	71.332	31.840	5.373	24.994	1.028
3800	9.801	80.198	71.562	32.819	5.539	26.171	1.036
3900	9.824	80.454	71.787	33.800	5.726	27.374	1.045
4000	9.847	80.702	72.006	34.784	5.937	28.601	1.053
4100	9.870	80.946	72.221	35.770	6.173	29.854	1.061
4200	9.893	81.184	72.432	36.758	6.439	31.131	1.069
4300	9.916	81.417	72.638	37.748	6.734	32.434	1.077
4400	9.938	81.646	72.840	38.741	7.065	33.761	1.085
4500	9.961	81.869	73.038	39.733	7.434	35.114	1.093
4600	9.984	82.088	73.233	40.733	7.844	36.491	1.101
4700	10.007	82.303	73.424	41.733	8.297	37.894	1.109
4800	10.029	82.514	73.611	42.735	8.797	39.324	1.118
4900	10.051	82.721	73.795	43.739	9.344	40.781	1.126
5000	10.075	82.924	73.975	44.745	9.949	42.263	1.134
5100	10.098	83.124	74.153	45.754	10.607	43.774	1.143
5200	10.120	83.320	74.327	46.765	11.322	45.317	1.152
5300	10.143	83.513	74.498	47.774	12.094	46.894	1.162
5400	10.165	83.703	74.667	48.783	12.930	48.504	1.171
5500	10.189	83.890	74.833	49.791	13.825	50.144	1.181
5600	10.211	84.074	74.997	50.831	14.781	51.811	1.191
5700	10.234	84.256	75.157	51.853	15.796	53.504	1.201
5800	10.257	84.433	75.316	52.878	16.872	55.224	1.212
5900	10.279	84.606	75.472	53.895	18.005	56.971	1.223
6000	10.302	84.781	75.625	54.934	19.195	58.746	1.235

Dec. 31, 1962; Dec. 31, 1967

POTASSIUM MONOXIDE (KO)

(IDEAL GAS)

GFW = 55.1014

Ground State Configuration [2π]

ΔH_f^o = [17.4 ± 1.0] kcal/molS_{298.15}^o = [56.9 ± 0.5] gibbs/molΔH_f^o₂₉₈ = [17.0 ± 1.0] kcal/mol

Electronic Levels and Quantum Heights

$$\frac{e_i, \text{ cm}^{-1}}{0} = \frac{g_i}{[4]}$$

$$\omega_e x_e = [350] \text{ cm}^{-1}$$

$$B_e = [0.3088] \text{ cm}^{-1}$$

$$\omega_e x_e = [2.2] \text{ cm}^{-1}$$

$$a_e = [0.0027] \text{ cm}^{-1}$$

$$\sigma = 1$$

$$r_e = [2.21] \text{ Å}$$

Heat of Formation

Brewer and Margrave (1) suggested that the ΔH_f^o value for KO(g) from the gaseous ions can be taken as the mean of the corresponding ΔH_f^o values for the alkali fluoride and chloride with a maximum uncertainty of 10 kcal/mol. We obtain the values ΔH_f^o = -137.94 and -117.7 kcal/mol for the reactions K⁺(g) + F⁻(g) = KF(g) and K⁺(g) + Cl⁻(g) = KCl(g), respectively. Assuming ΔH_f^o = -127.83 kcal/mol for the reaction K⁺(g) + O⁻(g) = KO(g), we calculate ΔH_f^o₂₉₈(KO, g) = 19.0 kcal/mol with the JANAF auxiliary values for the gaseous ions.

Based on the assumption that D₀(KO) = 1/2(D₀(K₂) + D₀(O₂)), or ΔH_f^o = 64.9 kcal/mol for the reaction KO(g) = K(g) + O(g), we evaluate ΔH_f^o₂₉₈(KO, g) = 15.6 kcal/mol or ΔH_f^o₂₉₈(KO, g) = 15.2 kcal/mol.

According to Somayajulu (2), in a sequence of similar diatomic molecules, k_rv_e/D₀ = constant, where k_r = force constant, r_e = equilibrium bond distance and D₀ = dissociation energy. Using r_e = 1.62 Å, D₀ = 77.9 kcal/mol for LiO(g), r_e = 2.2 Å and k_r(KO)/r_e(LiO) = 0.3015, we calculate D₀ = 55 kcal/mol for KO(g), yielding ΔH_f^o₂₉₈(KO, g) = 26.1 kcal/mol. The value k_r is derived from the relation k_r = 4π²ν²μ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass. The value of ΔH_f^o₂₉₈(KO, g) is tentatively adopted as 17 ± 10 kcal/mol.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for the OH(g) molecule, which has the same number of valence electrons. The values of ω_e and ω_ex_e are estimated by comparison with those for LiF(g) and KF(g). The bond distance is estimated from those for HO(g), HF(g) and KF(g). B_e and a_e are derived from r_e, ω_e and ω_ex_e by the method suggested by Herzberg (3).

References

1. L. Brewer and J. Margrave, J. Phys. Chem. **59**, 421 (1955).
2. G. R. Somayajulu, J. Chem. Phys. **33**, 1541 (1960).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o)/T	H ^o -H ^o 298	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0							
100							
200	8.577	54.062	54.062	+0.00	-33.000	-35.714	76.192
298							
300	8.592	54.115	54.062	+0.16	-33.013	-35.734	76.032
400	8.585	54.182	54.062	+0.88	-33.032	-35.771	75.816
500	8.565	54.246	54.062	1.768	-33.032	-35.771	75.616
600	8.956	60.211	55.777	2.660	-35.741	-37.171	13.540
700	9.009	61.596	56.512	3.559	-36.443	-37.353	11.662
800	9.051	62.802	57.224	4.462	-37.148	-37.434	10.227
900	9.087	63.860	57.894	5.379	-37.857	-37.429	9.049
1000	9.119	64.829	58.530	6.300	-38.575	-37.343	8.161
1100	9.149	65.700	59.161	7.193	-39.218	-36.161	7.195
1200	9.177	66.497	59.739	8.109	-39.720	-34.134	6.217
1300	9.203	67.232	60.268	9.024	-39.223	-32.064	5.300
1400	9.228	67.916	60.750	9.949	-38.725	-30.004	4.465
1500	9.254	68.553	61.187	10.874	-38.227	-27.931	3.711
1600	9.278	69.151	61.576	11.800	-37.730	-25.852	3.011
1700	9.302	69.714	61.926	12.729	-37.235	-23.765	2.350
1800	9.326	70.246	62.237	13.661	-36.742	-21.672	1.732
1900	9.349	70.751	62.510	14.594	-36.250	-19.575	1.155
2000	9.373	71.231	62.756	15.530	-35.758	-17.475	0.616
2100	9.396	71.689	62.974	16.469	-35.267	-15.371	0.108
2200	9.419	72.127	63.163	17.410	-34.775	-13.265	-0.357
2300	9.441	72.546	63.322	18.353	-34.282	-11.157	-0.865
2400	9.463	72.946	63.456	19.300	-33.789	-9.043	-1.345
2500	9.487	73.333	63.563	20.245	-33.295	-6.925	-1.797
2600	9.510	73.708	63.656	21.195	-32.802	-4.802	-2.230
2700	9.532	74.067	63.734	22.147	-32.309	-2.675	-2.645
2800	9.555	74.410	63.800	23.102	-31.816	-0.542	-3.045
2900	9.577	74.739	63.858	24.059	-31.323	1.585	-3.430
3000	9.599	75.075	63.906	25.017	-30.830	3.705	-3.795
3100	9.622	75.390	63.944	25.974	-30.337	5.825	-4.145
3200	9.644	75.696	63.972	26.931	-29.844	7.945	-4.485
3300	9.666	75.993	63.990	27.888	-29.351	10.065	-4.815
3400	9.688	76.280	63.998	28.845	-28.858	12.185	-5.135
3500	9.711	76.563	63.996	29.802	-28.365	14.305	-5.445
3600	9.733	76.837	63.983	30.759	-27.872	16.425	-5.745
3700	9.756	77.104	63.959	31.716	-27.379	18.545	-6.035
3800	9.778	77.364	63.924	32.673	-26.886	20.665	-6.315
3900	9.799	77.617	63.879	33.630	-26.393	22.785	-6.585
4000	9.822	77.867	63.824	34.587	-25.899	24.905	-6.845
4100	9.844	78.110	63.759	35.544	-25.406	27.025	-7.095
4200	9.867	78.347	63.684	36.501	-24.913	29.145	-7.335
4300	9.889	78.580	63.599	37.458	-24.420	31.265	-7.565
4400	9.911	78.809	63.504	38.415	-23.927	33.385	-7.785
4500	9.933	79.030	63.409	39.372	-23.434	35.505	-7.995
4600	9.955	79.249	63.314	40.329	-22.941	37.625	-8.195
4700	9.978	79.463	63.219	41.286	-22.448	39.745	-8.385
4800	10.000	79.674	63.124	42.243	-21.955	41.865	-8.565
4900	10.022	79.880	63.029	43.200	-21.462	43.985	-8.735
5000	10.044	80.083	62.934	44.157	-20.969	46.105	-8.895
5100	10.066	80.282	62.839	45.114	-20.476	48.225	-9.045
5200	10.088	80.477	62.744	46.071	-19.983	50.345	-9.185
5300	10.110	80.670	62.649	47.028	-19.490	52.465	-9.315
5400	10.132	80.861	62.554	47.985	-18.997	54.585	-9.435
5500	10.153	81.045	62.459	48.942	-18.504	56.705	-9.545
5600	10.175	81.228	62.364	49.899	-18.011	58.825	-9.645
5700	10.197	81.409	62.269	50.856	-17.518	60.945	-9.735
5800	10.219	81.586	62.174	51.813	-17.025	63.065	-9.815
5900	10.241	81.761	62.079	52.770	-16.532	65.185	-9.885
6000	10.263	81.933	62.000	53.727	-16.039	67.305	-9.945

Dec. 31, 1967

(IDEAL GAS)

POTASSIUM MONOXIDE UNINEGATIVE ION (K⁰⁻)

GFW = 55.10195

Ground State Configuration [1²]ΔH_f^o = [-33 ± 20] kcal/molS_{298.15} = [54.1 ± 0.3] gibbs/molΔH_f^o_{298.15} = [-33 ± 20] kcal/mol

Electronic Levels and Quantum Weights

$$\frac{g_i}{g_o} \frac{\omega_i}{\omega_o} = \frac{g_i}{g_o} \frac{\omega_i}{\omega_o}$$

$$\omega_i = [360] \text{ cm}^{-1}$$
$$\omega_o = [0.0027] \text{ cm}^{-1}$$
$$\sigma = 1$$
$$\tau_o = [2.2] \text{ Å}$$

Heat of Formation

The electron affinity (E. A.) of K⁰⁻(g) is unavailable, therefore the value of ΔH_f^o(K⁰⁻, g) is estimated. Assuming that the enthalpy change (ΔH_f^o) of the reaction (1) K⁰⁻(g) = K(g) + O²⁻(g) is approximately the average of the ΔH_f^o value for the reaction (2) K⁰⁻(g) = K(g) + O(g) and (3) K⁰⁻(g) = K(g) + F(g), we obtain ΔH_f^o = 1/2(63.5 + 117.3) = 90.4 kcal/mol for reaction (1). However, we compare the ΔH_f^o values for the reactions (4) HO(g) = H(g) + O(g), (5) HO⁻(g) = H(g) + O⁻(g), and (6) HF(g) = H(g) + F(g), and find that ΔH_f^o for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔH_f^o values for reactions (4) and (6). Based on this fact we estimated ΔH_f^o = 80 kcal/mol for reaction (1), yielding ΔH_f^o(K⁰⁻, g) = -33 kcal/mol. The value of ΔH_f^o(K⁰⁻, g) is tentatively adopted as -33 ± 20 kcal/mol. The electronic affinity of K⁰⁻(g) is derived to be 2.2 ± 0.8 eV. The value of E. A. for HO(g) is determined as 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of KF(g) which is isoelectronic with K⁰⁻(g). The values of ω_i, ω_o, x_i, and x_o are estimated by comparison with those for KF(g). The values of B_e and α_e are calculated from r_e, ω_e and ω_ex_e using the method recommended by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc. New York, 1950. The enthalpy at 0°K is -2.303 kcal/mol.

KO

Potassium, Diatomic (K_2)

(Ideal Gas) Mol. Wt. = 78.200

T, °K.	C _p ^o	S ^o - (F° - H° ₃₀₀)/T	cal. mole ⁻¹ deg. ⁻¹	-(F° - H° ₃₀₀)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₃₀₀	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞	∞
100	9.723	49.923	27.469	31.194	31.194	27.469	31.194	31.194	INFINITE
200	9.797	49.923	27.469	31.159	31.159	27.469	31.159	31.159	-60.904
298	9.847	49.923	27.469	31.142	31.142	27.469	31.142	31.142	-60.904
300	9.847	49.923	27.469	31.142	31.142	27.469	31.142	31.142	-60.904
400	9.858	49.923	27.469	31.137	31.137	27.469	31.137	31.137	-60.904
500	9.866	49.923	27.469	31.134	31.134	27.469	31.134	31.134	-60.904
600	9.872	49.923	27.469	31.132	31.132	27.469	31.132	31.132	-60.904
700	9.876	49.923	27.469	31.131	31.131	27.469	31.131	31.131	-60.904
800	9.878	49.923	27.469	31.130	31.130	27.469	31.130	31.130	-60.904
900	9.880	49.923	27.469	31.129	31.129	27.469	31.129	31.129	-60.904
1000	9.881	49.923	27.469	31.128	31.128	27.469	31.128	31.128	-60.904
1100	9.882	49.923	27.469	31.127	31.127	27.469	31.127	31.127	-60.904
1200	9.883	49.923	27.469	31.126	31.126	27.469	31.126	31.126	-60.904
1300	9.884	49.923	27.469	31.125	31.125	27.469	31.125	31.125	-60.904
1400	9.885	49.923	27.469	31.124	31.124	27.469	31.124	31.124	-60.904
1500	9.886	49.923	27.469	31.123	31.123	27.469	31.123	31.123	-60.904
1600	9.887	49.923	27.469	31.122	31.122	27.469	31.122	31.122	-60.904
1700	9.888	49.923	27.469	31.121	31.121	27.469	31.121	31.121	-60.904
1800	9.889	49.923	27.469	31.120	31.120	27.469	31.120	31.120	-60.904
1900	9.890	49.923	27.469	31.119	31.119	27.469	31.119	31.119	-60.904
2000	9.891	49.923	27.469	31.118	31.118	27.469	31.118	31.118	-60.904
2100	9.892	49.923	27.469	31.117	31.117	27.469	31.117	31.117	-60.904
2200	9.893	49.923	27.469	31.116	31.116	27.469	31.116	31.116	-60.904
2300	9.894	49.923	27.469	31.115	31.115	27.469	31.115	31.115	-60.904
2400	9.895	49.923	27.469	31.114	31.114	27.469	31.114	31.114	-60.904
2500	9.896	49.923	27.469	31.113	31.113	27.469	31.113	31.113	-60.904
2600	9.897	49.923	27.469	31.112	31.112	27.469	31.112	31.112	-60.904
2700	9.898	49.923	27.469	31.111	31.111	27.469	31.111	31.111	-60.904
2800	9.899	49.923	27.469	31.110	31.110	27.469	31.110	31.110	-60.904
2900	9.900	49.923	27.469	31.109	31.109	27.469	31.109	31.109	-60.904
3000	9.901	49.923	27.469	31.108	31.108	27.469	31.108	31.108	-60.904
3100	9.902	49.923	27.469	31.107	31.107	27.469	31.107	31.107	-60.904
3200	9.903	49.923	27.469	31.106	31.106	27.469	31.106	31.106	-60.904
3300	9.904	49.923	27.469	31.105	31.105	27.469	31.105	31.105	-60.904
3400	9.905	49.923	27.469	31.104	31.104	27.469	31.104	31.104	-60.904
3500	9.906	49.923	27.469	31.103	31.103	27.469	31.103	31.103	-60.904
3600	9.907	49.923	27.469	31.102	31.102	27.469	31.102	31.102	-60.904
3700	9.908	49.923	27.469	31.101	31.101	27.469	31.101	31.101	-60.904
3800	9.909	49.923	27.469	31.100	31.100	27.469	31.100	31.100	-60.904
3900	9.910	49.923	27.469	31.099	31.099	27.469	31.099	31.099	-60.904
4000	9.911	49.923	27.469	31.098	31.098	27.469	31.098	31.098	-60.904
4100	9.912	49.923	27.469	31.097	31.097	27.469	31.097	31.097	-60.904
4200	9.913	49.923	27.469	31.096	31.096	27.469	31.096	31.096	-60.904
4300	9.914	49.923	27.469	31.095	31.095	27.469	31.095	31.095	-60.904
4400	9.915	49.923	27.469	31.094	31.094	27.469	31.094	31.094	-60.904
4500	9.916	49.923	27.469	31.093	31.093	27.469	31.093	31.093	-60.904
4600	9.917	49.923	27.469	31.092	31.092	27.469	31.092	31.092	-60.904
4700	9.918	49.923	27.469	31.091	31.091	27.469	31.091	31.091	-60.904
4800	9.919	49.923	27.469	31.090	31.090	27.469	31.090	31.090	-60.904
4900	9.920	49.923	27.469	31.089	31.089	27.469	31.089	31.089	-60.904
5000	9.921	49.923	27.469	31.088	31.088	27.469	31.088	31.088	-60.904
5100	9.922	49.923	27.469	31.087	31.087	27.469	31.087	31.087	-60.904
5200	9.923	49.923	27.469	31.086	31.086	27.469	31.086	31.086	-60.904
5300	9.924	49.923	27.469	31.085	31.085	27.469	31.085	31.085	-60.904
5400	9.925	49.923	27.469	31.084	31.084	27.469	31.084	31.084	-60.904
5500	9.926	49.923	27.469	31.083	31.083	27.469	31.083	31.083	-60.904
5600	9.927	49.923	27.469	31.082	31.082	27.469	31.082	31.082	-60.904
5700	9.928	49.923	27.469	31.081	31.081	27.469	31.081	31.081	-60.904
5800	9.929	49.923	27.469	31.080	31.080	27.469	31.080	31.080	-60.904
5900	9.930	49.923	27.469	31.079	31.079	27.469	31.079	31.079	-60.904
6000	9.931	49.923	27.469	31.078	31.078	27.469	31.078	31.078	-60.904

December 31, 1961

POTASSIUM, DIATOMIC (K_2)

(IDEAL GAS)

MOL. WT. = 78.200

$\Delta H_f^o = 31.194$ kcal. mole⁻¹
Ground State = $1^2\Sigma$

$\Delta H_f^o = 30.374 \pm 0.5$ kcal. mole⁻¹
 $S_{298}^o = 59.666$ cal. mole⁻¹ deg.⁻¹

$\omega_e x_e = 92.64$ cm.⁻¹
 $B_e = 0.05622$ cm.⁻¹

$\omega_e x_e = 0.354$ cm.⁻¹
 $\omega_e = 8.3 \times 10^{-8}$ cm.⁻¹
 $\sigma = 2$

Thermodynamic Functions.

Spectroscopic data are the same as that selected by W. H. Evans, T. R. Munson, and D. D. Wagman [J. Research Natl. Bur. Standards **55**, 65 (1955)]. The calculated functions are in excellent agreement with their results.

Heat of Formation.

The heat of dissociation selected by Evans, Munson, and Wagman (loc. cit.) was used with the previously adopted heat of sublimation of the monomer to derive the heat of formation.

Dipotassium Monoxide (K_2O)
(Crystal) Mol. Wt. = 94.20

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0							
100							
200							
298	20.000	22.500	22.500	+0.00	- 86.800	- 76.986	56.430
300	20.050	22.624	22.500	+0.37	- 86.795	- 76.925	56.037
400	21.880	28.683	23.314	2.148	- 87.688	- 73.458	40.134
500	22.530	33.634	24.899	4.367	- 87.300	- 69.946	30.572
600	23.280	37.806	26.711	6.657	- 86.840	- 66.516	24.227
700	24.120	41.506	28.593	11.033	- 86.287	- 63.571	18.722
800	24.950	44.766	30.500	16.735	- 84.901	- 59.761	13.778
900	26.156	47.787	32.153	14.071	- 84.092	- 53.656	11.726
1000	27.130	50.593	33.858	16.735	- 84.092	- 53.656	11.726
1100	28.095	53.224	35.500	19.496	- 84.092	- 53.656	11.726
1200	28.970	55.770	37.082	22.258	- 84.092	- 53.656	11.726
1300	30.029	58.070	38.500	25.000	- 84.092	- 53.656	11.726
1400	30.999	60.335	40.078	28.360	- 84.092	- 53.656	11.726
1500	31.970	62.507	41.502	31.508	- 84.092	- 53.656	11.726
1600	32.94	64.602	42.880	34.794	- 84.092	- 53.656	11.726
1700	33.87	66.568	44.218	38.097	- 84.092	- 53.656	11.726
1800	34.89	68.599	45.500	41.500	- 84.092	- 53.656	11.726
1900	35.871	70.507	46.783	45.076	- 84.092	- 53.656	11.726
2000	36.850	72.372	48.016	48.712	- 84.092	- 53.656	11.726

June 30, 1963

K_2O

MOL. WT. = 94.20

(CRYSTAL)

DIPOTASSIUM MONOXIDE (K_2O)

$\Delta H^\circ_f 0 = \text{Unknown}$
 $S^\circ_{298.15} = [22.5 \pm 1.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H^\circ_f 298.15 = -86.8 \pm 0.5 \text{ kcal. mole}^{-1}$

$T_d = 1154^\circ K. (600 \text{ mm Hg})$

Heat of Formation.

$\Delta H^\circ_f 298.15$ was reported by M. Rengade, Ann. Chim. et phys. [8] 14, 540 (1908), based on the measurements of the heats of solution of K(c) and $K_2O(c)$ in H_2O . The same value of $\Delta H^\circ_f 298.15$ was also given by R. de Forcrand, Compt. rend. 159, 991 (1914).

Heat Capacity and Entropy.

Both C_p and $S^\circ_{298.15}$ were estimated by comparison with those of the $Na_2O(c)$.

Temperature of Decomposition.

T_d was taken from, "Data on Chemicals for Ceramic Use", National Research Council Bulletin 118 (1949).

Dipotassium Dioxide (K₂O₂)

(Crystal) Mol. Wt. = 110.20

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0						
100						
200						
298	23.940	27.000	0.000	-118.500	-102.723	75.204
300	23.940	27.000	0.044	-118.495	-102.624	74.758
400	27.400	29.447	5.208	-118.887	-91.567	60.566
500	28.450	32.022	8.037	-118.265	-86.279	51.425
600	30.581	34.268	11.000	-117.503	-81.005	45.250
700	32.700	36.289	14.145	-116.585	-75.854	40.771
800	34.706	38.087	17.444	-115.484	-70.718	36.826
900	36.691	40.604	20.887	-114.254	-65.519	33.426
1000	38.548	42.860	24.469	-150.885	-59.089	11.739
1100	37.992	44.850	28.194	-140.000	-50.825	9.256
1200	36.432	46.777	32.067	-146.980	-42.726	7.183
1300	34.444	48.646	36.086	-146.880	-34.680	5.436
1400	32.300	50.460	40.241	-162.559	-27.004	3.934
1500	30.063	52.224	44.542	-140.099	-19.480	2.547
1600	27.757	53.941	48.886	-137.533	-11.916	1.532
1700	25.378	55.615	53.573	-134.831	-4.603	0.559
1800	22.934	57.249	58.101	-131.998	2.554	-0.294
1900	20.431	58.846	62.570	-129.029	5.591	-1.154
2000						

Heat of Formation.

ΔH°_f 298.15 was reported by National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1952. The value was based on the measured decomposition pressure of K₂O₂(c) by M. Centner and M. Elmenthal, IX Congr. IUPAC, 3A, 201 (1955).

Heat Capacity and Entropy.

The heat capacities and S°_{298.15} were estimated by comparison with those for Na₂O₂(c), Na₂O(c), and K₂O(c).

Temperature of Melting.

T_m was reported by Centner and Elmenthal, loc. cit.



DIPOTASSIUM DIOXIDE (K₂O₂) (CRYSTAL) MOL. WT. = 110.20

ΔH°_f 0 = Unknown

S°_{298.15} = [27.0 ± 1.5] cal. deg.⁻¹ mole⁻¹

ΔH°_f 298.15 = -118.5 ± 1.0 kcal. mole⁻¹

ΔH°_m = Unknown

T_m = 763°K.



Lithium (Li)

(Reference State) At. Wt. = 6.940

T, °K.	C_p	$S^\circ - (F^\circ - H_{300}^\circ)/T$	ΔH_{300}°	ΔF°	Log K _F
0	0.000	14.141	1.105	0.000	0.000
100	3.199	11.122	0.996	0.000	0.000
200	5.156	8.742	0.846	0.000	0.000
298	5.847	6.954	0.000	0.000	0.000
300	5.856	6.950	0.011	0.000	0.000
400	6.559	6.674	0.632	0.000	0.000
500	7.200	11.415	2.050	0.000	0.000
600	7.060	13.216	8.610	0.000	0.000
700	6.926	14.294	9.387	0.000	0.000
800	6.816	15.218	10.024	0.000	0.000
900	6.704	16.032	10.688	0.000	0.000
1000	6.602	16.759	11.293	0.000	0.000
1100	6.480	17.415	11.757	0.000	0.000
1200	6.366	18.013	12.293	0.000	0.000
1300	6.266	18.562	12.718	0.000	0.000
1400	6.180	19.070	13.154	0.000	0.000
1500	6.100	19.541	13.584	0.000	0.000
1600	6.030	19.981	13.951	0.000	0.000
1700	4.971	41.790	15.100	45.374	0.000
1800	4.974	42.075	16.591	45.871	0.000
1900	4.978	42.346	18.082	46.368	0.000
2000	4.983	42.599	19.186	46.866	0.000
2100	4.991	42.842	20.287	47.365	0.000
2200	5.001	43.075	21.318	47.865	0.000
2300	5.014	43.297	22.269	48.365	0.000
2400	5.031	43.511	23.150	48.868	0.000
2500	5.051	43.717	23.968	49.372	0.000
2600	5.074	43.915	24.732	49.878	0.000
2700	5.102	44.107	25.446	50.387	0.000
2800	5.134	44.293	26.115	50.898	0.000
2900	5.169	44.474	26.745	51.414	0.000
3000	5.209	44.650	27.339	51.932	0.000
3100	5.253	44.822	27.900	52.456	0.000
3200	5.300	44.989	28.432	52.983	0.000
3300	5.349	45.153	28.936	53.516	0.000
3400	5.400	45.314	29.415	54.054	0.000
3500	5.467	45.471	29.872	54.597	0.000
3600	5.539	45.626	30.307	55.147	0.000
3700	5.596	45.778	30.723	55.703	0.000
3800	5.646	45.929	31.122	56.266	0.000
3900	5.699	46.077	31.503	56.836	0.000
4000	5.716	46.223	31.869	57.414	0.000
4100	5.901	46.366	32.221	58.000	0.000
4200	5.987	46.511	32.560	58.595	0.000
4300	6.079	46.653	32.886	59.194	0.000
4400	6.175	46.794	33.204	59.810	0.000
4500	6.277	46.938	33.508	60.433	0.000
4600	6.385	47.073	33.797	61.066	0.000
4700	6.500	47.211	34.081	61.710	0.000
4800	6.621	47.349	34.356	62.366	0.000
4900	6.748	47.487	34.623	63.035	0.000
5000	6.886	47.625	34.882	63.716	0.000
5100	7.032	47.763	35.133	64.412	0.000
5200	7.186	47.901	35.377	65.123	0.000
5300	7.349	48.039	35.615	65.850	0.000
5400	7.520	48.176	35.846	66.593	0.000
5500	7.701	48.318	36.071	67.355	0.000
5600	7.901	48.458	36.291	68.135	0.000
5700	8.106	48.600	36.506	68.935	0.000
5800	8.322	48.743	36.716	69.757	0.000
5900	8.547	48.888	36.921	70.600	0.000
6000	8.787	49.033	37.122	71.467	0.000

June 30, 1982

LITHIUM (Li)

(REFERENCE STATE)

At. Wt. = 6.940

0° to 453.69°K Crystal

453.69° to 1638°K Liquid

1638° to 6000°K Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

Li

Li

Lithium (Li)

(Crystal) At. Wt. = 6.940

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	.000	.000	INFINITE	1.105	.000	.000	INFINITE
100	3.193	1.875	7.875	.546	.000	.000	.000
200	5.193	3.193	6.954	.000	.000	.000	.000
298	5.894	3.894	6.954	.011	.000	.000	.000
300	5.894	3.894	6.954	.011	.000	.000	.000
400	7.222	5.222	7.067	1.330	.000	.000	.000
500	8.175	6.175	7.067	1.330	.000	.000	.000
600	8.824	6.824	7.067	1.330	.000	.000	.000
700	9.261	7.261	7.067	1.330	.000	.000	.000
800	9.536	7.536	7.067	1.330	.000	.000	.000
900	9.695	7.695	7.067	1.330	.000	.000	.000
1000	9.762	7.762	7.067	1.330	.000	.000	.000
1100	9.762	7.762	7.067	1.330	.000	.000	.000
1200	9.762	7.762	7.067	1.330	.000	.000	.000
1300	9.762	7.762	7.067	1.330	.000	.000	.000
1400	9.762	7.762	7.067	1.330	.000	.000	.000
1500	9.762	7.762	7.067	1.330	.000	.000	.000
1600	9.762	7.762	7.067	1.330	.000	.000	.000
1700	9.762	7.762	7.067	1.330	.000	.000	.000
1800	9.762	7.762	7.067	1.330	.000	.000	.000
1900	9.762	7.762	7.067	1.330	.000	.000	.000
2000	9.762	7.762	7.067	1.330	.000	.000	.000

LITHIUM (Li)

(CRYSTAL)

AT. WT. = 6.940

$$\Delta H_f^\circ 298.15 = 0$$

$$\Delta H_f^\circ 298.15 = 38.41 \pm 0.40 \text{ kcal. mole}^{-1} \text{ (Monatomic gas)}$$

$$\Delta H_f^\circ 298.15 = 50.41 \pm 0.30 \text{ kcal. mole}^{-1} \text{ (Diatomic gas)}$$

$$S_{298.15}^\circ = 6.954 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^\circ = 0.7171 \pm 0.0037 \text{ kcal. mole}^{-1}$$

$$T_m = 453.69^\circ\text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacities have been reported by the following authors for the temperature ranges indicated: L. M. Roberts, Proc. Phys. Soc. **70**, 744 (1957), 1.5 to 20°K (Li 99.5% pure); F. Simon and R. C. Swain, Z. Phys. Chem. **B20**, 169 (1935), 18° to 300°K; D. L. Martin, Proc. Roy. Soc. **A251**, 444 (1960), 22° to 300°K (Li 99.95% pure); T. B. Douglas, L. R. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. **77**, 2144 (1955), 299° to 1200°K (Li 99.98% pure). Martin, in a series of determinations, found that C_p depended on the thermal history of the sample; a peak at roughly 107°K was ascribed to a martensitic transformation. There is excellent continuity between the results of Roberts and of Martin, while those of Martin and Douglas et al. differ by 1% at 300°K and have been smoothly joined. The values of Simon and Swain were not used as they were 5% lower than Martin's and did not show the peak at 107°K; also their values for Al_2O_3 , reported at the same time, are lower than recent measurements. Heat capacities between 1200°K and the normal boiling point were obtained from the heat content equation given by Douglas et al. between 420° and 900°K.

Melting.

Douglas et al. (loc. cit.) report the triple point to be 180.54°K, which is here adopted as the melting point since the densities of solid and liquid lithium at 180°K are not available for calculating dT_m/dP . The same authors give the heat of melting as 432.3 ± 2.2 abs. Joule g^{-1} .

Heat of Sublimation.

Lithium vapor contains an appreciable amount of dimer, whose heat of dissociation has been selected by W. H. Evans, R. Jacobson, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bureau of Standards **55**, 83 (1955), from spectroscopic and molecular beam measurements to be 25.76 ± 0.10 kcal. mole⁻¹ at 0°K. This heat of dissociation, together with the thermodynamic functions calculated in this work, has been used to find the partial pressures of Li(g) and Li₂(g) from the measured total vapor pressures. H. Hartmann and R. Schneider, Z. anorg. allgem. Chem. **180**, 275 (1929), report values from 1204° to 1353°K; while M. Mencherat, C. Rendus **208**, 499 (1939), reports effusion measurements from 735° to 915°K. Mencherat's pressures are calculated on the assumption of monatomic vapor and have been recalculated to find the true total pressure. Effusion measurements by L. C. Lewis, Z. Physik **69**, 766 (1931), and A. Bogros, C. Rendus **191**, 560 (1950) and Ann. Phys. **17**, 199 (1952), have been disregarded. Mencherat considers them to be inaccurate because of impurities in the lithium used, and Lewis used a doubtful calibration method. Heats of sublimation to monatomic vapor calculated from the vapor pressures of Hartmann and Schneider and of Mencherat agree to within 2% and the average value has been adopted. The heat of sublimation of the dimer was then calculated using this value.

Lithium (Li)

(Liquid) At. Wt. = 6.940

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f°	ΔF_f°	Log K _P
0					
100	7.441	8.113	0.000	.223	.164
200	7.487	8.159	0.014	.221	.161
300	7.530	8.205	.042	.218	.158
400	7.569	8.251	.082	.215	.155
500	7.606	8.297	.125	.212	.152
600	7.640	8.343	.170	.209	.149
700	7.671	8.389	.216	.206	.146
800	7.699	8.435	.263	.203	.143
900	7.725	8.481	.310	.200	.140
1000	7.750	8.527	.357	.197	.137
1100	7.774	8.573	.404	.194	.134
1200	7.797	8.619	.451	.191	.131
1300	7.819	8.665	.498	.188	.128
1400	7.840	8.711	.545	.185	.125
1500	7.860	8.757	.592	.182	.122
1600	7.879	8.803	.639	.179	.119
1700	7.897	8.849	.686	.176	.116
1800	7.914	8.895	.733	.173	.113
1900	7.930	8.941	.780	.170	.110
2000	7.946	8.987	.827	.167	.107
2100	7.961	9.033	.874	.164	.104
2200	7.975	9.079	.921	.161	.101
2300	7.989	9.125	.968	.158	.098
2400	7.999	9.171	.1015	.155	.095
2500	8.009	9.217	.1048	.152	.092
2600	8.018	9.263	.1081	.149	.089
2700	8.026	9.309	.1114	.146	.086
2800	8.034	9.355	.1147	.143	.083
2900	8.041	9.401	.1180	.140	.080
3000	8.048	9.447	.1213	.137	.077
3100	8.054	9.493	.1246	.134	.074
3200	8.060	9.539	.1279	.131	.071
3300	8.065	9.585	.1312	.128	.068
3400	8.070	9.631	.1345	.125	.065
3500	8.075	9.677	.1378	.122	.062
3600	8.079	9.723	.1411	.119	.059
3700	8.083	9.769	.1444	.116	.056
3800	8.087	9.815	.1477	.113	.053
3900	8.090	9.861	.1510	.110	.050
4000	8.093	9.907	.1543	.107	.047

June 30, 1962

Li

LITHIUM (Li)

(LIQUID)

At. Wt. = 6.940

 $\Delta H_f^\circ 298.15 = 0.569 \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = 8.113 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_m^\circ = 0.7171 \pm 0.0035 \text{ kcal. mole}^{-1}$ $T_m = 453.69^\circ\text{K}$ $T_b = 1620^\circ\text{K}$ (equilibrium mixture) T_b (Monatomic gas) = 1639°K $\Delta H_v 1638 = 35.16 \text{ kcal. mole}^{-1}$

Heat of Formation.

Obtained from the heat of fusion by adding $H_{453.69}^\circ - H_{298.15}^\circ$ for the solid and subtracting $H_{453.69}^\circ - H_{298.15}^\circ$ for the liquid.

Heat Capacity.

The data of T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. 77, 2144 (1955) were taken and extrapolated below T_m and above 1200°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K .

Vaporization.

Lithium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1620°K ; the vapor pressure of the monatomic gas reaches 1 atm. at 1639°K and the heat of vaporization to monatomic gas is $35.16 \text{ kcal. mole}^{-1}$. See also Li(crystal).

Lithium, Monatomic (Li)
(Ideal Gas) At. Wt. = 6.940

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	.000	INFINITE	1.481	38.034	38.034	INFINITE
100	4.968	27.716	.984	38.412	38.412	76.272
200	4.968	31.158	.815	38.460	38.460	83.015
298	4.968	33.183	.680	38.480	38.480	86.241
300	4.968	33.174	.679	38.480	38.480	86.241
400	4.966	34.603	.506	38.284	38.284	82.257
500	4.968	35.712	1.003	37.363	37.363	75.252
600	4.968	36.618	1.500	37.147	37.147	70.130
700	4.968	37.384	2.031	36.943	36.943	64.416
800	4.966	38.047	2.493	36.748	36.748	58.488
900	4.968	38.632	2.990	36.554	36.554	52.050
1000	4.968	39.156	3.487	36.361	36.361	45.937
1100	4.968	39.629	3.884	36.170	36.170	40.131
1200	4.968	40.061	4.281	35.979	35.979	34.734
1300	4.968	40.459	4.677	35.789	35.789	29.723
1400	4.968	40.827	5.074	35.601	35.601	25.121
1500	4.969	41.170	5.471	35.415	35.415	20.913
1600	4.970	41.491	5.868	35.231	35.231	17.111
1700	4.971	41.792	6.265	35.047	35.047	13.711
1800	4.974	42.076	6.662	34.863	34.863	10.711
1900	4.976	42.345	7.059	34.679	34.679	8.211
2000	4.983	42.601	7.456	34.495	34.495	6.211
2100	4.991	42.844	7.853	34.311	34.311	4.711
2200	5.001	43.076	8.250	34.127	34.127	3.211
2300	5.014	43.299	8.647	33.943	33.943	2.211
2400	5.031	43.513	9.044	33.759	33.759	1.211
2500	5.051	43.719	9.441	33.575	33.575	.711
2600	5.074	43.917	9.838	33.391	33.391	.211
2700	5.102	44.109	10.235	33.207	33.207	-.289
2800	5.134	44.295	10.632	33.023	33.023	-.789
2900	5.169	44.476	11.029	32.839	32.839	-1.289
3000	5.209	44.652	11.426	32.655	32.655	-1.789
3100	5.253	44.823	11.823	32.471	32.471	-2.289
3200	5.300	44.991	12.220	32.287	32.287	-2.789
3300	5.352	45.155	12.617	32.103	32.103	-3.289
3400	5.407	45.315	13.014	31.919	31.919	-3.789
3500	5.466	45.473	13.411	31.735	31.735	-4.289
3600	5.529	45.628	13.808	31.551	31.551	-4.789
3700	5.596	45.780	14.205	31.367	31.367	-5.289
3800	5.666	45.930	14.602	31.183	31.183	-5.789
3900	5.740	46.078	15.000	30.999	30.999	-6.289
4000	5.818	46.225	15.397	30.815	30.815	-6.789
4100	5.901	46.369	15.794	30.631	30.631	-7.289
4200	5.987	46.513	16.191	30.447	30.447	-7.789
4300	6.079	46.655	16.588	30.263	30.263	-8.289
4400	6.175	46.795	16.985	30.079	30.079	-8.789
4500	6.277	46.935	17.382	29.895	29.895	-9.289
4600	6.385	47.074	17.779	29.711	29.711	-9.789
4700	6.500	47.213	18.176	29.527	29.527	-10.289
4800	6.621	47.351	18.573	29.343	29.343	-10.789
4900	6.750	47.489	18.970	29.159	29.159	-11.289
5000	6.886	47.627	19.367	28.975	28.975	-11.789
5100	7.032	47.764	19.764	28.791	28.791	-12.289
5200	7.186	47.902	20.161	28.607	28.607	-12.789
5300	7.349	48.041	20.558	28.423	28.423	-13.289
5400	7.523	48.180	20.955	28.239	28.239	-13.789
5500	7.707	48.320	21.352	28.055	28.055	-14.289
5600	7.901	48.460	21.749	27.871	27.871	-14.789
5700	8.106	48.602	22.146	27.687	27.687	-15.289
5800	8.322	48.745	22.543	27.503	27.503	-15.789
5900	8.549	48.889	22.940	27.319	27.319	-16.289
6000	8.787	49.038	23.337	27.135	27.135	-16.789

June 30, 1962

AT. WT. = 6.940

(IDEAL GAS)

LITHIUM, MONATOMIC (Li)

ΔH_f^o 298.15 = 38.41 ± 0.40 kcal. mole⁻¹
S_{298.15} = 33.143 cal. deg. mole⁻¹

ΔH_f^o = 38.034 kcal. mole⁻¹
Ground State Configuration 2s¹/2

Electronic Levels and Multiplicities

E ₁ cm. ⁻¹	E ₁	E ₁ cm. ⁻¹	E ₁
0	2	36596	50
14504	6	38300	2
27206	2	39823	50
30325	6	41756	70
31283	10	42756	52
35012	2	43319	162

Heat of Formation.
Same as the heat of sublimation to the monatomic gas; see notes on Li(crystal).

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 467," U. S. Government Printing Office, Washington (1949) p. 9. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

Li⁺

Lithium Unipositive Ion (Li⁺)

(Ideal Gas) At. Wt. = 6.940

LITHIUM UNIPOSITIVE ION (Li⁺) (IDEAL GAS)

AT. WT. = 6.940

Ground State Configuration ¹S₀ ΔH_f⁰ = 182.379 kcal. mole⁻¹
S_{298.15} = 31.766 cal. deg.⁻¹ mole⁻¹ ΔH_f⁰ 298.15 = 164.236 kcal. mole⁻¹

Electronic Levels and Multiplicities

E, cm. ⁻¹	E ₁
0	1
492008	18
581765	39
582517	61
595039	125
601915	65

Heat of Formation.

The heat of formation at 0°K. was obtained from that of the ideal monatomic lithium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels" Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation Li(ref. state) - e⁻(ref. state) = Li⁺(monatomic gas), thus Li⁺ involves the difference in enthalpies of two reference states as well as its own enthalpy.

Heat Capacity and Entropy.

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore loc. cit.

T, °K.	C _v	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0							
100	4.968	31.766	31.766	0.000	164.236	155.351	-113.870
200	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
300	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
400	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
500	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
600	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
700	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
800	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
900	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1000	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1100	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1200	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1300	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1400	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1500	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1600	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1700	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1800	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
1900	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2000	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2100	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2200	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2300	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2400	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2500	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2600	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2700	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2800	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
2900	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3000	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3100	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3200	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3300	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3400	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3500	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3600	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3700	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3800	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
3900	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4000	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4100	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4200	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4300	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4400	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4500	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4600	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4700	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4800	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
4900	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5000	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5100	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5200	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5300	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5400	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5500	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5600	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5700	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5800	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
5900	4.968	31.766	31.766	0.009	164.243	155.295	-113.127
6000	4.968	31.766	31.766	0.009	164.243	155.295	-113.127

Mar. 31, 1965

Li⁺

(Ideal Gas) GFW = 20.9457

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	ΔH° _f kcal/mol	ΔG° _f	Log K _p
0	∞	INFINITE	79.990	79.990	INFINITE
100	4.000	41.807	80.219	79.123	170.731
200	7.126	46.719	80.142	76.066	83.099
298	7.848	49.744	80.000	74.065	54.291
300	7.857	49.793	79.997	74.028	53.929
400	8.241	52.110	79.834	72.063	38.263
500	8.490	53.377	79.692	70.217	30.692
600	8.655	55.541	78.690	68.501	24.951
700	8.772	56.884	78.498	66.817	20.661
800	8.858	58.062	78.316	65.160	17.801
900	8.926	59.109	78.135	63.527	15.427
1000	8.980	60.052	77.954	61.914	13.251
1100	9.026	60.910	77.772	60.319	11.984
1200	9.067	61.698	77.588	58.739	10.698
1300	9.102	62.425	77.405	57.176	9.612
1400	9.135	63.100	77.221	55.628	8.684
1500	9.165	63.732	77.039	54.090	7.881
1600	9.193	64.324	76.858	52.568	7.180
1700	9.220	64.882	76.682	51.063	6.734
1800	9.246	65.410	76.510	50.017	6.437
1900	9.271	65.911	76.342	49.034	6.171
2000	9.295	66.387	76.181	48.102	5.932
2100	9.318	66.841	76.025	47.224	5.715
2200	9.341	67.275	75.874	46.398	5.518
2300	9.364	67.691	75.728	45.622	5.338
2400	9.386	68.090	75.587	44.895	5.173
2500	9.408	68.473	75.450	44.216	5.022
2600	9.430	68.843	75.318	43.584	4.881
2700	9.451	69.199	75.190	43.000	4.752
2800	9.473	69.543	75.066	42.462	4.632
2900	9.494	69.876	74.946	41.969	4.520
3000	9.515	70.198	74.830	41.511	4.415
3100	9.536	70.510	74.718	41.089	4.317
3200	9.556	70.813	74.610	40.700	4.226
3300	9.577	71.108	74.506	40.344	4.140
3400	9.598	71.394	74.406	40.020	4.059
3500	9.618	71.673	74.310	39.728	3.982
3600	9.639	71.944	74.218	39.466	3.911
3700	9.659	72.208	74.130	39.234	3.843
3800	9.679	72.466	74.046	39.030	3.778
3900	9.699	72.718	73.966	38.854	3.717
4000	9.720	72.963	73.890	38.700	3.660
4100	9.740	73.204	73.818	38.566	3.605
4200	9.760	73.439	73.750	38.452	3.552
4300	9.780	73.669	73.686	38.358	3.502
4400	9.800	73.894	73.626	38.284	3.455
4500	9.821	74.114	73.570	38.220	3.410
4600	9.841	74.330	73.518	38.166	3.367
4700	9.861	74.542	73.469	38.122	3.326
4800	9.881	74.750	73.424	38.086	3.286
4900	9.901	74.954	73.383	38.056	3.248
5000	9.921	75.154	73.346	38.030	3.213
5100	9.941	75.351	73.312	38.008	3.178
5200	9.960	75.544	73.281	37.989	3.145
5300	9.980	75.734	73.252	37.972	3.113
5400	10.000	75.921	73.226	37.957	3.083
5500	10.020	76.104	73.202	37.943	3.054
5600	10.040	76.285	73.179	37.930	3.026
5700	10.060	76.463	73.158	37.918	3.000
5800	10.080	76.638	73.138	37.907	2.974
5900	10.100	76.810	73.119	37.897	2.950
6000	10.120	76.980	73.100	37.888	2.926

Dec. 31, 1960; Sept. 30, 1966; Dec. 31, 1966

LITHIUM NITRIDE (LIN)

(IDEAL GAS)

GFW = 20.9457

Ground State Configuration [3 Σ]

ΔH_f° = 80 ± 40 kcal/molS°_{298.15} = [49.7] gibbs/molΔH_f°_{298.15} = 80 ± 40 kcal/mol

Electronic Levels and Quantum Weights

$$\frac{\epsilon_i}{\epsilon_1}, \text{ cm}^{-1} = \frac{E_i}{[3]}$$

 $\omega_e = [700] \text{ cm}^{-1}$ $\omega_e x_e = [7] \text{ cm}^{-1}$ $\sigma = 1$ $B_e = [1.25] \text{ cm}^{-1}$ $\alpha_e = [0.0183] \text{ cm}^{-1}$ $r_e = [1.71] \text{ Å}$

Heat of Formation.

The adopted ΔH_f°_{298.15} = 80 ± 40 kcal/mol is calculated from the following estimates:

Method	D° kcal/mol	76	75	ΔH _f ° _{298.15} kcal/mol
Estimate D° from geometric mean for Li ₂ and N ₂				
Estimate from D° for series N ₂ (g), CN(g), and BeN(g)		40 - 100	110 - 50	
Estimate from D° for series HN(g), HO(g), LiF(g) and LiO(g)		20 - 60	130 - 90	

J. L. Margrave and P. Schapitanonda, J. Phys. Chem. 59, 1231 (1955), report estimated dissociation energies in the range 111-178 kcal/mol, based on approximate ionic binding energies calculated from ionic radii for N⁻ in the range 0.70 to 1.08 Å.

Heat Capacity and Entropy.

The molecular constants ω_e , r_e and $\omega_e x_e$ are estimated by comparison with those of CN, BN, CO, BO and LiO. The values of α_e and B_e are calculated from the above constants. The ground state configuration is assumed to be 3Σ by analogy with NH and OH⁺.

Lithium Nitroxide (LiON)
(Ideal Gas) $G^{\circ}F = 36.9451$

LiNO

OPW = 36.9451

(IDEAL GAS)

LITHIUM NITROXIDE (LiON)

Point Group C_{2v}

$S^{\circ}_{298.15} = 58.61$ gibbs/mol

Ground State Quantum Weight = [1]

$\Delta H^{\circ}_f = [43.5 \pm 10]$ kcal/mol
 $\Delta H^{\circ}_{298.15} = [43.0 \pm 10]$ kcal/mol

Vibrational Frequencies and Degeneracies

ω , cm^{-1}	
1350 (1)	
330 (1)	
650 (1)	

$O-N = 1.30 \pm 0.05 \text{ \AA}$

$\sigma = 1$

Bond Angle: $Li-O-N = 100 \pm 10^{\circ}$

Product of the Moments of Inertia: $I_A I_B I_C = 2.6523 \times 10^{-116} \text{ g}^3 \text{ cm}^6$

Heat of Formation

The heat of formation (ΔH°_{298}) for $LiON(g)$ has not been determined experimentally. The ΔH°_{298} value adopted is calculated from the estimated Li-O and O-N bond energies. The value, $D(Li-O) = 88$ kcal/mol, is obtained by averaging the bonds in $Li_2O(g)$. The value, $D(O-N) = 69$ kcal/mol, is calculated on the assumption that $D(ClON-O) = D(N-Of)$. The ΔH°_{298} of $LiOH(g)$, calculated similarly from bond energies (i.e. $D(Li-O) = 88$ kcal/mol and $D(O-H) = 111$ kcal/mol), is 10 kcal/mol more than the measured value. Therefore, we subtract 10 kcal/mol from the ΔH°_{298} of $LiON$, 53 kcal/mol, estimated from the above bond energies, and arrive at 43 kcal/mol for the adopted value.

Heat Capacity and Entropy

The vibrational frequencies, bond distances and bond angle were obtained from W. L. S. Andrews and G. C. Fimentel, loc. cit. The three principal moments of inertia are: $I_A = 1.2706 \times 10^{-56}$, $I_B = 3.9776 \times 10^{-39}$ and $I_C = 5.2482 \times 10^{-39} \text{ g cm}^2$.

LiNO

Sept. 30, 1966

T, K	C_p°	S°	$-(G^{\circ}-H^{\circ}_{298})/T$	$H^{\circ}-H^{\circ}_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-2.701	43.478	43.478	INFINITE
100	8.359	48.573	0.000	1.098	42.785	42.785	93.507
200	10.617	58.608	0.000	0.000	43.478	43.478	30.587
300	10.633	58.674	58.608	0.020	42.996	41.719	30.193
400	11.373	61.839	59.035	1.222	42.773	41.328	22.581
500	11.932	64.440	59.863	2.284	41.804	41.069	17.951
600	12.351	66.654	60.915	3.503	41.873	40.945	14.914
700	12.663	68.583	61.700	4.765	41.371	40.495	12.756
800	12.897	70.200	62.748	6.033	41.187	40.793	11.144
900	13.075	71.819	63.672	7.332	41.009	40.756	9.897
1000	13.212	73.204	64.555	8.647	40.833	40.738	8.903
1100	13.319	74.469	65.402	9.974	40.658	40.736	8.093
1200	13.404	75.632	66.207	11.310	40.482	40.750	7.422
1300	13.473	76.707	66.973	12.654	40.306	40.780	6.856
1400	13.529	77.708	67.705	14.004	40.129	40.823	6.373
1500	13.575	78.643	68.403	15.360	39.951	40.878	5.956
1600	13.613	79.520	69.071	16.719	39.773	40.947	5.593
1700	13.645	80.347	69.710	18.082	42.353	42.353	5.445
1800	13.672	81.127	70.323	19.448	44.546	44.546	5.434
1900	13.696	81.867	70.911	20.816	46.544	46.544	5.457
2000	13.716	82.570	71.477	22.187	48.027	48.027	5.485
2100	13.733	83.240	72.021	23.559	49.527	51.250	5.536
2200	13.749	83.876	72.546	24.934	51.047	53.477	5.586
2300	13.762	84.490	73.052	26.309	52.582	55.703	5.633
2400	13.774	85.087	73.541	27.686	54.131	57.930	5.675
2500	13.784	85.659	74.013	29.064	55.695	60.157	5.719
2600	13.793	86.180	74.471	30.443	57.264	62.385	5.764
2700	13.802	86.700	74.914	31.822	58.837	64.617	5.810
2800	13.809	87.203	75.344	33.203	60.414	66.846	5.856
2900	13.816	87.687	75.762	34.584	62.003	69.083	5.906
3000	13.822	88.156	76.167	35.966	63.595	71.318	5.955
3100	13.828	88.609	76.561	37.349	65.186	73.556	5.999
3200	13.833	89.048	76.944	38.732	66.779	75.794	6.041
3300	13.837	89.474	77.318	40.115	68.374	78.035	6.081
3400	13.841	89.887	77.681	41.499	69.969	80.282	6.125
3500	13.845	90.288	78.036	42.883	71.564	82.526	6.169
3600	13.849	90.678	78.382	44.268	73.159	84.778	6.213
3700	13.852	91.058	78.719	45.653	74.754	87.027	6.257
3800	13.855	91.427	79.049	47.038	76.349	89.288	6.301
3900	13.858	91.787	79.371	48.424	77.944	91.546	6.345
4000	13.860	92.138	79.686	49.810	79.539	93.805	6.389
4100	13.863	92.480	79.994	51.196	81.134	96.074	6.433
4200	13.865	92.814	80.295	52.582	82.729	98.342	6.477
4300	13.867	93.141	80.590	53.969	84.324	100.614	6.521
4400	13.869	93.460	80.879	55.356	85.919	102.890	6.565
4500	13.871	93.771	81.162	56.743	87.514	105.175	6.609
4600	13.872	94.076	81.439	58.130	89.109	107.462	6.653
4700	13.874	94.374	81.711	59.517	90.704	109.750	6.697
4800	13.875	94.667	81.978	60.905	92.299	112.042	6.741
4900	13.877	94.953	82.240	62.292	93.894	114.338	6.785
5000	13.878	95.233	82.497	63.680	95.489	116.639	6.829
5100	13.879	95.508	82.749	65.068	97.084	118.938	6.873
5200	13.880	95.777	82.997	66.456	98.679	121.236	6.917
5300	13.882	96.042	83.241	67.844	100.274	123.533	6.961
5400	13.883	96.301	83.481	69.232	101.869	125.831	7.005
5500	13.884	96.556	83.716	70.621	103.464	128.128	7.049
5600	13.885	96.806	83.947	72.009	105.059	130.425	7.093
5700	13.885	97.052	84.175	73.397	106.654	132.722	7.137
5800	13.886	97.293	84.399	74.786	108.249	135.019	7.181
5900	13.887	97.531	84.620	76.175	109.844	137.316	7.225
6000	13.888	97.764	84.837	77.564	111.439	139.613	7.269

Lithium Sodium Oxide (LiNaO)

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 45.931

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	0.000	INFINITE	INFINITE	2.421	23.938	23.938	INFINITE
100	0.160	51.433	60.659	1.623	23.935	23.259	57.362
200	0.195	57.391	62.176	.957	24.436	28.398	20.030
298	0.206	61.270	61.270	.000	25.000	30.222	22.152
300	0.210	61.315	61.270	.049	25.040	30.254	22.039
400	0.257	65.666	62.566	1.100	25.250	31.682	18.682
500	0.299	67.026	62.502	2.262	27.613	33.117	14.475
600	0.339	69.247	63.446	3.481	28.205	34.161	12.443
700	0.374	71.188	64.416	4.740	28.741	35.113	10.962
800	0.406	72.906	65.372	6.027	29.240	35.988	9.831
900	0.436	74.433	66.320	7.345	29.700	36.822	8.836
1000	0.462	75.840	67.162	8.658	30.191	37.584	8.029
1100	0.487	77.112	68.028	9.992	30.660	38.280	7.405
1200	0.510	78.260	68.834	11.335	31.109	38.925	7.011
1300	0.531	79.361	69.603	12.685	31.536	39.527	6.747
1400	0.550	80.421	70.340	14.040	31.944	40.088	6.507
1500	0.567	81.394	71.036	15.401	32.336	40.616	6.287
1600	0.583	82.164	71.706	16.765	32.714	41.116	6.084
1700	0.598	82.833	72.347	18.132	33.079	41.590	5.897
1800	0.612	83.438	72.951	19.502	33.432	42.040	5.726
1900	0.625	83.978	73.521	20.872	33.774	42.468	5.576
2000	0.637	84.454	74.058	22.248	34.104	42.876	5.442
2100	0.648	84.864	74.564	23.623	34.421	43.266	5.321
2200	0.658	85.210	75.039	25.000	34.726	43.639	5.211
2300	0.667	85.500	75.486	26.378	35.020	43.996	5.110
2400	0.675	85.736	75.906	27.756	35.304	44.338	5.017
2500	0.683	85.928	76.297	29.137	35.578	44.666	4.936
2600	0.690	86.076	76.662	30.517	35.843	44.981	4.864
2700	0.696	86.190	76.996	31.899	36.099	45.284	4.800
2800	0.701	86.270	77.296	33.281	36.346	45.576	4.742
2900	0.706	86.326	77.564	34.664	36.584	45.856	4.689
3000	0.710	86.357	77.800	36.046	36.814	46.124	4.641
3100	0.714	86.364	78.015	37.431	37.036	46.381	4.597
3200	0.717	86.348	78.200	38.816	37.250	46.628	4.557
3300	0.720	86.300	78.374	40.200	37.456	46.866	4.520
3400	0.722	86.225	78.526	41.586	37.654	47.096	4.486
3500	0.724	86.125	78.659	42.971	37.844	47.318	4.454
3600	0.725	86.000	78.764	44.351	38.026	47.532	4.424
3700	0.726	85.850	78.840	45.726	38.200	47.738	4.396
3800	0.726	85.675	78.888	47.100	38.366	47.936	4.370
3900	0.726	85.475	78.906	48.475	38.524	48.126	4.346
4000	0.725	85.250	78.894	49.850	38.674	48.308	4.324
4100	0.724	85.000	78.840	51.225	38.816	48.482	4.304
4200	0.722	84.725	78.750	52.600	38.950	48.648	4.286
4300	0.720	84.425	78.625	53.975	39.076	48.806	4.270
4400	0.717	84.100	78.460	55.350	39.194	48.956	4.256
4500	0.714	83.750	78.250	56.725	39.304	49.100	4.244
4600	0.710	83.375	78.000	58.100	39.406	49.238	4.234
4700	0.706	82.975	77.712	59.475	39.500	49.370	4.226
4800	0.701	82.550	77.388	60.850	39.586	49.496	4.220
4900	0.696	82.100	77.025	62.225	39.664	49.616	4.216
5000	0.690	81.625	76.625	63.600	39.734	49.730	4.214
5100	0.684	81.125	76.188	64.975	39.796	49.838	4.212
5200	0.678	80.600	75.712	66.350	39.850	49.940	4.210
5300	0.671	80.050	75.200	67.725	39.896	50.036	4.208
5400	0.664	79.475	74.650	69.100	39.934	50.126	4.206
5500	0.657	78.875	74.062	70.475	39.964	50.210	4.204
5600	0.649	78.250	73.438	71.850	39.986	50.288	4.202
5700	0.641	77.600	72.775	73.225	39.999	50.360	4.200
5800	0.633	76.925	72.075	74.600	40.004	50.426	4.198
5900	0.625	76.225	71.338	75.975	40.004	50.486	4.196
6000	0.617	75.500	70.562	77.350	40.000	50.540	4.194

June 30, 1961

LiNaO

Lithium Sodium Oxide (LiNaO) (Ideal Gas)

Mol. Wt. = 45.931

 $\Delta H_f^\circ 298.15 = [-25 \pm 30] \text{ kcal. mole}^{-1}$ $S^\circ 298.15 = [61.270] \text{ cal. deg}^{-1} \text{ mole}^{-1}$

Vibrational Levels and Multiplicities

(ν, cm^{-1})
[400] (1)
[1000] (1)
[900] (1)

Li-O-Ne angle = $[105^\circ]$, O-Li distance = $[1.82] \text{ \AA}$, O-Ne distance = $[2.21] \text{ \AA}$ Product of moments of inertia, $I_A I_B I_C = [3.179 \times 10^{-115}] \text{ g}^3 \text{ cm}^6$
 $\sigma = 1$

Heat of Formation. Estimated from bond energies derived from heats of formation used in JANAP tables.

Heat Capacity and Entropy. The molecular constants have been estimated by comparison of similar molecules.

LiNaO

T, °K.	C _p ^o	S ^o	-(F ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	INFINITE	2.438	20.105	20.105	INFINITE
100	0.866	42.517	56.040	1.443	20.124	20.124	40.045
200	7.252	74.447	51.088	1.786	20.251	16.361	17.856
300	7.743	86.395	50.495	2.000	20.350	14.453	17.594
400	7.754	90.443	50.395	0.14	20.097	14.418	10.803
500	8.142	92.730	50.704	0.810	19.916	12.552	6.858
600	8.400	94.577	51.300	1.618	18.961	10.810	4.725
700	8.573	96.125	51.979	2.488	18.720	9.204	3.352
800	8.694	97.456	52.608	3.351	18.494	7.635	2.384
900	8.782	98.623	53.181	4.215	18.277	6.098	1.666
1000	8.848	99.661	53.687	5.107	18.061	4.589	1.114
1100	8.901	100.596	54.122	5.995	17.854	3.104	0.678
1200	8.945	101.447	54.586	6.887	17.650	1.660	0.326
1300	8.981	102.227	55.071	7.783	17.454	0.195	0.036
1400	9.013	102.947	55.568	8.683	17.269	-1.231	-0.207
1500	9.042	103.616	56.069	9.586	17.095	-2.641	-0.412
1600	9.067	104.241	56.574	10.491	16.932	-4.035	-0.588
1700	9.091	104.827	57.082	11.399	16.781	-5.415	-0.740
1800	9.113	105.378	57.594	12.309	16.637	-6.784	-0.871
1900	9.133	105.900	58.108	13.222	16.502	-8.142	-0.985
2000	9.153	106.394	58.624	14.136	16.375	-9.488	-1.087
2100	9.172	106.864	59.138	15.052	16.258	-10.821	-1.178
2200	9.190	107.312	59.650	15.970	16.146	-12.142	-1.259
2300	9.207	107.740	60.163	16.890	16.039	-13.457	-1.331
2400	9.224	108.150	60.675	17.812	15.936	-14.767	-1.394
2500	9.241	108.543	61.186	18.735	15.838	-16.071	-1.449
2600	9.257	108.920	61.696	19.660	15.744	-17.370	-1.505
2700	9.273	109.283	62.208	20.586	15.654	-18.664	-1.561
2800	9.289	109.634	62.721	21.514	15.568	-19.954	-1.617
2900	9.305	109.972	63.234	22.444	15.486	-21.240	-1.673
3000	9.320	110.299	63.748	23.375	15.408	-22.522	-1.729
3100	9.335	110.615	64.262	24.308	15.334	-23.800	-1.785
3200	9.350	110.921	64.778	25.242	15.262	-25.074	-1.841
3300	9.365	111.218	65.293	26.178	15.193	-26.344	-1.897
3400	9.380	111.507	65.809	27.116	15.126	-27.610	-1.953
3500	9.395	111.787	66.326	28.054	15.061	-28.874	-2.009
3600	9.410	112.059	66.843	28.995	15.000	-30.136	-2.065
3700	9.424	112.325	67.360	29.936	14.942	-31.396	-2.121
3800	9.439	112.583	67.877	30.879	14.886	-32.652	-2.177
3900	9.453	112.834	68.394	31.824	14.832	-33.904	-2.233
4000	9.468	113.081	68.911	32.770	14.780	-35.152	-2.289
4100	9.482	113.321	69.428	33.718	14.730	-36.396	-2.345
4200	9.497	113.555	69.945	34.667	14.681	-37.636	-2.401
4300	9.511	113.784	70.462	35.617	14.633	-38.872	-2.457
4400	9.525	114.008	70.979	36.569	14.586	-40.104	-2.513
4500	9.539	114.227	71.496	37.522	14.540	-41.332	-2.569
4600	9.554	114.442	72.013	38.477	14.495	-42.556	-2.625
4700	9.568	114.652	72.530	39.433	14.451	-43.776	-2.681
4800	9.582	114.856	73.047	40.390	14.408	-44.992	-2.737
4900	9.596	115.060	73.564	41.349	14.366	-46.204	-2.793
5000	9.610	115.258	74.081	42.310	14.324	-47.412	-2.849
5100	9.624	115.452	74.598	43.271	14.283	-48.616	-2.905
5200	9.639	115.643	75.115	44.234	14.242	-49.816	-2.961
5300	9.653	115.830	75.632	45.199	14.202	-51.012	-3.017
5400	9.667	116.014	76.150	46.165	14.162	-52.204	-3.073
5500	9.681	116.195	76.667	47.132	14.122	-53.392	-3.129
5600	9.695	116.373	77.184	48.101	14.082	-54.576	-3.185
5700	9.709	116.547	77.701	49.071	14.042	-55.756	-3.241
5800	9.723	116.719	78.219	50.043	14.002	-56.932	-3.297
5900	9.737	116.889	78.738	51.016	13.962	-58.104	-3.353
6000	9.751	117.055	79.258	52.000	13.922	-59.272	-3.409
6100	9.765	117.219	79.777	52.986	13.882	-60.436	-3.465

Dec. 31, 1960 Mar. 31, 1964

LITHIUM MONOXIDE (LiO)

MOL. WT. = 22.940

(IDEAL GAS)

Ground State Configuration $[^2P]$
 $S_{298.15}^{\circ} = 50.395 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^{\circ} 0 = 20.1 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^{\circ} 298.15 = 20.1 \pm 5 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{\epsilon_i, \text{ cm.}^{-1}}{0} \frac{g_i}{4}$$

$\omega_e = 745 \text{ cm.}^{-1}$
 $\omega_e x_e = [4.835] \text{ cm.}^{-1}$
 $\alpha_e = [0.01288] \text{ cm.}^{-1}$
 $\sigma = 1$
 $r_e = [1.62] \text{ \AA}$

Heat of Formation.

D. White, K. S. Sehadri, D. P. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963) calculated the heat of formation from their mass spectral data by two different methods.

For the first calculation (a) they combined the slope of the log Π vs $1/T$ curve for LiO^+ with the slopes for Li^+ and Li_2O^+ for the reaction $\text{Li}_2\text{O}^+ (\text{g}) \rightarrow \text{Li} (\text{g}) + \text{LiO} (\text{g})$. For the second calculation (b) they assumed a cross section $\sigma_{\text{LiO}}/\sigma_{\text{Li}_2\text{O}} = 1$ and from this they calculated a partial pressure for $\text{LiO} (\text{g})$ at 1500°K and an equilibrium constant for the reaction $\text{Li}_2\text{O} (\text{g}) \rightarrow \text{Li} (\text{g}) + \text{LiO} (\text{g})$. They obtained (a) $\Delta H_f^{\circ} 298 = 18.3 \text{ kcal. mole}^{-1}$ and (b) $\Delta H_f^{\circ} 298 = 16.3 \text{ kcal. mole}^{-1}$, and used the average value from the two methods for the heat of formation of $\text{LiO} (\text{g})$. The JANAF heat of formation, $20.1 \pm 5 \text{ kcal. mole}^{-1}$, was obtained in the same way using their data and the present tables i.e. (a) $\Delta H_f^{\circ} 298 = 22.0 \text{ kcal. mole}^{-1}$ and (b) $\Delta H_f^{\circ} 298 = 18.3 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The molecular constants, ω_e , x_e , α_e , and σ , were calculated from ω_e and r_e , reported by White et al. The ground state configuration, 2P , was estimated by J. S. Gordon, Thiokol Chemical Corp., Reaction Motor Division, Denville, N. J., "Thermodynamic Data for Combustion Products", January, 1960, by A. Buchler and J. L. Stauffer, J. Chem. Phys. **39**, 2299 (1963) and by White et al.

Lithium Monoxide Uninegative Ion (LiO⁻)
(Ideal Gas) GFW = 22.93895

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
100	7.734	47.593	47.593	16.000	19.324	14.165
200	7.742	47.641	47.593	16.012	19.345	14.093
300	7.742	47.641	47.593	16.012	19.345	14.093
400	8.131	49.025	47.002	16.009	20.354	11.121
500	8.390	51.769	48.496	1.636	21.112	9.228
600	8.564	53.315	49.174	2.084	21.536	7.881
700	8.685	54.445	49.863	2.397	22.037	6.880
800	8.773	55.810	50.535	2.520	22.337	6.102
900	8.840	56.848	51.180	2.551	22.546	5.475
1000	8.893	57.782	51.794	2.588	22.675	4.956
1100	8.936	58.632	52.378	2.622	22.733	4.517
1200	8.972	59.411	52.932	2.654	22.788	4.139
1300	9.004	60.130	53.458	2.687	22.841	3.810
1400	9.032	60.799	53.959	2.719	22.890	3.519
1500	9.057	61.423	54.436	2.750	22.938	3.259
1600	9.080	62.008	54.891	2.780	22.987	3.025
1700	9.101	62.559	55.324	2.809	23.036	2.823
1800	9.121	63.080	55.742	2.837	23.084	2.643
1900	9.141	63.573	56.142	2.865	23.132	2.483
2000	9.159	64.043	56.525	2.892	23.180	2.343
2100	9.176	64.490	56.894	2.919	23.228	2.223
2200	9.193	64.917	57.249	2.946	23.276	2.123
2300	9.210	65.326	57.591	2.973	23.324	2.043
2400	9.226	65.719	57.922	2.999	23.372	1.983
2500	9.242	66.096	58.241	3.025	23.420	1.933
2600	9.257	66.458	58.550	3.051	23.468	1.893
2700	9.272	66.808	58.850	3.077	23.516	1.863
2800	9.287	67.145	59.140	3.103	23.564	1.833
2900	9.302	67.472	59.422	3.129	23.612	1.803
3000	9.317	67.787	59.695	3.155	23.660	1.773
3100	9.331	68.093	59.961	3.181	23.708	1.743
3200	9.346	68.389	60.220	3.207	23.756	1.713
3300	9.360	68.677	60.472	3.233	23.804	1.683
3400	9.374	68.957	60.717	3.259	23.852	1.653
3500	9.389	69.229	60.957	3.285	23.900	1.623
3600	9.403	69.494	61.190	3.311	23.948	1.593
3700	9.417	69.751	61.418	3.337	23.996	1.563
3800	9.430	70.003	61.641	3.363	24.044	1.533
3900	9.444	70.248	61.859	3.389	24.092	1.503
4000	9.458	70.487	62.071	3.415	24.140	1.473
4100	9.472	70.721	62.279	3.441	24.188	1.443
4200	9.486	70.949	62.483	3.467	24.236	1.413
4300	9.499	71.173	62.682	3.493	24.284	1.383
4400	9.513	71.391	62.878	3.519	24.332	1.353
4500	9.527	71.605	63.069	3.545	24.380	1.323
4600	9.540	71.815	63.257	3.571	24.428	1.293
4700	9.554	72.020	63.442	3.597	24.476	1.263
4800	9.567	72.221	63.622	3.623	24.524	1.233
4900	9.581	72.419	63.800	3.649	24.572	1.203
5000	9.594	72.612	63.974	3.675	24.620	1.173
5100	9.608	72.802	64.145	3.701	24.668	1.143
5200	9.621	72.989	64.314	3.727	24.716	1.113
5300	9.635	73.172	64.479	3.753	24.764	1.083
5400	9.648	73.353	64.642	3.779	24.812	1.053
5500	9.662	73.530	64.802	3.805	24.860	1.023
5600	9.675	73.704	64.959	3.831	24.908	0.993
5700	9.689	73.875	65.114	3.857	24.956	0.963
5800	9.702	74.044	65.267	3.883	25.004	0.933
5900	9.715	74.210	65.417	3.909	25.052	0.903
6000	9.729	74.373	65.565	3.935	25.100	0.873

Dec. 31, 1967

LITHIUM MONOXIDE UNINEGATIVE ION (LiO⁻) (IDEAL GAS) GFW = 22.93895

Ground State Configuration [↑↓]
 $\Delta H_f^\circ = [-16 \pm 15] \text{ kcal/mol}$
 $\Delta H_f^\circ_{298.15} = [-16 \pm 15] \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_i, \text{ cm}^{-1}$ $\frac{g_i}{O}$ $\frac{g_i}{[1]}$

$\omega_e x_e = [4.5] \text{ cm}^{-1}$ $\sigma = 1$
 $\omega_e = [1.360] \text{ cm}^{-1}$ $r_e = [1.6] \text{ \AA}$

Heat of Formation

Data on the electron affinity (E.A.) of LiO (g) are unavailable, therefore the value of $\Delta H_f^\circ(\text{LiO}^-, \text{g})$ is estimated. We first assume that the enthalpy change (ΔH_r°) of the reaction (1) $\text{LiO}^-(\text{g}) = \text{Li}(\text{g}) + \text{O}^-(\text{g})$ is close to the average of the ΔH_r° values for the reactions (2) $\text{LiO}(\text{g}) = \text{Li}(\text{g}) + \text{O}(\text{g})$ and (3) $\text{LiF}(\text{g}) = \text{Li}(\text{g}) + \text{F}(\text{g})$. The atom F(g) is isoelectronic with O⁻(g). In other words, the ΔH_r° for reaction (1) is approximately $1/2(76.91 + 135.84) = 106.4 \text{ kcal/mol}$. Then we compare the ΔH_r° values for the reactions (4) $\text{HO}(\text{g}) = \text{H}(\text{g}) + \text{O}(\text{g})$, (5) $\text{HO}^-(\text{g}) = \text{H}(\text{g}) + \text{O}^-(\text{g})$, and (6) $\text{HF}(\text{g}) = \text{H}(\text{g}) + \text{F}(\text{g})$, and find that ΔH_r° for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔH_r° values for reactions (4) and (6). Based on this fact we estimate $\Delta H_r^\circ = 96.4 \text{ kcal/mol}$ for reaction (1), yielding $\Delta H_f^\circ(\text{LiO}^-, \text{g}) = -15.5 \text{ kcal/mol}$.

Applying the difference in electron affinity between H(g) and Li(g) to OH(g) gives an approximate value, E. A. = 1.7 eV (39.2 kcal/mol) for LiO(g). The value of E. A. for H(g), Li(g) and OH(g) are taken from U. S. Bur. Std. Rept. 8628, Jan. 1, 1965. Based on $\Delta H_r^\circ = 39.2 \text{ kcal/mol}$ for the reaction $\text{LiO}^-(\text{g}) = \text{LiO}(\text{g}) + \text{e}^-(\text{g})$, we derive $\Delta H_f^\circ = -19.1 \text{ kcal/mol}$ for $\text{LiO}^-(\text{g})$, which is in reasonable agreement with the above estimated value.

The value of ΔH_f° for $\text{LiO}^-(\text{g})$ is tentatively adopted as $-16 \pm 15 \text{ kcal/mol}$. Using this ΔH_f° value, we derive E. A. = $1.6 \pm 0.7 \text{ eV}$ for LiO(g). The electron affinity of OH(g) is $1.8 \pm 0.1 \text{ eV}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of LiF(g) which is isoelectronic with LiO⁻(g). The values of ω_e , $\omega_e x_e$ and r_e are estimated by comparison with the observed data for LiF(g). The values of B_e and a_e are calculated from r_e , ω_e and $\omega_e x_e$ by use of the method suggested by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950. The enthalpy at 0°K is -2.137 kcal/mol .

T, °K.	C_p^0	S^0	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0	7.809	38.310	INFINITE	2.312	50.788	50.788	INFINITE
100	8.009	38.310	5.408	50.782	50.782	50.782	47.685
200	8.214	43.684	47.428	50.623	47.685	47.685	47.685
298	8.622	47.050	47.050	50.400	40.519	29.700	40.519
300	8.627	47.104	47.051	50.394	40.457	29.471	40.457
400	8.826	48.104	48.104	50.394	40.457	29.471	40.457
500	8.942	51.599	48.042	48.058	34.184	18.923	34.184
600	9.022	53.236	48.775	2.677	31.468	11.462	31.468
700	9.084	54.632	49.514	3.582	28.826	8.999	28.826
800	9.132	55.827	50.272	4.650	26.253	6.172	26.253
900	9.168	56.941	51.041	5.881	23.761	3.291	23.761
1000	9.224	57.987	51.567	6.330	21.279	0.450	21.279
1100	9.264	58.778	52.183	7.254	18.863	3.748	18.863
1200	9.291	59.365	52.767	8.162	16.487	3.003	16.487
1300	9.378	60.621	53.360	9.046	14.152	2.316	14.152
1400	9.409	61.673	53.347	10.989	11.951	1.394	11.951
1500	9.484	62.281	54.024	11.932	7.327	1.001	7.327
1600	9.478	62.955	55.279	12.878	7.763	1.998	7.763
1700	9.512	63.817	57.116	13.867	9.850	1.195	9.850
1800	9.537	64.808	58.523	14.905	11.956	1.529	11.956
1900	9.579	64.403	59.535	15.736	13.956	1.529	13.956
2000	9.612	64.871	59.921	16.696	16.073	1.673	16.073
2100	9.646	65.319	57.292	17.659	18.157	1.804	18.157
2200	9.673	65.648	57.697	18.625	20.239	1.923	20.239
2300	9.712	65.161	57.697	19.565	22.313	2.134	22.313
2400	9.745	66.558	58.331	20.567	24.488	2.427	24.488
2500	9.778	66.941	58.655	21.543	26.598	2.714	26.598
2600	9.810	67.311	58.969	22.523	28.658	2.995	28.658
2700	9.840	67.673	59.273	23.506	30.679	3.276	30.679
2800	9.873	68.028	59.568	24.491	32.668	3.550	32.668
2900	9.909	68.350	59.856	25.481	34.626	3.819	34.626
3000	9.941	68.675	60.135	26.473	36.565	4.084	36.565
3100	9.964	68.991	60.407	27.469	38.484	4.345	38.484
3200	9.989	69.298	60.673	28.469	40.393	4.602	40.393
3300	10.039	69.598	60.930	29.470	42.291	4.856	42.291
3400	10.072	69.889	61.182	30.476	44.181	5.107	44.181
3500	10.104	70.173	61.428	31.485	46.064	5.356	46.064
3600	10.137	70.451	61.668	32.497	47.944	5.602	47.944
3700	10.169	70.723	61.903	33.512	49.819	5.846	49.819
3800	10.202	70.986	62.132	34.528	51.690	6.088	51.690
3900	10.234	71.245	62.357	35.552	53.558	6.329	53.558
4000	10.267	71.498	62.576	36.577	55.424	6.569	55.424
4100	10.299	71.746	62.792	37.606	57.288	6.808	57.288
4200	10.332	71.988	63.003	38.637	59.150	7.046	59.150
4300	10.364	72.225	63.203	39.669	61.009	7.283	61.009
4400	10.396	72.459	63.413	40.710	62.865	7.519	62.865
4500	10.429	72.688	63.612	41.751	64.719	7.754	64.719
4600	10.461	72.913	63.807	42.796	66.572	7.988	66.572
4700	10.493	73.134	63.998	43.844	68.424	8.221	68.424
4800	10.526	73.350	64.188	44.894	70.275	8.453	70.275
4900	10.559	73.563	64.373	45.949	72.126	8.685	72.126
5000	10.591	73.773	64.556	47.006	73.977	8.917	73.977
5100	10.623	73.979	64.735	48.067	75.828	9.149	75.828
5200	10.655	74.184	64.910	49.132	77.679	9.381	77.679
5300	10.687	74.388	65.083	50.198	79.530	9.613	79.530
5400	10.719	74.581	65.255	51.264	81.381	9.845	81.381
5500	10.751	74.771	65.424	52.342	83.232	10.077	83.232
5600	10.783	74.959	65.599	53.419	85.083	10.309	85.083
5700	10.815	75.146	65.773	54.496	86.934	10.541	86.934
5800	10.847	75.333	65.946	55.573	88.785	10.773	88.785
5900	10.879	75.517	66.117	56.650	90.636	11.005	90.636
6000	10.911	75.699	66.288	57.727	92.487	11.237	92.487

LITHIUM, DIATOMIC (Li_2)

(IDEAL GAS)

MOL. WT. = 13.880

$\Delta H_f^0 = 50.298 \text{ kcal. mole}^{-1}$
Ground State Configuration Σ^+
 $\Delta H_f^0 = 50.298 \text{ kcal. mole}^{-1}$
 $S_{298.15}^0 = 47.050 \text{ cal. deg. mole}^{-1}$

$\omega_e = 353.59 \text{ cm}^{-1}$
 $\omega_e x_e = 2.625 \text{ cm}^{-1}$
 $\alpha_e = 0.00718 \text{ cm}^{-1}$
 $r_e = 2.673 \text{ \AA}$
 $d = 2$

Heat of Formation.
Same as the heat of sublimation to the diatomic gas; see notes on Li (crystal).

Heat Capacity and Entropy.

The spectroscopic constants of Li_2 listed by G. Herzberg, "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Co., Inc., New York (1950) have been corrected for the presence of 7.5% Li^6 in naturally occurring lithium, J. R. Stehn and E. P. Clancy, "Chart of the Nuclides", General Electric Co., Schenectady (1956).

$$\Delta H_f^\circ = 9.056 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^\circ = -143.1 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^\circ = 14 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^\circ = 9.056 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 1843^\circ \text{K.}$$

Dilithium Monoxide (Li₂O)

(Crystal) Mol. Wt. = 29.880

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	0.000	0.000	INFINITE	-1.732	-141.585	-139.774	INFINITE
100	2.497	8.868	17.547	-1.668	-142.115	-139.774	305.461
200	6.892	4.680	10.125	-1.089	-142.756	-137.172	149.687
298	12.927	9.056	9.056	0.000	-143.100	-134.348	98.475
300	12.997	9.136	9.056	-0.24	-143.105	-134.294	97.829
400	15.297	13.221	9.497	1.449	-143.277	-131.528	71.751
500	16.630	16.766	10.687	3.050	-144.678	-128.175	56.023
600	17.644	19.905	11.969	4.762	-144.969	-124.824	45.465
700	18.500	22.091	13.105	6.470	-144.950	-121.456	37.922
800	19.240	23.518	14.083	8.178	-144.874	-118.073	31.922
900	19.840	24.518	14.943	9.846	-144.749	-114.679	27.673
1000	20.405	25.654	17.209	12.448	-144.440	-111.480	24.363
1100	21.225	31.648	18.432	14.538	-144.143	-108.198	21.496
1200	21.900	33.519	19.612	16.689	-143.792	-104.746	19.102
1300	22.475	35.049	20.748	18.800	-143.400	-101.230	16.981
1400	22.975	36.549	21.848	21.141	-142.962	-97.556	15.381
1500	23.400	38.025	22.908	23.426	-142.489	-93.782	13.896
1600	23.760	40.018	23.931	25.739	-141.947	-89.908	12.601
1700	24.060	41.435	24.919	28.077	-141.354	-85.944	11.422
1800	24.310	42.976	25.763	30.450	-140.710	-81.890	10.350
1900	24.530	44.636	26.570	32.860	-140.020	-77.740	9.371
2000	24.740	46.316	27.484	35.244	-139.280	-73.499	8.469
2100	24.947	48.004	28.562	37.678	-138.500	-69.166	7.635
2200	25.140	49.692	29.403	40.153	-137.660	-64.740	6.865
2300	25.320	51.380	30.115	42.670	-136.770	-60.220	6.150
2400	25.485	53.068	30.705	45.104	-135.830	-55.610	5.485
2500	25.640	54.756	31.187	47.461	-134.840	-50.910	4.870
2600	25.785	56.444	31.559	50.154	-133.800	-46.120	4.305
2700	25.920	58.132	31.821	52.708	-132.710	-41.250	3.790
2800	26.045	59.820	32.073	55.162	-131.570	-36.300	3.325
2900	26.160	61.508	32.315	57.467	-130.380	-31.270	2.910
3000	26.265	63.196	32.547	60.482	-129.140	-26.180	2.545

Dec. 31, 1960; Mar. 31, 1964

Heat of Formation.

The selected heat of formation was calculated as follows:

Reaction	ΔH _f ° 298.15 kcal. mole ⁻¹	Ref.
(I) Li ₂ O(c) + H ₂ O(l) = 2LiOH(∞H ₂ O)	-31.74 ± 0.08	(a)
(II) Li(c) + 1/2 O ₂ (g) = LiOH(∞H ₂ O)	-121.572 ± 0.019	(b)
(III) H ₂ (g) + 1/2 O ₂ (g) = H ₂ O(l)	-68.3174	(c)
(IV) 2Li(c) + 1/2 O ₂ (g) = Li ₂ O(c)	-143.1 ± 0.5	(d)
(a) V. F. Kolesov, S. M. Skuratov, and I. D. Zaklin, <i>Russian J. Inorganic Chemistry</i> , 3 , 558 (1959).		
(b) S. R. Gunn and L. G. Green, <i>J. Am. Chem. Soc.</i> , 80 , 4782 (1958).		
(c) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties" National Bureau of Standards Circular 500, 1952 (reprinted 1961).		
(d) Reaction (IV) is the sum of -(I) + 2(II) - (III).		

Kolesov, et al. (loc. cit.) measured the enthalpy of the reaction of Li₂O with water at 20° in 5 experiments.

The mean ΔH_f° was -31.41 ± 0.08 kcal. This was brought to 298°K by Kolesov using enthalpy data of (a) H. L. Johnston and T. W. Bauer, *J. Am. Chem. Soc.*, **73**, 1119 (1951), for Li₂O, (b) N. S. Osborne, J. F. Stinson, and D. C. Ginnings, *J. Res. Natl. Bur. Stems*, **A**, **23**, 197 (1959) for H₂O, (c) F. T. Quaker and K. N. Schmarke, *J. Am. Chem. Soc.*, **55**, 1013 (1933) for C_p of LiOH(aq) and (d) Rossini, et al., (loc. cit.) for aqueous LiOH. In addition to the above, N. N. Beketov, *Bull. Acad. Sci. Russ. Ser. 32, 186 (1888) and H. R. Forrester, *Compt Rend.*, **144**, 1403 (1907) have reported experimental heats for Li₂O. Rossini et al. and Johnston and Bauer have reported heats of formation for Li₂O recalculated from older data. L. G. Panolino, in a Natl. Research Corp. Quarterly Report, July 1 to Sept. 30, 1962, reported a ΔH_f° 298 of -141.1 ± 4.2 kcal. He measured the heat of combustion of Li(c) in O₂(g) in a Parr bomb.*

Heat Capacity and Entropy.

The low temperature C_p data of H. L. Johnston and T. W. Bauer, (loc. cit.) from [17° -298°K.] was joined graphically to the high temperature C_p data of C. H. Shomate and A. J. Cohen, *J. Am. Chem. Soc.*, **77**, 285 (1955) [425°-1045°K.] and E. N. Rodgina, and K. A. Gomelakli, *Russian J. Phys. Chem.*, **35**, 898 (1961) [370°-1125°K.]. The S°_{298.15} was reported by Johnston and Bauer using S°₁₆ (extrap.) = 0.003 cal. deg.⁻¹ mole⁻¹.

Melting Data.

The melting point of Li₂O is uncertain. The selected melting point, 1843°K., was measured by A. E. van Arkel, E. A. Flood, and N. F. H. Bright, *Can. J. Chem.*, **31**, 1009 (1953). L. Brewer and J. L. Margrave, *J. Phys. Chem.*, **59**, 421 (1955) reported the melting point 1700°K. They also stated that H. van Konster and F. Jaeger, *Proc. Roy. Acad. Sci., Amsterdam*, **16**, 857 (1914) had reported 1700° (1973°K) as the melting point. The heat of melting, [14] kcal. mole⁻¹, was estimated by A. Glaesner, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K.", Argonne National Laboratory, University of Chicago, ANL-5750, 1957.

Heat of Sublimation.

Li₂O(c) vaporizes to Li₂O(g), LiO(g), Li₂O₂(g), Li(g), and O₂(g) [J. Berkhovitz, W. A. Chupka, G. D. Blue and J. L. Margrave, *J. Phys. Chem.*, **63**, 644 (1959); D. White, K. S. Sehadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, *J. Chem. Phys.*, **39**, 2465 (1963); D. L. Hildenbrand, W. F. Hall, and N. D. Potter, *J. Chem. Phys.*, **39**, 296 (1963); D. L. Hildenbrand, L. P. Theard, W. F. Hall, and N. D. Potter, Fifth Quarterly Technical Report, U-2289, Aeronutronic Division of Philco Corporation, 15 September 1963; L. P. Firsova and A. N. Nesmeyanov, *Russian J. Phys. Chem.*, **34**, 1232 (1960)]. The major species (0°-1700°K.) are reported to be Li₂O(g), Li(g), and O₂(g) with lesser amounts of LiO(g) and Li₂O₂(g). Hildenbrand, et al., U-2289, have reported about equal amounts of Li₂O⁺ and Li⁺ (1300 to 1550°K.) and about 1/30th of this amount of LiO⁺. White, et al., calculated ΔH_{sub} from their mass spectra data. They made two different calculations (a) for Li₂O(c) → Li₂O(g) and (b) for Li₂O(g) → 2Li(g) + 1/2 O₂(g), and found (a) 102.5 kcal. and (b) 99.0 kcal. They used a weighted average of (a) and (b) and obtained 101.6 kcal. at 0°K. The selected ΔH_{sub}° 298 of 102.5 ± 3 kcal. was obtained in the same manner using their data and the present JANAF functions, 1.e. (a) 104.2 kcal. and (b) 100.3 kcal. Knudsen-effusion data of White et al., corrected for dissociation pressure with JANAF values gives Li₂O pressures slightly different than those reported. The recalculated pressures give a 3rd law ΔH_{sub}° 298 of 101.7 kcal. for both cells. The corresponding 2nd law values are 85 and 95.5 kcal. for cell 7 and 8. The 3rd law treatment of both sets of data show relatively large trends of ΔH_{sub} with T which are probably too large to be only due to errors in the functions. (Continued on Lithium Oxide Li₂O(g) table)

Dilithium Monoxide (Li₂O)

(Liquid) Mol. Wt. = 29.880

Li₂O

(LIQUID) MOL. WT. = 29.880

DILITHIUM MONOXIDE (Li₂O)

Log K_p

T, °K. C_p° - (F° - H₂₉₈°)/T kcal. mole⁻¹ ΔH_f° ΔF_f°

T, °K.	C _p °	S° - (F° - H ₂₉₈ °)/T	kcal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0						
100						
200	12.927	13.160	0.000	-132.129	-124.601	91.930
300	12.927	13.160	0.024	-132.134	-124.555	90.734
400	12.927	13.160	0.047	-132.138	-124.508	89.538
500	16.630	20.880	3.066	-131.411	-114.255	85.124
600	24.000	24.006	16.069	-131.098	-114.313	82.365
700	24.000	27.706	17.162	-131.387	-113.416	80.408
800	24.000	31.411	18.058	-132.770	-110.805	80.214
900	24.000	35.116	18.743	-134.152	-108.194	80.020
1000	24.000	38.821	19.428	-135.532	-105.583	79.826
1100	24.000	42.526	20.113	-136.912	-102.972	79.632
1200	24.000	46.231	20.798	-138.292	-100.361	79.438
1300	24.000	49.936	21.483	-139.672	-97.750	79.244
1400	24.000	53.641	22.168	-141.052	-95.139	79.050
1500	24.000	57.346	22.853	-142.432	-92.528	78.856
1600	24.000	61.051	23.538	-143.812	-89.917	78.662
1700	24.000	64.756	24.223	-145.192	-87.306	78.468
1800	24.000	68.461	24.908	-146.572	-84.695	78.274
1900	24.000	72.166	25.593	-147.952	-82.084	78.080
2000	24.000	75.871	26.278	-149.332	-79.473	77.886
2100	24.000	79.576	26.963	-150.712	-76.862	77.692
2200	24.000	83.281	27.648	-152.092	-74.251	77.498
2300	24.000	86.986	28.333	-153.472	-71.640	77.304
2400	24.000	90.691	29.018	-154.852	-69.029	77.110
2500	24.000	94.396	29.703	-156.232	-66.418	76.916
2600	24.000	98.101	30.388	-157.612	-63.807	76.722
2700	24.000	101.806	31.073	-158.992	-61.196	76.528
2800	24.000	105.511	31.758	-160.372	-58.585	76.334
2900	24.000	109.216	32.443	-161.752	-55.974	76.140
3000	24.000	112.921	33.128	-163.132	-53.363	75.946
3100	24.000	116.626	33.813	-164.512	-50.752	75.752
3200	24.000	120.331	34.498	-165.892	-48.141	75.558
3300	24.000	124.036	35.183	-167.272	-45.530	75.364
3400	24.000	127.741	35.868	-168.652	-42.919	75.170
3500	24.000	131.446	36.553	-169.992	-40.308	74.976
3600	24.000	135.151	37.238	-171.372	-37.697	74.782
3700	24.000	138.856	37.923	-172.752	-35.086	74.588
3800	24.000	142.561	38.608	-174.132	-32.475	74.394
3900	24.000	146.266	39.293	-175.512	-29.864	74.200
4000	24.000	149.971	39.978	-176.892	-27.253	74.006

S_{298.15} = 13.160 cal. deg.⁻¹ mole⁻¹
 ΔH_f° 298.15 = -132.129 kcal. mole⁻¹
 ΔH_m° = [14] kcal. mole⁻¹
 ΔH_v° = Unknown

T_m = 1843°K.

T_b = [2838°K.]

Heat of Formation.

ΔH_f° (l) was obtained from ΔH_f° (c) by adding ΔH_m and the difference between H₁₈₄₃-H₂₉₈ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated at 8 cal. deg.⁻¹ g. atom⁻¹ from comparisons with similar compounds and from Kopp's rule. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See melting data given on the Li₂O crystal table.

Vaporization Data.

The vapor over Li₂O(c) at 1700°K. is composed of Li₂O(g), Li(g), O₂(g), LiO(g), and Li₂O₂(g). Thus a boiling point becomes almost meaningless. The value, 2836°K. listed above is the temperature at which the free energy of Li₂O(g) and the free energy of Li₂O(l) are equal. L. Brewer, Chem. Rev. 52, (1953) estimated a boiling point of 2600°K.

Li₂O

Dilithium Monoxide (Li₂O)

(Ideal Gas) Mol. Wt. = 29.880

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	0.000	0.000	INFINITE	-2.584	-39.636	-39.636	INFINITE
100	0.825	42.987	64.663	2.116	-39.613	-41.284	-40.221	97.101
200	10.946	50.184	55.790	1.121	-39.688	-43.105	-44.767	32.633
298	11.893	54.732	54.732	+0.00	-39.600	-44.767	-44.767	32.633
300	11.910	54.806	54.733	+0.22	-39.606	-44.797	-44.797	32.633
400	12.287	58.256	54.733	1.125	-39.636	-46.535	-46.535	20.849
500	13.287	61.250	56.137	2.557	-42.171	-47.700	-47.700	17.761
600	13.682	63.710	57.199	3.907	-42.624	-48.762	-48.762	15.533
700	13.957	65.841	58.285	5.289	-43.031	-49.754	-49.754	13.847
800	14.152	67.718	59.369	6.694	-43.408	-50.689	-50.689	12.457
900	14.288	69.384	60.453	8.125	-43.754	-51.577	-51.577	11.457
1000	14.401	70.905	61.562	9.593	-44.133	-52.424	-52.424	10.576
1100	14.483	72.282	62.984	10.997	-44.484	-53.236	-53.236	9.837
1200	14.547	73.545	63.171	12.469	-44.832	-54.017	-54.017	9.207
1300	14.598	74.701	63.319	13.906	-45.175	-54.769	-54.769	8.687
1400	14.638	75.791	63.437	15.306	-45.513	-55.493	-55.493	8.187
1500	14.671	76.806	63.543	16.684	-45.851	-56.192	-56.192	7.768
1600	14.698	77.753	63.645	18.042	-46.184	-56.872	-56.872	7.054
1700	14.721	78.645	63.741	19.373	-46.508	-57.535	-57.535	6.221
1800	14.740	79.487	63.834	20.684	-46.824	-58.181	-58.181	5.476
1900	14.756	80.284	63.924	21.971	-47.131	-58.812	-58.812	4.806
2000	14.771	81.036	64.010	23.245	-47.426	-59.426	-59.426	4.200
2100	14.783	81.763	64.093	24.507	-47.715	-60.023	-60.023	3.669
2200	14.794	82.451	64.171	25.756	-48.000	-60.603	-60.603	3.147
2300	14.803	83.109	64.245	26.994	-48.281	-61.166	-61.166	2.650
2400	14.811	83.744	64.314	28.221	-48.558	-61.714	-61.714	2.181
2500	14.818	84.344	64.379	29.439	-48.831	-62.246	-62.246	1.870
2600	14.825	84.925	64.442	30.648	-49.100	-62.763	-62.763	1.508
2700	14.830	85.485	64.501	31.844	-49.364	-63.266	-63.266	1.171
2800	14.836	86.024	64.551	33.024	-49.624	-63.754	-63.754	0.858
2900	14.840	86.545	64.604	34.191	-49.879	-64.226	-64.226	0.565
3000	14.844	87.048	64.654	35.345	-50.129	-64.681	-64.681	0.291
3100	14.848	87.535	64.701	36.487	-50.375	-65.118	-65.118	0.035
3200	14.852	88.006	64.745	37.617	-50.617	-65.549	-65.549	+0.206
3300	14.855	88.463	64.785	38.734	-50.853	-65.966	-65.966	+0.434
3400	14.858	88.907	64.821	39.839	-51.084	-66.369	-66.369	+0.648
3500	14.860	89.337	64.854	40.934	-51.311	-66.758	-66.758	+0.851
3600	14.863	89.756	64.884	42.019	-51.534	-67.134	-67.134	+1.043
3700	14.865	90.163	64.911	43.094	-51.753	-67.497	-67.497	+1.225
3800	14.867	90.560	64.934	44.159	-51.968	-67.847	-67.847	+1.398
3900	14.869	90.946	64.954	45.214	-52.179	-68.184	-68.184	+1.562
4000	14.871	91.322	64.971	46.259	-52.385	-68.509	-68.509	+1.719
4100	14.872	91.690	64.987	47.295	-52.589	-68.824	-68.824	+1.868
4200	14.874	92.048	64.999	48.321	-52.789	-69.129	-69.129	+2.011
4300	14.875	92.398	65.009	49.339	-52.984	-69.424	-69.424	+2.147
4400	14.876	92.740	65.014	50.349	-53.175	-69.709	-69.709	+2.278
4500	14.878	93.074	65.019	51.350	-53.361	-70.000	-70.000	+2.403
4600	14.879	93.401	65.024	52.344	-53.544	-70.286	-70.286	+2.524
4700	14.880	93.721	65.029	53.331	-53.724	-70.566	-70.566	+2.639
4800	14.881	94.035	65.034	54.311	-53.900	-70.841	-70.841	+2.750
4900	14.882	94.341	65.039	55.284	-54.074	-71.111	-71.111	+2.857
5000	14.883	94.642	65.044	56.250	-54.244	-71.376	-71.376	+2.961
5100	14.884	94.937	65.049	57.209	-54.411	-71.637	-71.637	+3.060
5200	14.884	95.226	65.054	58.161	-54.574	-71.894	-71.894	+3.156
5300	14.885	95.509	65.059	59.107	-54.734	-72.146	-72.146	+3.249
5400	14.886	95.788	65.064	60.047	-54.891	-72.394	-72.394	+3.339
5500	14.886	96.061	65.069	60.981	-55.044	-72.637	-72.637	+3.426
5600	14.887	96.329	65.074	61.909	-55.194	-72.876	-72.876	+3.511
5700	14.888	96.593	65.079	62.831	-55.341	-73.111	-73.111	+3.593
5800	14.888	96.851	65.084	63.747	-55.484	-73.344	-73.344	+3.673
5900	14.889	97.106	65.089	64.658	-55.624	-73.574	-73.574	+3.750
6000	14.889	97.356	65.094	65.564	-55.761	-73.800	-73.800	+3.824

Dec. 31, 1960 Mar. 31, 1964

DILITHIUM MONOXIDE (Li₂O) (IDEAL GAS)

MOL. WT. = 29.880

Point Group P_{∞h}

ΔH_f^o = -39.6 ± 2.5 kcal. mole⁻¹

ΔH_f^o 298.15 = -39.9 ± 2.5 kcal. mole⁻¹

S^o 298.15 = 54.732 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	
[760] (1)	
[140] (2)	
987 (1)	

σ = 2

Bond Distances: Li-O = [1.59] Å

Bond Angle: Li-O-Li = 180°

Rotational Constant: B₀ = 0.46045 cm.⁻¹

Heat of Formation.

The heat of formation was calculated from the heat of formation of the crystal and the heat of sublimation.

Heat Capacity and Entropy.

D. White, K. S. Seshairi, and D. P. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. 39, 2463 (1963) made an estimate of the bond distance Li-O = 1.59 Å based on an analysis of their vibrational spectra. They found that Li₂O was a linear molecule. A. Buchler and J. L. Stauffer, J. Chem. Phys. 39, 2299 (1963) have shown from electric deflection experiments that Li₂O is very probably linear. They also report from the results of an effusion experiment evidence that the electron diffraction data and Li-O bond distance, 1.82 Å reported by F. A. Akishin and N. G. Rambidi, Dokl. Akad. Nauk. SSSR 118, 973 (1958) [English Translation, Proc. Acad. Sci. USSR, Phys. Chem. Sect. 118, 83 (1958)] are for Mo-O in Li₂MoO₄ rather than for Li-O in Li₂O. Buchler and Stauffer (loc. cit.) estimate an Li-O distance of 1.55 Å. White, et al., (loc. cit.) have estimated the vibrational frequencies ν₁ = [760] cm.⁻¹ and ν₂ = [140] cm.⁻¹ and assigned ν₃ = 987 cm.⁻¹ from their infrared matrix spectra. The principal moments of inertia calculated from the molecular constants are: I_A = 0, and I_B = I_C = 5.8256 X 10⁻³⁹ g. cm.².

Heat of Sublimation (continued from Li₂O(c) table).

A sample of LiAlO₂ was melted 7 times in argon in an arc-image furnace, H. Prophet, "Melting Point of Lithium Aluminate", ARPA-1-150, Dow Chemical Co., Mar. 9, 1961. The sample decomposed on fusion and successive melting points approached that of Al₂O₃. The residue was found to be 95% Al₂O₃ and 5% LiAl₂O₆. The sample and residue were characterized by X-ray diffraction. A reasonable assumption from this is that ΔF₂(3000°K) = 0 for 2LiAlO₂(c) = Al₂O₃(c) + Li₂O(g). From this ΔF₂, a ΔH_f^o 298 for Li₂O of 50 kcal. was calculated. A vapor pressure study of the molecular species over the decomposing LiAlO₂ might help resolve the discrepancies in lithium oxide ΔH_f^o values.

Li₂O

Lithium Dioxide (Li_2O_2)
(Crystal) Mol. Wt. = 45.880



MOL. WT. = 45.880

(CRYSTAL)

LITHIUM DIOXIDE (Li_2O_2)

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
100							
200							
298	16.880	13.500		+0.00	-151.200	-136.468	100.029
300	16.920	13.505		+0.31	-151.204	-136.377	99.346
400	19.760	14.911	14.205	1.883	-151.305	-131.414	71.798
500	21.700	17.536	15.618	3.659	-152.796	-126.288	55.198
600	23.200	19.438	17.286	5.211	-152.795	-120.930	44.269
700	24.700	21.336	19.093	6.612	-152.502	-115.719	36.127
800	26.070	23.236	20.786	11.152	-152.164	-110.487	30.182
900	27.350	25.136	22.512	13.824	-151.668	-105.307	25.571
1000	28.610	27.036	24.196	16.622	-151.077	-100.185	21.894
1100	29.850	28.936	25.835	19.565	-150.369	-95.130	18.600
1200	31.070	30.836	27.627	22.591	-149.567	-90.144	15.617
1300	32.261	32.736	29.473	25.758	-148.604	-85.232	12.828
1400	33.438	34.636	31.356	29.063	-147.558	-80.365	10.250
1500	34.600	36.536	33.238	32.445	-146.393	-75.638	7.692
1600	35.748	38.436	35.120	35.902	-145.115	-70.960	5.190
1700	36.883	40.336	37.002	39.594	-143.710	-63.712	2.669
1800	38.003	42.236	38.884	43.438	-142.196	-54.932	0.119
1900	39.108	44.136	40.766	47.424	-140.571	-44.760	
2000	40.200	46.036	42.648	51.559	-138.846	-33.699	

June 30, 1963; Sept. 30, 1963

ΔH_f° = Unknown

ΔH_f° 298.15 = -151.2 ± 2.0 kcal. mole⁻¹

S° 298.15 = [13.5 ± 1.0] cal. deg⁻¹ mole⁻¹

T_d = 468°K.

Heat of Formation.

ΔH_f° 298.15 was reported by R. de Forcrand, Compt. rend. 130, 1465 (1900), based on the measured heats of the reactions of $\text{Li}_2\text{O}_2(\text{c})$ with $\text{HCl}(\text{aq.})$ and $\text{LiOH}(\text{aq.})$ with $\text{H}_2\text{O}_2(\text{aq.})$.

Heat Capacity and Entropy.

Both C_p and S°_{298.15} were estimated by comparison with those of the $\text{Na}_2\text{O}_2(\text{c})$, respectively.

Temperature of Decomposition.

T_d was reported to be about 300°C. by N. M. Wiederhorn, N. F. Surprenant, and A. J. Lefrier, "Research on New Methods of Separation of Air into O₂ and N₂ Components," C-53825, First-Quarterly Progress Report, September 1961, Arthur D. Little, Inc. The value adopted was reported by Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use", June, 1949, obtained from M. Centnerzwer and M. Blumenthal, Bull. intern. acad. polonaise, Classe. sci. math. nat., A 499 (1933).



Lithium Dioxide (Li₂O₂)
(Ideal Gas) Mol. Wt. = 45.880

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f	ΔF _f	Log K _p
0	∞	∞	∞	∞	∞	∞
100	10.45	49.4	79.212	57.504	58.403	126.935
200	11.28	58.0	158.424	57.600	58.493	126.935
298	11.383	65.357	249.000	58.400	58.729	4.698
300	17.409	65.465	250.000	58.400	58.729	4.698
400	18.378	70.622	349.000	58.400	58.729	4.698
500	18.880	74.783	449.000	58.400	58.729	4.698
600	19.169	78.253	549.000	58.400	58.729	4.698
700	19.349	81.223	649.000	58.400	58.729	4.698
800	19.469	83.615	749.000	58.400	58.729	4.698
900	19.552	85.113	849.000	58.400	58.729	4.698
1000	19.611	86.117	949.000	58.400	58.729	4.698
1100	19.656	86.747	1049.000	58.400	58.729	4.698
1200	19.690	87.139	1149.000	58.400	58.729	4.698
1300	19.717	87.336	1249.000	58.400	58.729	4.698
1400	19.738	87.478	1349.000	58.400	58.729	4.698
1500	19.755	87.561	1449.000	58.400	58.729	4.698
1600	19.770	87.603	1549.000	58.400	58.729	4.698
1700	19.781	87.635	1649.000	58.400	58.729	4.698
1800	19.791	87.666	1749.000	58.400	58.729	4.698
1900	19.799	87.696	1849.000	58.400	58.729	4.698
2000	19.806	87.724	1949.000	58.400	58.729	4.698
2100	19.813	87.750	2049.000	58.400	58.729	4.698
2200	19.818	87.774	2149.000	58.400	58.729	4.698
2300	19.823	87.796	2249.000	58.400	58.729	4.698
2400	19.827	87.816	2349.000	58.400	58.729	4.698
2500	19.830	87.834	2449.000	58.400	58.729	4.698
2600	19.833	87.850	2549.000	58.400	58.729	4.698
2700	19.836	87.864	2649.000	58.400	58.729	4.698
2800	19.839	87.877	2749.000	58.400	58.729	4.698
2900	19.841	87.889	2849.000	58.400	58.729	4.698
3000	19.843	87.900	2949.000	58.400	58.729	4.698
3100	19.845	87.910	3049.000	58.400	58.729	4.698
3200	19.847	87.919	3149.000	58.400	58.729	4.698
3300	19.848	87.927	3249.000	58.400	58.729	4.698
3400	19.850	87.934	3349.000	58.400	58.729	4.698
3500	19.851	87.940	3449.000	58.400	58.729	4.698
3600	19.852	87.945	3549.000	58.400	58.729	4.698
3700	19.853	87.949	3649.000	58.400	58.729	4.698
3800	19.854	87.953	3749.000	58.400	58.729	4.698
3900	19.855	87.956	3849.000	58.400	58.729	4.698
4000	19.856	87.959	3949.000	58.400	58.729	4.698
4100	19.857	87.961	4049.000	58.400	58.729	4.698
4200	19.858	87.963	4149.000	58.400	58.729	4.698
4300	19.859	87.965	4249.000	58.400	58.729	4.698
4400	19.860	87.967	4349.000	58.400	58.729	4.698
4500	19.861	87.969	4449.000	58.400	58.729	4.698
4600	19.862	87.971	4549.000	58.400	58.729	4.698
4700	19.863	87.973	4649.000	58.400	58.729	4.698
4800	19.864	87.975	4749.000	58.400	58.729	4.698
4900	19.865	87.977	4849.000	58.400	58.729	4.698
5000	19.866	87.979	4949.000	58.400	58.729	4.698
5100	19.867	87.981	5049.000	58.400	58.729	4.698
5200	19.868	87.983	5149.000	58.400	58.729	4.698
5300	19.869	87.985	5249.000	58.400	58.729	4.698
5400	19.870	87.987	5349.000	58.400	58.729	4.698
5500	19.871	87.989	5449.000	58.400	58.729	4.698
5600	19.872	87.991	5549.000	58.400	58.729	4.698
5700	19.873	87.993	5649.000	58.400	58.729	4.698
5800	19.874	87.995	5749.000	58.400	58.729	4.698
5900	19.875	87.997	5849.000	58.400	58.729	4.698
6000	19.876	87.999	5949.000	58.400	58.729	4.698

Mar. 31, 1964



MOL. WT. = 45.880

DILITHIUM DIOXIDE (Li₂O₂) (IDEAL GAS)

Point Group [D_{2h}]
 $\Delta H_f^0 = [-57.5 \pm 6] \text{ kcal. mole}^{-1}$
 $\Delta H_f^{298.15} = [-58.0 \pm 6] \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω cm. ⁻¹	ω cm. ⁻¹
[400] (1)	[270] (1)
[250] (1)	[330] (1)
[300] (1)	[530] (1)

Bond Distances Li-O = [1.90] Å

Bond Angle O-Li-O = [116]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.66304 \times 10^{-115}] \text{ g.}^3 \text{ cm.}^6$

σ = 4

Heat of Formation.

The heat of formation, -58 kcal., was calculated from an equilibrium constant for the reaction $\frac{1}{2} \text{O}_2(\text{g}) + \text{Li}_2\text{O}(\text{g}) \rightarrow \text{Li}_2\text{O}_2(\text{g})$ and the current JANAF functions. The equilibrium constant, 0.39, was estimated by D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2465 (1965), from their mass spectrometric data.

Heat Capacity and Entropy.

White, et al., (loc. cit.), from their spectral data have assigned two observed frequencies and estimated the remaining frequencies using the ionic model calculations of J. Berkowitz, J. Chem. Phys. **29**, 1386 (1958); **32**, 1519 (1960) as a guide. They proposed a planar rhombic structure of D_{2h} symmetry, similar to the alkali halide dimers, for the previously undetected Li₂O₂ molecule, and estimated the angle, 116°, and bond distance, 1.90 Å, from their matrix spectra. The principal moments calculated from these molecular constants are: $I_A = 13.793 \times 10^{-39}$, $I_B = 2.356 \times 10^{-39}$, and $I_C = 16.129 \times 10^{-39} \text{ g. cm.}^2$.



Lithium Metasilicate (Li_2SiO_3)
(Crystal) GFW = 89.9622

T, °K	Cp ^o	$\frac{\text{gibbs/mol}}{\text{S}^o}$	$-(\text{G}^o - \text{H}^o_{\text{298}})/\text{T}$	$\text{H}^o - \text{H}^o_{\text{298}}$	$\frac{\text{kcal/mol}}{\Delta \text{H}^o}$	ΔG^o	Log Kp
0	0.000	INFINITE		-3.479	-391.627	-391.627	INFINITE
100	6.513	2.934	35.600	-3.267	-392.758	-392.758	844.474
200	17.217	10.746	21.191	-2.086	-393.748	-393.748	934.548
298	24.936	18.191		-1.000	-394.750	-394.750	975.092
300	24.142	19.340	19.191	-0.845	-394.245	-372.424	271.311
400	28.800	26.919	20.196	-2.689	-392.417	-365.117	159.491
500	30.347	33.498	22.215	-5.642	-395.941	-357.635	150.322
600	32.100	39.209	24.592	-9.776	-395.933	-349.972	127.877
700	34.377	44.254	27.019	-12.051	-395.810	-342.121	106.877
800	36.520	48.788	29.479	-15.447	-395.595	-334.697	91.435
900	38.508	52.912	31.857	-18.930	-395.307	-327.099	79.430
1000	38.401	56.700	34.154	-22.546	-394.956	-319.534	69.635
1100	37.184	60.206	36.345	-26.224	-394.565	-312.015	61.992
1200	37.400	63.673	38.449	-29.980	-394.084	-304.538	55.463
1300	36.550	66.532	40.510	-33.603	-393.574	-297.092	49.946
1400	35.183	69.412	42.491	-37.690	-393.018	-289.620	45.223
1500	33.800	72.117	44.378	-41.639	-392.415	-282.131	41.136
1600	30.400	74.725	46.194	-45.602	-391.768	-275.012	37.565
1700	26.990	77.192	47.946	-49.719	-391.144	-268.274	34.065
1800	24.540	79.551	49.636	-53.846	-390.546	-262.756	30.699
1900	22.110	81.813	51.271	-58.030	-390.816	-257.498	27.676
2000	20.440	83.986	52.853	-62.268	-390.975	-252.525	24.972
2100	18.149	86.079	54.395	-66.537	-390.991	-247.505	22.532
2200	16.140	88.098	55.872	-70.897	-390.969	-242.546	20.320
2300	14.412	90.048	57.316	-75.295	-390.905	-237.549	18.306
2400	12.935	91.835	58.719	-79.719	-390.810	-232.519	16.465
2500	11.600	93.763	60.095	-84.197	-390.682	-227.462	14.777

Sept. 30, 1961; March 31, 1964; June 30, 1967

(CRYSTAL)

LITHIUM METASILICATE (Li_2SiO_3)

GFW = 89.9622



$\Delta \text{H}^o_{\text{f}} = -391.63 \pm 1.0 \text{ kcal/mol}$
 $\Delta \text{H}^o_{\text{f}} 298.15 = -394.24 \pm 1.0 \text{ kcal/mol}$
 $\Delta \text{H}^o = 6.7 \pm 0.5 \text{ kcal/mol}$

$S^o_{298.15} = 19.19 \pm 0.3 \text{ gibbs/mol}$

$T_m = 1474 \pm 1^\circ \text{K}$

Heat of Formation

The heats of solution of $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Li}_2\text{SiO}_3(\text{c})$ in 20 per cent hydrofluoric acid at 74.7°C were measured by F. C. Kresak, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). The authors derived two values of $\Delta \text{H}^o_{\text{f}}$ of $\text{Li}_2\text{O}(\text{c})$ from those of $\text{LiCl}(\text{c})$ and $\text{Li}_2\text{SO}_4(\text{c})$, presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate $\Delta \text{H}^o_{\text{f}}$ of $\text{Li}_2\text{O}(\text{c})$ as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal/mol (sulfate scheme, originally -60.86), using recent $\Delta \text{H}^o_{\text{f}}$ values for $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{HCl}(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and $\text{Li}_2\text{O}(\text{c})$. The corresponding enthalpy changes, $\Delta \text{H}^o_{\text{f}}$, for the reaction $\text{Li}_2\text{O}(\text{c}) + \text{SiO}_2(\text{quartz}) = \text{Li}_2\text{SiO}_3(\text{c})$ are derived as -33.08 and -34.17 kcal/mol. Adopting the weighted average $\Delta \text{H}^o_{\text{f}} 298 = -33.44$ kcal/mol with $\Delta \text{H}^o_{\text{f}} 298(\text{Li}_2\text{O}, \text{c}) = -143.1$ kcal/mol and $\Delta \text{H}^o_{\text{f}} 298(\text{SiO}_2, \text{quartz}) = -217.7$ kcal/mol, we obtain $\Delta \text{H}^o_{\text{f}} 298 = -394.24$ kcal/mol for $\text{Li}_2\text{SiO}_3(\text{c})$. This $\Delta \text{H}^o_{\text{f}} 298(\text{Li}_2\text{SiO}_3, \text{c})$ value is independent of future changes in $\Delta \text{H}^o_{\text{f}} 298$ of $\text{Li}_2\text{O}(\text{c})$ but the values of $\Delta \text{H}^o_{\text{f}}$ and ΔH^o are not independent.

The heats of solution of $\text{LiOH}(\text{c})$ and $\text{Li}_2\text{SiO}_3(\text{c})$ in 20 percent HF(aq) at 50°C were measured by W. E. Hatton, D. L. Hildenbrand, G. C. Sinke, and D. R. Stull, unpublished work, Thermal Laboratory, The Dow Chemical Co., Midland, Michigan, 1959. The Li_2SiO_3 sample was prepared from lithium carbonate and silica by fusion under vacuum at 1500°C . Analysis gave 66.74 percent SiO_2 and 15.12 percent Li . The corresponding calculated values are 66.79 and 15.43. Also present were 0.5 percent K and 0.06 percent Na. Corrections were made for impurities in the heat of formation measurements. The results are given as follows:

$2\text{LiOH}(\text{c}, 25^\circ \text{C}) + 2\text{HF}(\text{sol}, 50^\circ \text{C}) + 2\text{LiF}(\text{sol}, 50^\circ \text{C}) + 2\text{H}_2\text{O}(\text{sol}, 50^\circ \text{C})$
 $\text{SiO}_2(\text{c}, 25^\circ \text{C}) + 6\text{HF}(\text{sol}, 50^\circ \text{C}) + \text{H}_2\text{SiF}_6(\text{sol}, 50^\circ \text{C}) + 2\text{H}_2\text{O}(\text{sol}, 50^\circ \text{C})$
 $3\text{H}_2\text{O}(\text{sol}, 50^\circ \text{C}) + 2\text{LiF}(\text{sol}, 50^\circ \text{C}) + \text{H}_2\text{SiF}_6(\text{sol}, 50^\circ \text{C}) + \text{Li}_2\text{SiO}_3(\text{c}, 25^\circ \text{C}) + 8\text{HF}(\text{sol}, 50^\circ \text{C})$
 $\text{H}_2\text{O}(\text{sol}, 50^\circ \text{C}) + \text{H}_2\text{O}(\text{f}, 25^\circ \text{C})$
 $2\text{LiOH}(\text{c}, 25^\circ \text{C}) + \text{SiO}_2(\text{c}, 25^\circ \text{C}) + \text{Li}_2\text{SiO}_3(\text{c}, 25^\circ \text{C}) + \text{H}_2\text{O}(\text{f}, 25^\circ \text{C})$

The $\Delta \text{H}^o_{\text{f}} 298$ for the second reaction was determined by D. R. Torgeson and T. G. Sahama, J. Am. Chem. Soc. 70, 2156 (1948). Based on the calculated enthalpy change for the overall reaction, $\Delta \text{H}^o_{\text{f}} 298 = -13.14$ kcal/mol and $\Delta \text{H}^o_{\text{f}} 298 = -115.84$, -217.7 and -88.32 kcal/mol for $\text{LiOH}(\text{c})$, $\text{SiO}_2(\text{low quartz})$, and $\text{H}_2\text{O}(\text{f})$, respectively, we derived $\Delta \text{H}^o_{\text{f}} 298(\text{Li}_2\text{SiO}_3, \text{c}) = -394.21 \pm 1.0$ kcal/mol, which is in agreement with the adopted value.

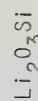
C. Kroger and E. Fingas, Z. Anorg. Allgem. Chem. 213, 12 (1933), measured the equilibrium pressure of CO_2 over a mixture of $\text{Li}_2\text{CO}_3(\text{c})$, $\text{SiO}_2(\text{quartz})$, and $\text{Li}_2\text{SiO}_3(\text{c})$ from 585 to 781°K . The enthalpy change ($\Delta \text{H}^o_{\text{f}} 298$) of the reaction $\text{Li}_2\text{CO}_3(\text{c}) + \text{SiO}_2(\text{c}) + \text{Li}_2\text{SiO}_3(\text{c}) + \text{CO}_2(\text{g})$ is evaluated by the second and third law methods to be 30.94 and 29.47 kcal/mol, respectively. Using $\Delta \text{H}^o_{\text{f}} 298 = -290.84$, -217.7 and -84.05 kcal/mol for $\text{Li}_2\text{CO}_3(\text{c})$, $\text{SiO}_2(\text{c})$ and $\text{CO}_2(\text{g})$, respectively, and third law $\Delta \text{H}^o_{\text{f}} 298$, we obtain $\Delta \text{H}^o_{\text{f}} 298(\text{Li}_2\text{SiO}_3, \text{c}) = -384.82 \pm 5$ kcal/mol, which is not used.

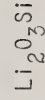
Heat Capacity and Entropy

The low temperature heat capacities, 25 - 340°K , were measured by Hatton et al., loc. cit., with an adiabatic vacuum calorimeter, using a nickel-plated copper sample container. During the filling and sealing of the calorimeter, the compound was handled in an anhydrous, CO_2 -free atmosphere so as to avoid contamination. The purity of the sample is not well established. The high temperature heat capacities are estimated by summation of the Cp's of the constituent oxides Li_2O and SiO_2 , and a subsequent correction based upon a comparison of the heat capacities of $\text{Na}_2\text{SiO}_3(\text{c})$ and its constituent oxides. These estimated Cp values are plotted, and the resulting curve is joined smoothly with the low temperature Cp curve at 298°K . The entropy, S^o_{298} , is derived using the measured low temperature heat capacities, based on $S^o_{25} = 0.023$ eu.

Melting Data

See $\text{Li}_2\text{SiO}_3(\text{l})$ table for details.





(Liquid) $\text{GFw} = 89.9622$

T, °K	C_p°	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(C_p^\circ - H_{298}^\circ)/T$	$\frac{\text{kcal/mol}}{H^\circ - H_{298}^\circ}$	ΔH°	ΔG°	Log Kp
0							
100							
200							
298	24.036	22.958	22.958	- .000	- 389.441	- 367.982	269.665
300	24.142	23.107	22.959	.045	- 389.447	- 367.755	267.910
400	28.400	30.686	23.663	2.689	- 388.618	- 360.825	197.146
500	30.547	37.285	25.982	5.642	- 390.142	- 353.719	154.611
600	32.100	42.676	28.349	8.776	- 390.134	- 346.423	126.188
700	33.520	47.525	31.246	12.076	- 389.031	- 339.030	100.890
800	34.520	52.555	33.246	15.497	- 389.726	- 331.911	90.674
900	35.508	56.679	35.624	18.920	- 389.508	- 324.516	78.846
1000	40.000	60.467	37.921	22.546	- 389.157	- 317.506	69.391
1100	40.000	64.280	40.147	26.546	- 389.426	- 310.377	61.666
1200	40.000	67.992	42.385	30.546	- 387.714	- 303.409	54.614
1300	40.000	71.692	44.585	34.546	- 387.032	- 296.339	48.614
1400	40.000	75.385	46.746	38.546	- 386.363	- 289.355	42.170
1500	40.000	79.078	48.872	42.546	- 385.710	- 282.449	35.153
1600	40.000	82.767	50.976	46.546	- 385.073	- 275.593	27.693
1700	40.000	86.456	53.052	50.546	- 384.451	- 268.788	20.207
1800	40.000	90.145	55.117	54.546	- 383.845	- 262.032	12.707
1900	40.000	93.834	57.162	58.546	- 383.255	- 255.326	5.207
2000	40.000	97.523	59.187	62.546	- 382.680	- 248.670	2.707
2100	40.000	101.212	61.192	66.546	- 382.120	- 242.064	0.207
2200	40.000	104.901	63.187	70.546	- 381.575	- 235.508	
2300	40.000	108.590	65.172	74.546	- 381.045	- 229.002	
2400	40.000	112.279	67.147	78.546	- 380.529	- 222.546	
2500	40.000	115.968	69.112	82.546	- 380.027	- 216.140	
2600	40.000	119.657	71.067	86.546	- 379.539	- 209.784	
2700	40.000	123.346	73.002	90.546	- 379.064	- 203.478	
2800	40.000	127.035	74.917	94.546	- 378.603	- 197.222	
2900	40.000	130.724	76.812	98.546	- 378.156	- 191.016	
3000	40.000	134.413	78.687	102.546	- 377.724	- 184.860	
3100	40.000	138.102	80.542	106.546	- 377.306	- 178.754	
3200	40.000	141.791	82.377	110.546	- 376.902	- 172.698	
3300	40.000	145.480	84.192	114.546	- 376.512	- 166.692	
3400	40.000	149.169	86.003	118.546	- 376.135	- 160.736	
3500	40.000	152.858	87.794	122.546	- 375.772	- 154.830	
3600	40.000	156.547	89.565	126.546	- 375.423	- 148.974	
3700	40.000	160.236	91.316	130.546	- 375.088	- 143.168	
3800	40.000	163.925	93.047	134.546	- 374.767	- 137.412	
3900	40.000	167.614	94.758	138.546	- 374.460	- 131.706	
4000	40.000	171.303	96.449	142.546	- 374.167	- 126.050	

LITHIUM METASILICATE (Li_2SiO_3) (LIQUID)

$S_{298.15}^\circ = 22.958$ gibbs/mol

$\Delta H_{298.15}^\circ = -389.441$ kcal/mol

$\Delta H_m^\circ = 6.7 \pm 0.5$ kcal/mol

$T_m = 1474 \pm 1^\circ\text{K}$

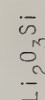
Heat of Formation
 $\Delta H_{298}^\circ(t)$ is obtained from $\Delta H_{298}^\circ(c)$ by adding ΔH_m° and the difference between H_{1474}° - H_{298}° for crystal and liquid.
 Tschernobaeff, Rev. Met. 21, 729 (1905), measured the heat of reaction between SiO_2 and Li_2CO_3 in a bomb calorimeter, using carbon as the auxiliary combustible material. Based on the derived $\Delta H_{298}^\circ = 24.99$ kcal/mol for the reaction $\text{Li}_2\text{CO}_3(c) + \text{SiO}_2(c) \rightarrow \text{Li}_2\text{SiO}_3(\text{gl}) + \text{CO}_2(g)$, the heat of formation for $\text{Li}_2\text{SiO}_3(\text{gl})$ is evaluated as -389.30 kcal/mol, which is in fair agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $\text{Na}_2\text{SiO}_3(l)$, $\text{Na}_2\text{O}(l)$ and $\text{Li}_2\text{O}(l)$. A glass transition is assumed at 1000°K; i.e., the heat capacities below 1000°K are taken to be the same as those for $\text{Li}_2\text{SiO}_3(c)$. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point has been reported as 1474 ± 1 and 1461°K by F. C. Kracek, J. Phys. Chem. 34, 2841 (1930), and H. S. Van Klooster, Z. Anorg. Chem. 89, 135 (1911), respectively. The value reported by Kracek is adopted.
 R. Schwarz and H. Sturm, Ber. 47, 1730 (1914), used a cooling-curve method to compare the heats of fusion of $\text{Li}_2\text{SiO}_3(c)$ and $\text{NaCl}(c)$. From the reported ratio, $\epsilon(\text{Li}_2\text{SiO}_3)/\epsilon(\text{NaCl}) = 0.261/0.402$, where ϵ = heat of fusion in kcal/g, and heat of fusion of $\text{NaCl}(c)$, the value $\Delta H_m^\circ = 6.7$ kcal/mol is derived.



Lithium Metatitanate (Li_2TiO_3)
(Crystal) Mol. Wt. = 109.780



MOL. WT. = 109.780

(CRYSTAL)

LITHIUM METATITANATE (Li_2TiO_3)

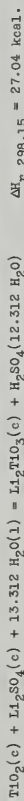
T, °K.	C _p	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f °	ΔF°	Log K _p
0	0.000	0.000	INFINITE	-3.942	-396.770	-396.770	INFINITE
100	7.443	3.377	40.417	-3.704	-397.073	-391.555	855.658
200	16.757	12.640	24.215	-2.315	-398.942	-384.682	420.352
298	26.256	21.930	21.930	0.000	-399.300	-377.591	276.768
300	26.470	22.093	21.931	-0.049	-399.304	-377.456	276.964
400	30.440	30.263	23.018	2.898	-399.383	-370.156	202.234
500	32.420	37.285	25.188	6.049	-400.814	-362.703	158.530
600	33.820	43.328	27.720	9.365	-400.729	-355.085	128.333
700	34.690	48.522	30.335	12.597	-400.554	-347.487	102.487
800	35.150	52.952	32.535	15.254	-400.354	-340.930	80.713
900	35.250	57.562	35.428	19.921	-400.053	-332.396	61.713
1000	35.780	61.409	37.816	23.573	-399.762	-324.893	51.002
1100	37.240	64.937	40.142	27.275	-399.448	-317.422	43.063
1200	37.560	68.134	42.346	31.018	-399.059	-309.984	36.775
1300	37.800	70.976	44.332	34.794	-398.584	-294.976	31.503
1400	38.120	74.032	46.605	38.594	-398.034	-284.976	26.603
1500	42.200	78.560	48.410	45.224	-396.227	-287.559	21.839
1600	43.000	81.309	50.481	49.484	-395.455	-280.337	18.290
1700	43.800	83.940	52.278	53.924	-394.713	-270.513	15.240
1800	44.500	86.399	53.976	57.744	-394.000	-257.864	12.740
1900	45.200	88.728	55.596	61.044	-393.316	-243.464	10.634
2000	46.200	91.248	57.986	67.324	-464.420	-236.470	9.169
2100	47.000	93.521	59.243	71.984	-462.916	-225.108	8.226
2200	47.800	95.566	60.452	76.724	-461.344	-213.850	7.440
2300	48.400	97.366	61.524	81.444	-459.716	-202.684	6.794
2400	49.400	99.954	63.916	86.444	-457.987	-191.464	6.264
2500	50.200	101.987	65.417	91.424	-456.207	-180.396	5.839
2600	51.000	103.971	66.862	96.484	-454.357	-169.403	5.439
2700	51.600	105.803	68.272	101.624	-452.462	-158.476	5.057
2800	52.000	107.403	69.554	106.844	-450.524	-147.624	4.697
2900	53.400	109.669	70.999	112.144	-448.442	-136.855	4.312
3000	54.200	111.493	72.318	117.524	-446.298	-126.136	3.919

June 30, 1961; Mar. 31, 1964

$\Delta H_f^\circ 0 = -396.8 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -399.3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 21.930 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -399.3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 2.75 \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = 26.33 \text{ kcal. mole}^{-1}$
 $T_m = 1820^\circ\text{K.}$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was calculated from measurements of solution calorimetry by S. S. Todd and K. K. Kelley, "Heat and Free Energy Data for Tricalcium Dittitanate, Spinel, Lithium Metatitanate and Zinc Titanium Spinel", U. S. Bureau Mines Report Invest. 5193 (1956), according to the following equation:



The $\Delta H_r^\circ 298.15$ value for rutile was obtained from the JANAF Tables and the other $\Delta H_f^\circ 298.15$ values were obtained from "Selected Values of Chemical Thermodynamic Properties" NBS Circular 500 (1952).

Heat Capacity and Entropy.

The low temperature heat capacities were taken from E. G. King, J. Am. Chem. Soc. 77, 2150 (1955). These low temperature heat capacities were fit to the high temperature heat contents from A. U. Christensen, K. C. Conway, and K. K. Kelley, "High Temperature Heat Contents and Entropies of Aluminates and Ferrites of Lithium, Sodium, and of Lithium Titanate", U. S. Bur. Mines Rept. Invest. 5565 (1960).

The $S_{298.15}^\circ = 21.9$ was obtained from E. G. King, loc. cit. based on the measured $S_{298.15}^\circ$ and the extrapolated S_{51}° - S_0° .

Transition Data.

A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit. reported that lithium metatitanate undergoes a transition from the α to the β form at $1,485^\circ\text{K.}$ with an absorption of $2.750 \text{ kcal. mole}^{-1}$.

Melting Data.

The T_m and ΔH_m° were obtained from A. U. Christensen, K. C. Conway, and K. K. Kelley, loc. cit.



Lithium Metatitanate (Li_2TiO_3)
(Liquid) Mol. Wt. = 109.780



LITHIUM METATITANATE (Li_2TiO_3) (LIQUID) MOL. WT. = 109.780

T, °K.	C_p	S°	$-\int_0^T (C_p - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0							
100	26.256	35.355	35.355	0.000	-374.374	-356.667	261.432
200	26.470	35.518	35.518	0.049	-374.378	-356.558	259.740
300	30.440	43.088	36.443	2.898	-374.457	-356.600	191.550
400	32.420	50.710	38.613	6.049	-375.868	-354.459	150.569
500	33.820	56.753	41.145	9.365	-375.803	-338.214	123.189
600	34.860	62.047	43.760	12.801	-375.428	-331.965	103.639
700	35.620	66.754	46.346	16.327	-375.393	-325.744	88.985
800	36.250	70.987	48.853	19.921	-375.127	-319.552	77.594
900	36.780	74.834	51.261	23.573	-374.836	-313.392	68.486
1000	37.240	78.362	53.567	27.275	-374.522	-307.263	61.045
1100	37.600	81.618	55.771	31.018	-375.143	-301.128	54.840
1200	37.880	84.634	57.900	34.792	-375.704	-295.004	49.592
1300	38.000	87.468	59.989	38.600	-376.204	-288.983	45.110
1400	38.000	90.156	62.026	42.442	-376.644	-283.059	41.240
1500	38.000	92.609	64.012	46.320	-377.033	-277.220	37.865
1600	38.000	94.877	65.939	50.232	-377.373	-271.468	34.556
1700	38.000	96.961	67.809	54.172	-377.668	-265.788	31.428
1800	38.000	98.786	69.623	58.142	-377.918	-260.168	28.440
1900	38.000	100.366	71.382	62.142	-378.123	-254.608	25.580
2000	38.000	101.729	73.087	66.172	-378.283	-249.108	22.858
2100	38.000	102.900	74.742	70.232	-378.398	-243.668	20.270
2200	38.000	103.890	76.347	74.322	-378.468	-238.288	17.810
2300	38.000	104.620	77.906	78.442	-378.493	-232.968	15.470
2400	38.000	105.110	79.420	82.592	-378.473	-227.708	13.240
2500	38.000	105.480	80.891	86.772	-378.408	-222.508	11.110
2600	38.000	105.740	82.322	90.992	-378.298	-217.368	9.080
2700	38.000	105.900	83.714	95.252	-378.143	-212.288	7.150
2800	38.000	105.980	85.069	99.552	-377.943	-207.268	5.320
2900	38.000	105.990	86.389	103.892	-377.698	-202.308	3.590
3000	38.000	105.930	87.676	108.262	-377.418	-197.408	1.960
3100	38.000	105.810	88.930	112.572	-377.093	-192.568	0.430
3200	38.000	105.630	90.154	116.812	-376.723	-187.788	-0.100
3300	38.000	105.400	91.349	120.982	-376.308	-183.068	-0.630
3400	38.000	105.120	92.516	125.092	-375.848	-178.408	-1.160
3500	38.000	104.790	93.656	129.142	-375.343	-173.808	-1.690
3600	38.000	104.410	94.771	133.132	-374.793	-169.268	-2.220
3700	38.000	103.980	95.861	137.062	-374.198	-164.788	-2.750
3800	38.000	103.500	96.927	140.932	-373.558	-160.368	-3.280
3900	38.000	102.970	97.971	144.742	-372.873	-155.908	-3.810
4000	38.000	102.390	98.991	148.492	-372.143	-151.408	-4.340

$S_{298.15}^\circ = 35.355 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$
 $\Delta H_f^\circ 298.15 = -374.374 \text{ kcal. mole}^{-1}$
 $\Delta F_f^\circ 298.15 = -356.667 \text{ kcal. mole}^{-1}$
 $T_m = 1820^\circ\text{K.}$

Heat of Formation.

The $\Delta H_f^\circ 298.15$ was obtained from the heat of formation of the crystal by adding ΔH_m and the difference between $H_{1820}^\circ - H_{298}^\circ$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacities were reported by A. U. Christensen, K. C. Conway, and K. K. Kelley, "High-Temperature Heat Contents and Entropies of Aluminates and Ferrites of Lithium, Sodium, and of Lithium Titanate", U. S. Bureau Mines Report Invest. 5565 (1960). The measured heat capacity is extrapolated to an assumed glass transition temperature of 1214°K. , below which the heat capacity is taken to be equal to that of the crystal.

The $S_{298.15}^\circ$ was obtained in a manner analogous to that of the heat of formation.

Melting Data.

The T_m and ΔH_m were obtained from A. U. Christensen, K. C. Conway and K. K. Kelley, loc. cit.



T, °K	C _p	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔC _p	Log K _p
0							
100							
200							
298	33.300	30.000	10.000	.000	- 612.070	- 577.459	423.636
300	33.200	30.205	10.001	.061	- 612.081	- 577.447	420.669
400	41.038	31.419	10.003	3.847	- 612.329	- 565.447	309.144
500	44.350	33.344	10.005	8.249	- 613.678	- 554.085	242.190
600	49.160	37.831	10.019	13.014	- 613.359	- 542.192	197.493
700	51.360	41.494	10.047	18.047	- 612.445	- 530.370	165.569
800	53.200	44.256	10.085	23.274	- 612.195	- 514.436	141.685
900	54.850	46.119	10.132	28.681	- 611.431	- 506.992	123.112
1000	56.250	47.172	10.187	34.237	- 610.571	- 495.421	108.274
1100	57.504	48.494	10.257	39.926	- 609.625	- 483.952	96.152
1200	58.630	49.944	10.343	45.733	- 608.604	- 472.574	86.087
1300	59.636	51.511	10.445	51.655	- 607.507	- 461.294	77.551
1400	60.540	53.193	10.562	57.682	- 606.339	- 450.107	70.265
1500	61.315	54.947	10.695	63.872	- 605.143	- 438.994	63.962
1600	61.900	56.761	10.843	69.999	- 603.940	- 427.965	58.487
1700	62.350	58.619	11.006	76.182	- 602.742	- 416.163	53.242
1800	62.600	60.516	11.184	82.405	- 601.562	- 404.585	48.271
1900	62.738	62.447	11.376	88.658	- 600.413	- 393.264	43.635
2000	62.800	64.404	11.582	94.931	- 599.291	- 382.193	39.653
2100	62.853	66.376	11.801	101.213	- 598.195	- 371.360	36.259
2200	62.900	68.361	12.034	107.501	- 597.126	- 360.761	33.000
2300	62.940	70.359	12.281	113.793	- 596.086	- 350.394	30.032
2400	62.973	72.371	12.541	120.089	- 595.072	- 340.254	27.317
2500	63.000	74.394	12.814	126.384	- 594.081	- 330.333	24.827

ΔH_f⁰ = Unknown

ΔH_f^{298.15} = -612.07 ± 1.0 kcal/mol

ΔH_f⁰ = 0.225 kcal/mol

ΔH_m⁰ = [12.86] kcal/mol

T_m = 1307 ± 1°K

S_{298.15} = [30] gibbs/mol

T_t = 1209°K

Heat of Formation

The heats of solution of $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ in 20 per cent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. of the Geophysical Laboratory, No. 1215, 69 (1933). The authors derived two values of ΔHsoln of $\text{Li}_2\text{O}(\text{c})$ from those of $\text{LiCl}(\text{c})$ and $\text{Li}_2\text{SO}_4(\text{c})$, presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate ΔHsoln of $\text{Li}_2\text{O}(\text{c})$ as -58.74 (chloride scheme, originally -59.36) and -59.83 kcal/mol (sulfate scheme, originally -60.86), using recent ΔH_f²⁹⁸ values for $\text{LiCl}(\text{c})$, $\text{Li}_2\text{SO}_4(\text{c})$, $\text{HCl}(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and $\text{Li}_2\text{O}(\text{c})$. The corresponding enthalpy changes, ΔH_f²⁹⁸, for the reaction $\text{Li}_2\text{O}(\text{c}) + 2\text{SiO}_2(\text{quartz}) = \text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ are derived as -33.21 and -34.30 kcal/mol. Adopting the weighted average ΔH_f²⁹⁸ = -33.57 kcal/mol with ΔH_f²⁹⁸(Li_2O , c) = -143.1 kcal/mol and ΔH_f²⁹⁸(SiO_2 , quartz) = -217.7 kcal/mol, we obtain ΔH_f²⁹⁸ = -612.07 kcal/mol for $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$. This ΔH_f²⁹⁸($\text{Li}_2\text{Si}_2\text{O}_5$, c) value is independent of future changes in ΔH_f²⁹⁸ of $\text{Li}_2\text{O}(\text{c})$ but the values of ΔHsoln and ΔH_f⁰ are not independent.

The heats of solution of $\text{LiOH}(\text{c})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ in 20 per cent HF(aq) at 80°C were measured by W. E. Hatton, G. C. Sinke, D. L. Hildenbrand, and D. R. Stull, unpublished work, Thermal Laboratory, The Dow Chemical Co., Midland, Michigan, 1959. By use of a reaction scheme similar to that described on the $\text{Li}_2\text{SiO}_3(\text{c})$ table, the enthalpy change at 298°K for the reaction $2\text{LiOH}(\text{c}) + 2\text{SiO}_2(\text{c}) + \text{Li}_2\text{Si}_2\text{O}_5(\text{c}) + \text{H}_2\text{O}(\text{l})$ was calculated to be -13.44 kcal/mol. Incorporating this value with ΔH_f²⁹⁸ = -115.84, -217.7 and -68.315 kcal/mol for $\text{LiOH}(\text{c})$, $\text{SiO}_2(\text{c})$, and $\text{H}_2\text{O}(\text{l})$, respectively, we obtain ΔH_f²⁹⁸($\text{Li}_2\text{Si}_2\text{O}_5$, c) = -612.20 ± 2.0 kcal/mol, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy

Both heat capacities and S₂₉₈ are estimated by comparison with those for $\text{Na}_2\text{Si}_2\text{O}_5(\text{c})$, $\text{Na}_2\text{O}(\text{c})$ and $\text{Li}_2\text{O}(\text{c})$.

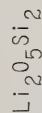
Transition Data

The transition temperature, T_t = 1209°K, is taken from F. C. Kracek, J. Am. Chem. Soc. 61, 2863 (1939). The author estimated a heat of transition of 1 to 2 cal/g based on the arrest in the cooling and heating curves. The value of ΔH_t⁰ is calculated assuming the heat of transition at 1209°K is 1.5 cal/g.

Melting Data

Incongruent melting of $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ at 1033° has been reported by F. C. Kracek, J. Phys. Chem. 34, 2641 (1930); J. Am. Chem. Soc. 61, 2863 (1939). The liquidus temperature of 1034° at the composition 19.92 per cent Li_2O and 80.08 per cent SiO_2 , reported by Kracek (1939), is adopted as T_m. The heat of melting is evaluated such that ΔH_m⁰ + ΔH_f²⁹⁸ = 11.43 kcal/mol, where the value 11.43 kcal/mol is the difference between ΔH_f²⁹⁸ for $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{l})$. The latter were determined by solution calorimetry by Kracek (see Heat of Formation sections in $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{l})$ tables).

Lithium Disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$)
(Liquid) GFW = 150.047



GFW = 150.047

(LIQUID)

LITHIUM DISILICATE ($\text{Li}_2\text{Si}_2\text{O}_5$)

$\Delta H_f^{298.15} = -600.640 \pm 1.0$ kcal/mol

$\Delta H_m^* = [12.86]$ kcal/mol

$S_{298.15}^* = [38.237]$ gibbs/mol

$T_m = 1307^\circ\text{K}$

Heat of Formation

The heats of solution of LiCl(c) , $\text{Li}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$ in 20 percent hydrofluoric acid at 74.7°C were measured by F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953). Following the same procedure as described in $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ table, we derived the enthalpy changes, ΔH_f^{298} , for the reaction $\text{Li}_2\text{O(c)} + 2\text{SiO}_2(\text{quartz}) = \text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$ as -21.78 and -22.87 kcal/mol. Adopting the weighted average $\Delta H_f^{298} = -72.14$ kcal/mol with $\Delta H_f^{298}(\text{Li}_2\text{O, c}) = -143.1$ kcal/mol and $\Delta H_f^{298}(\text{SiO}_2, \text{quartz}) = -217.7$ kcal/mol, we obtain $\Delta H_f^{298} = -600.640$ kcal/mol for $\text{Li}_2\text{Si}_2\text{O}_5(\text{gl})$. This $\Delta H_f^{298}(\text{Li}_2\text{Si}_2\text{O}_5, \text{gl})$ value is independent of future changes in ΔH_f^* of $\text{Li}_2\text{O(c)}$ but the values of ΔH_{soln} and ΔH_m^* are not independent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $\text{Na}_2\text{Si}_2\text{O}_5(\text{c})$, $\text{Na}_2\text{SiO}_3(\text{c})$ and $\text{Li}_2\text{SiO}_3(\text{c})$. A glass transition temperature at 800°K is assumed, i.e. the heat capacities below 800°K are taken from those for $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ and above 800°K are assumed to be constant.

The S_{298}^* value is obtained from $S_{298}^*(\text{c})$ by adding ΔS_m^* and the difference between $S_{1307}^* - S_{298}^*$ for crystal and liquid.

Melting Data

See $\text{Li}_2\text{Si}_2\text{O}_5(\text{c})$ table for details.

Log Kp

ΔG_f^*

kcal/mol
 ΔH_f^*

$H_f^* - H_{298}^*$

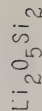
$-(G^* - H_{298}^*)/T$

gibbs/mol
 S^*

C_p^*

T, $^\circ\text{K}$

100	33,000	38,297	38,297	1,001	-600.640	-568.703	616.870
200	33,200	38,502	38,298	1,061	-600.651	-569.506	614.156
300	41,500	49,335	39,716	3,947	-600.899	-557.736	304.733
400	48,050	59,140	42,641	8,244	-602.248	-546.504	239.008
500	49,160	67,824	46,128	13,018	-601.929	-535.740	195.143
600	51,360	75,572	49,791	18,047	-601.415	-524.749	163.634
700	60,000	82,555	53,458	23,276	-600.763	-513.644	140.376
800	60,000	89,621	57,091	29,278	-599.404	-503.057	122.159
900	60,000	95,943	60,666	35,278	-598.100	-492.421	107.618
1000	60,000	101,662	64,137	41,278	-596.843	-481.916	95.748
1200	60,000	106,882	67,484	47,278	-595.629	-471.522	85.876
1300	60,000	111,695	70,702	53,278	-594.454	-461.229	77.440
1400	60,000	116,131	73,790	59,278	-593.314	-451.023	70.408
1500	60,000	120,271	76,753	65,278	-592.207	-440.894	64.239
1600	60,000	124,143	79,595	71,278	-591.132	-430.844	58.951
1700	60,000	127,781	82,323	77,278	-589.167	-417.992	53.736
1800	60,000	131,210	84,945	83,278	-587.263	-402.372	48.855
1900	60,000	134,454	87,466	89,278	-585.415	-386.839	44.497
2000	60,000	137,532	89,893	95,278	-583.761	-371.387	40.563
2100	60,000	140,459	92,232	101,278	-582.321	-356.003	37.050
2200	60,000	143,251	94,488	107,278	-581.001	-340.691	33.844
2300	60,000	145,918	96,667	113,278	-579.801	-325.442	30.924
2400	60,000	148,471	98,772	119,278	-578.712	-310.246	28.252
2500	60,000	150,921	100,810	125,278	-577.730	-295.120	25.799
2600	60,000	153,274	102,782	131,278	-576.861	-280.061	23.540
2700	60,000	155,538	104,695	137,278	-576.035	-265.017	21.452
2800	60,000	157,720	106,550	143,278	-575.250	-250.035	19.516
2900	60,000	159,826	108,351	149,278	-574.507	-235.105	17.718
3000	60,000	161,860	110,101	155,278	-573.800	-220.220	16.043



LITHIUM NITRIDE (Li₃N)

(CRYSTAL)

GFW = 34.8237

T, °K	C _p ^a	gkcal/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log K _p
0							
100							
200							
298	18.480	9.000	9.000	0.000	- 47.200	- 36.840	27.005
300	18.530	9.114	9.000	0.034	- 47.205	- 36.777	26.792
400	20.990	14.785	9.757	2.011	- 47.440	- 33.261	18.173
500	24.240	18.722	11.266	4.728	- 48.829	- 29.471	12.882
600	25.660	24.184	13.082	6.679	- 49.872	- 25.389	9.248
700	27.840	28.308	14.941	9.357	- 49.658	- 21.324	6.658
800	29.640	32.149	16.855	12.235	- 49.228	- 17.305	4.727
900	30.960	35.720	18.755	15.268	- 48.647	- 13.347	3.241
1000	31.900	39.033	20.619	18.414	- 47.959	- 9.461	2.068
1100	32.540	42.105	22.434	21.638	- 47.193	- 5.647	1.122
1200	32.970	44.956	24.194	24.914	- 46.381	- 1.908	0.367
1300	33.250	47.606	25.804	28.226	- 45.532	1.764	- 0.297
1400	33.450	50.078	27.534	31.561	- 44.663	5.371	- 0.838
1500	33.600	52.391	29.115	34.914	- 43.773	8.913	- 1.299
1600	33.720	54.564	30.638	38.281	- 42.868	12.398	- 1.693
1700	33.800	56.611	32.107	41.657	- 41.904	19.806	- 2.546
1800	33.840	58.544	33.522	45.039	- 40.828	29.586	- 3.592
1900	33.890	60.374	34.888	48.425	- 39.645	38.284	- 4.519
2000	33.920	62.113	36.206	51.815	- 38.352	46.898	- 5.343
2100	33.960	63.769	37.479	55.209	- 36.948	58.438	- 6.082
2200	34.000	65.350	38.710	58.607	- 35.476	67.913	- 6.747

ΔH_f⁰ = UnknownΔH_f⁰_{298.15} = -47.2 ± 1.0 kcal/molS_{298.15} = [9 + 2] gibbs/mol

Heat of Formation.

The adopted ΔH_f⁰_{298.15} = -47.2 ± 1.0 kcal/mol was determined calorimetrically by Neumann et al.¹ by heating Li (c) at 600°C under 5 atm N₂ pressure for 1 minute. The ΔH_f⁰_{298.15} = -131.1 kcal/mol of reaction Li₃N(c) + 3 H₂O (l) = 3 LiOH (aq) + NH₃ (aq) was measured by Guntz.² Based on this ΔH_f⁰_{298.15} the heat of formation was calculated to be -47.02 ± 2 kcal/mol which is in very good agreement with that of Neumann et al.¹. Unfortunately the author does not report the amount of water in LiOH (aq) and we assumed 300 H₂O as the best estimate. Heats of formation for NH₃(aq) = [-19.17] kcal/mol and H₂O (l) = [-68.315] kcal/mol were taken from Wagman et al.³. The ΔH_f⁰ of LiOH + 300 H₂O (-121.30 kcal/mol) was derived from the heats of formation and solution of LiOH(c) (see JANAF table) and the heat of dilution selected by Parker.⁴

References: 1. B. Neumann, C. Kroger and H. Haebler, Z. anorg. allgem. Chem. **204**, 81-96 (1932).2. A. Guntz, Compt. rend **123**, 995-8 (1896).

3. D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm,

"Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1,

Washington, 1965.

4. V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes,"

NSRDS-NBS 2, Washington, D. C., 1965.

Heat Capacity and Entropy.

S. Satoh, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **35**, 162 (1939), has measured enthalpies (273-578°K) and derived an equation for the specific heat of Li₃N. The adopted heat capacities were obtained from this equation. Above 773°K the heat capacities were graphically extrapolated. The entropy was estimated from the contribution 3.5 eu per Li given by W. M. Latimer, "Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, 1952, and a -1.5 eu contribution for N.

Dec. 31, 1960; Sept. 30, 1966

Magnesium (Mg)

(Reference State) At. Wt. = 24.32

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	- 1.196	0.000	0.000	0.000
100	3.768	2.273	12.602	- 1.042	0.000	0.000	0.000
200	5.440	5.533	7.693	- 4.480	0.000	0.000	0.000
298	5.973	7.814	7.814	0.000	0.000	0.000	0.000
300	5.980	7.851	7.814	0.011	0.000	0.000	0.000
400	6.290	9.613	8.052	1.425	0.000	0.000	0.000
500	6.560	11.047	8.512	1.267	0.000	0.000	0.000
600	6.802	12.264	9.036	1.936	0.000	0.000	0.000
700	7.080	13.333	9.577	2.659	0.000	0.000	0.000
800	7.420	14.300	10.108	3.354	0.000	0.000	0.000
900	7.810	15.156	10.624	4.034	0.000	0.000	0.000
1000	8.260	15.939	11.130	4.703	0.000	0.000	0.000
1100	8.740	16.702	11.604	5.363	0.000	0.000	0.000
1200	9.260	17.452	12.042	6.016	0.000	0.000	0.000
1300	9.820	18.184	12.450	6.663	0.000	0.000	0.000
1400	10.420	18.900	12.830	7.300	0.000	0.000	0.000
1500	11.060	19.600	13.180	7.930	0.000	0.000	0.000
1600	11.740	20.290	13.510	8.550	0.000	0.000	0.000
1700	12.460	20.970	13.820	9.160	0.000	0.000	0.000
1800	13.220	21.640	14.120	9.760	0.000	0.000	0.000
1900	14.020	22.300	14.410	10.350	0.000	0.000	0.000
2000	14.860	22.950	14.690	10.930	0.000	0.000	0.000
2100	15.740	23.600	14.960	11.500	0.000	0.000	0.000
2200	16.660	24.240	15.220	12.070	0.000	0.000	0.000
2300	17.620	24.880	15.480	12.630	0.000	0.000	0.000
2400	18.620	25.520	15.740	13.190	0.000	0.000	0.000
2500	19.660	26.160	16.000	13.750	0.000	0.000	0.000
2600	20.740	26.800	16.260	14.310	0.000	0.000	0.000
2700	21.860	27.440	16.520	14.870	0.000	0.000	0.000
2800	23.020	28.080	16.780	15.430	0.000	0.000	0.000
2900	24.220	28.720	17.040	16.000	0.000	0.000	0.000
3000	25.460	29.360	17.300	16.560	0.000	0.000	0.000
3100	26.740	30.000	17.560	17.120	0.000	0.000	0.000
3200	28.060	30.640	17.820	17.680	0.000	0.000	0.000
3300	29.420	31.280	18.080	18.240	0.000	0.000	0.000
3400	30.820	31.920	18.340	18.800	0.000	0.000	0.000
3500	32.260	32.560	18.600	19.360	0.000	0.000	0.000
3600	33.740	33.200	18.860	19.920	0.000	0.000	0.000
3700	35.260	33.840	19.120	20.480	0.000	0.000	0.000
3800	36.820	34.480	19.380	21.040	0.000	0.000	0.000
3900	38.420	35.120	19.640	21.600	0.000	0.000	0.000
4000	40.060	35.760	19.900	22.160	0.000	0.000	0.000
4100	41.740	36.400	20.160	22.720	0.000	0.000	0.000
4200	43.460	37.040	20.420	23.280	0.000	0.000	0.000
4300	45.220	37.680	20.680	23.840	0.000	0.000	0.000
4400	47.020	38.320	20.940	24.400	0.000	0.000	0.000
4500	48.860	38.960	21.200	24.960	0.000	0.000	0.000
4600	50.740	39.600	21.460	25.520	0.000	0.000	0.000
4700	52.660	40.240	21.720	26.080	0.000	0.000	0.000
4800	54.620	40.880	21.980	26.640	0.000	0.000	0.000
4900	56.620	41.520	22.240	27.200	0.000	0.000	0.000
5000	58.660	42.160	22.500	27.760	0.000	0.000	0.000
5100	60.740	42.800	22.760	28.320	0.000	0.000	0.000
5200	62.860	43.440	23.020	28.880	0.000	0.000	0.000
5300	65.020	44.080	23.280	29.440	0.000	0.000	0.000
5400	67.220	44.720	23.540	30.000	0.000	0.000	0.000
5500	69.460	45.360	23.800	30.560	0.000	0.000	0.000
5600	71.740	46.000	24.060	31.120	0.000	0.000	0.000
5700	74.060	46.640	24.320	31.680	0.000	0.000	0.000
5800	76.420	47.280	24.580	32.240	0.000	0.000	0.000
5900	78.820	47.920	24.840	32.800	0.000	0.000	0.000
6000	81.260	48.560	25.100	33.360	0.000	0.000	0.000

Dec. 31, 1960; Sept. 30, 1962

(REFERENCE STATE)

MAGNESIUM (ME)

Crystal
Liquid
Ideal gas, monatomic

Below 922°K
922°K to 1378°K
above 1378°K

See crystal, liquid, and ideal monatomic gas for details.

Mg

At. Wt. = 24.32

Mg

T, °K.	C_p	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_f° , kcal. mole ⁻¹	ΔF_f°	Log K _p
0	.000	INFINITE	1.196	.000	INFINITE
100	3.768	2.273	1.042	.000	.000
200	5.440	5.533	.480	.000	.000
298	5.953	7.814	.000	.000	.000
300	5.960	7.851	.011	.000	.005
400	6.290	9.613	.652	.000	.000
500	6.560	11.047	1.267	.000	.000
600	6.802	12.264	1.936	.000	.000
700	7.020	13.305	2.624	.000	.000
800	7.210	14.197	3.320	.000	.000
900	7.380	14.956	4.015	.000	.000
1000	7.530	15.606	4.719	.000	.000
1100	7.660	16.165	5.431	.008	.081
1200	7.770	16.640	6.150	.015	.115
1300	7.860	17.030	6.875	.022	.142
1400	7.930	17.340	7.605	.028	.168
1500	7.980	17.580	8.340	.032	.192
1600	8.020	17.750	9.080	.035	.215
1700	8.050	17.860	9.825	.038	.238
1800	8.070	17.920	10.575	.040	.260
1900	8.080	17.950	11.330	.041	.281
2000	8.090	17.960	12.090	.042	.302

Dec. 31, 1960; Sept. 30, 1962

MAGNESIUM (Mg)

(CRYSTAL)

At. Wt. = 24.32

$\Delta H_f^\circ 0 = 0$

$\Delta H_f^\circ 298.15 = 0$

$\Delta H_f^\circ 298.15 = 35.28 \pm 0.01 \text{ kcal. mole}^{-1}$

$\Delta H_f^\circ 298.15 = 7.814 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$T_m = 922 \pm 0.5^\circ\text{K}$

$\Delta H_m = 2.14 \text{ kcal. mole}^{-1}$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

The following heat capacity measurements were considered in drawing a smooth curve of C_p with T : P. L. Smith (1.25-4.2°K) Phil. Mag. 46, 744 (1955); J. R. Clement and H. R. Jeffers (3-13°K) Phys. Rev. 105, 1435 (1957); K. Clausius and J. V. Vaughn (11.3-228.4°K) J. Am. Chem. Soc. 52, 4686, (1930); R. S. Craig, C. A. Krier, L. W. Coffey, E. A. Bates, and W. E. Wallace (12-320°K) J. Am. Chem. Soc. 76, 238 (1954); W. Mannchen and K. Bornkessel (190-300°K) Z. Metallkunde 51, 482-5 (1960); H. Seelkamp (291-773°K) Z. anorg. Chem. 195, 345 (1931); and D. R. Stull and R. A. McDonald (700-900°K) J. Am. Chem. Soc. 77, 5293 (1955). The following heat capacity measurements were noted but not used as the data were either not tabulated, or erratic, or inconsistent or would not have altered the C_p curve: D. L. Martin (0.4-1.5°K) Proc. Phys. Soc. (London) 78, 1482-8 (1961); I. Estermann, S. A. Friedberg, and J. E. Goldman (1.6-4.2°K) Phys. Rev. 87, 582 (1952); E. P. Eastman and W. H. Rodenbush (74.9-288.5°K) J. Am. Chem. Soc. 40, 469 (1918); W. G. Saba, K. P. Sterrett, R. S. Craig, and W. R. Wallace (298-543°K) J. Am. Chem. Soc. 79, 3537 (1957); F. M. Jaeger and T. J. Poppema (273-873°K) Rec. Trav. chim. 55, 492 (1936); J. H. Averbey and E. Griffiths (323-899°K) Proc. Phys. Soc. 36, 378 (1926); E. D. Eastman, A. M. Williams and T. F. Young (373-873°K) J. Am. Chem. Soc. 45, 1178 (1926); and P. Schübel (323-773°K) Z. anorg. Chem. 87, 81 (1914). ΔH_m was obtained by numerical integration using the low temperature C_p data cited above.

Melting.

Melting point is from J. L. Houghton and R. J. M. Payne (922 ± 0.5°K) J. Inst. Met. 54, 279 (1934). Also noted but not used were: R. Chadwick (923°K) J. Inst. Met. 39, 285-300 (1928); W. R. D. Jones (920.5°K) J. Inst. Met. 45, 395-419 (1931).

The heat of melting is from D. R. Stull and R. A. McDonald (loc. cit.)

Heat of Sublimation.

Is obtained by third law calculations from the vapor pressure data on the solid by F. F. Coleman and A. E. Egerton, Phil. Trans Roy. Soc. (London) A234, 177-204 (1935) and the value is confirmed by similar use of the vapor pressure data on the liquid by E. Scheil and P. Wolf, Z. Metallkunde 50, 229-33 (1959); A. Wejmarth, Tek. Tid. 72, 33-9, 44-8 (1942); A. Schneider and E. K. Stoll, Z. Elektrochem. 47, 519-26 (1941); E. Baur and R. Brunner, Helv. Chim. Acta, 17, 958-69 (1934); and H. Hartmann and R. Schneider, Z. anorg. Chem. 180, 275-83 (1929). Additional data noted but not used on the vapor pressure as values were not tabulated or they were erratic of the solid are by J. F. Smith and R. L. Smythe, Acta Metallurgica, 1, 261-7 (1959); A. Eucken, Metallwirtschaft, 15, 64-5 (1936); W. Leitzgeb, Metallwirtschaft, 14, 289 (1935); and of the liquid by P. A. Vetter and O. Kubaschewski, Z. Elektrochem. 57, 243 (1953); W. Leitzgeb, Z. anorg. Chem. 202, 312 (1931); C. Zwikker, Physica, 9, 246 (1928); O. Ruff and H. Hartmann, Z. anorg. Chem. 135, 29-45 (1924); and J. Johnston, Ind. Eng. Chem. 9, 876 (1917).

Magnesium (Mg)

(Liquid) At. Wt. = 24.32

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298	5.953	10.159	0.000	2.158	1.459	1.060
300	5.960	10.196	0.011	2.158	1.455	1.060
400	6.290	11.958	0.925	2.158	1.219	0.960
500	6.560	13.392	1.267	2.158	0.986	0.831
600	6.802	14.609	1.936	2.158	0.750	0.773
700	7.090	15.679	2.630	2.158	0.517	0.761
800	7.338	16.568	3.348	2.158	0.288	0.778
900	7.540	17.324	4.090	2.158	0.068	0.812
1000	7.690	17.967	4.857	2.158	0.000	0.850
1100	8.140	18.102	5.675	0.000	0.000	0.900
1200	8.400	18.601	6.502	0.000	0.000	0.960
1300	8.520	18.956	7.338	0.000	0.000	1.020
1400	8.590	19.255	8.175	0.000	0.000	1.072
1500	8.180	21.779	9.139	29.960	2.666	0.988
1600	9.440	27.380	10.070	29.526	4.826	0.659
1700	9.700	27.960	11.077	29.066	6.960	0.695
1800	9.820	28.476	12.060	28.576	9.076	0.732
1900	10.220	28.067	13.019	28.057	11.192	0.782
2000	10.460	28.598	14.034	27.529	13.192	0.842
2100	10.740	28.116	15.115	26.965	15.213	0.913
2200	11.000	28.622	16.202	26.375	17.210	1.000
2300	11.240	29.116	17.297	25.765	19.177	1.092
2400	11.520	29.603	18.412	25.117	21.117	1.192
2500	11.780	29.076	19.619	24.450	23.029	1.303

MAGNESIUM (Mg)

(LIQUID)

AT. WT. = 24.32

$$S_{298.15}^o = [0.159] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^o = 2.140 \text{ cal. mole}^{-1}$$

$$\Delta H_v^o = 30.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o 298.15 = [2.158] \text{ kcal. mole}^{-1}$$

$$T_m = 922 \pm 0.5^\circ \text{K}$$

$$T_b = 1379^\circ \text{K}$$

Heat of Formation.

$\Delta H_f^o 298.15$ (= $\Delta H_m 298.15$) obtained from $\Delta H_m 922$ by adding $H_{922} - H_{298.15}$ for solid and subtracting $H_{922} - H_{298.15}$ for liquid.

Heat Capacity and Entropy.

The heat capacity measurements of D. R. Stull and R. A. McDonald (950-1100°K) J. Am. Chem. Soc. 77, 5293 (1955) were used. Outside of the observed range C_p was extrapolated linearly with temperature. Below T_m the linear extrapolation was continued until the C_p curve for the solid is encountered at 710°K. At lower temperatures the C_p of the crystal is used. $S_{298.15}^o$ was calculated from that of the solid.

Melting.

See crystal for details.

Vaporization.

The normal boiling point was calculated by the third law and $\Delta H_v 298.15$. This compares with 1377°K computed from the general vapor pressure equation for liquid Mg given on p 221 of Gmelins Handbuch der anorganischen Chemie, System-Nummer 27 (1952), and experimentally determined values; 1376 ± 5°K by A. Schneider and U. Esch, Z. Elektrochem 45, 888 (1939); 1380°K by E. Baur and R. Brunner, Helv. Chim. Acta 17, 958 (1934); 1370°K by W. Leitgeb, Z. anorg. Chem. 202, 305 (1931); and 1395°K by Greenwood, Chem. News 104, 31 (1911).

The $\Delta H_v 1378$ is based on the liquid and ideal gas tables.

Mg

AT. WT. = 24.32

(IDEAL GAS)

MAGNESIUM, MONATOMIC (Mg)

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _f
0	.000	INFINITE	INFINITE	1.481	34.996	INFINITE	INFINITE
100	4.968	30.076	30.021	.984	35.339	32.558	-71.153
200	4.968	31.520	31.058	.488	35.273	29.676	-34.427
298	4.968	31.504	31.044	.000	35.281	27.023	-18.809
300	4.968	31.535	31.044	.009	35.279	26.974	-19.650
400	4.968	31.664	31.099	.506	35.162	24.222	-13.233
500	4.968	31.072	31.067	1.003	35.017	21.504	-9.399
600	4.968	30.978	31.079	1.500	34.845	18.816	-6.053
700	4.968	30.744	31.092	1.996	34.648	16.161	-5.045
800	4.968	30.407	31.291	2.493	34.420	13.534	-3.697
900	4.968	30.093	31.670	2.990	34.156	10.939	-2.656
1000	4.968	31.516	31.029	3.487	31.734	8.557	-1.870
1100	4.968	31.990	30.368	3.984	31.439	6.252	-1.242
1200	4.968	32.422	30.688	4.481	31.099	3.977	-.724
1300	4.968	32.820	30.991	4.977	30.742	1.732	-.000
1400	4.968	33.186	31.278	5.471	.000	.000	.000
1500	4.968	33.530	31.550	5.971	.000	.000	.000
1600	4.968	33.851	31.809	6.468	.000	.000	.000
1700	4.968	34.152	40.056	6.965	.000	.000	.000
1800	4.968	34.436	40.291	7.461	.000	.000	.000
1900	4.968	34.705	40.516	7.958	.000	.000	.000
2000	4.969	34.960	40.732	8.455	.000	.000	.000
2100	4.969	35.202	40.939	8.952	.000	.000	.000
2200	4.970	35.433	41.138	9.449	.000	.000	.000
2300	4.972	35.654	41.330	9.946	.000	.000	.000
2400	4.974	35.866	41.515	10.443	.000	.000	.000
2500	4.978	36.069	41.693	10.941	.000	.000	.000
2600	4.983	36.264	41.865	11.439	.000	.000	.000
2700	4.989	36.453	42.031	11.938	.000	.000	.000
2800	4.998	36.634	42.192	12.437	.000	.000	.000
2900	5.009	36.810	42.349	12.937	.000	.000	.000
3000	5.023	36.980	42.500	13.439	.000	.000	.000
3100	5.040	37.145	42.647	13.942	.000	.000	.000
3200	5.060	37.305	42.790	14.447	.000	.000	.000
3300	5.085	37.461	42.930	14.954	.000	.000	.000
3400	5.114	37.613	43.065	15.464	.000	.000	.000
3500	5.148	37.762	43.197	15.977	.000	.000	.000
3600	5.186	37.908	43.326	16.494	.000	.000	.000
3700	5.229	38.050	43.452	17.014	.000	.000	.000
3800	5.278	38.190	43.575	17.540	.000	.000	.000
3900	5.332	38.328	43.695	18.070	.000	.000	.000
4000	5.392	38.464	43.812	18.606	.000	.000	.000
4100	5.457	38.598	43.927	19.140	.000	.000	.000
4200	5.528	38.730	44.040	19.678	.000	.000	.000
4300	5.604	38.861	44.151	20.224	.000	.000	.000
4400	5.686	38.991	44.259	20.781	.000	.000	.000
4500	5.773	39.120	44.366	21.342	.000	.000	.000
4600	5.865	39.246	44.471	21.907	.000	.000	.000
4700	5.964	39.375	44.574	22.476	.000	.000	.000
4800	6.067	39.501	44.675	23.047	.000	.000	.000
4900	6.176	39.628	44.775	23.619	.000	.000	.000
5000	6.289	39.754	44.873	24.192	.000	.000	.000
5100	6.407	39.879	44.970	24.767	.000	.000	.000
5200	6.530	39.995	45.066	25.344	.000	.000	.000
5300	6.658	40.110	45.160	25.923	.000	.000	.000
5400	6.790	40.226	45.253	26.503	.000	.000	.000
5500	6.927	40.342	45.345	27.084	.000	.000	.000
5600	7.069	40.458	45.436	27.666	.000	.000	.000
5700	7.215	40.574	45.527	28.249	.000	.000	.000
5800	7.367	40.691	45.616	28.834	.000	.000	.000
5900	7.523	40.808	45.704	29.420	.000	.000	.000
6000	7.684	40.926	45.791	30.007	.000	.000	.000

Dec. 31, 1960; Sept. 30, 1962

$\Delta H_f^0 = 35.0 \pm 0.01 \text{ kcal. mole}^{-1}$ $\Delta H_f^{298.15} = 35.28 \pm 0.01 \text{ kcal. mole}^{-1}$
 Ground State 1S_0 $S_{298.15}^{298.15} = 35.504 \text{ cal. mole}^{-1} \text{ deg}^{-1}$

Electronic Levels and Multiplicities

$\epsilon_i, \text{cm}^{-1}$	g_i	$\epsilon_i, \text{cm}^{-1}$	g_i
0.00	1	46403.14	5
21850.37	1	57020	9
21870.43	3	57204	28
21911.14	5	57854	12
35051.36	3	49346.6	58
41197.37	3	51872.4	51
43503.0	1	52556.4	1
		53134.7	5
		60397	102
		60887	194

Heat of Formation.

$\Delta H_f^{298.15} (-\Delta H_s^{298.15})$ is calculated as described on the table for crystal.

Heat Capacity and Entropy.

Thermodynamic functions were calculated using electronic levels and multiplicities from C. E. Moore [Nat]. Bur. Standards Circ. 467, Vol. 1 (1949)]. Higher levels were averaged.

Magnesium Unipositive Ion (Mg⁺)

(Ideal Gas) GFW = 24.31145

T, °K	C _p ^o	S ^o -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^o kcal/mol	ΔG ^o	Log Kp
100	4.268	36.879	0.00	211.559	201.406	-18.635
200	4.268	36.879	0.00	211.559	201.406	-18.635
298	4.268	36.879	0.00	211.559	201.406	-18.635
300	4.268	36.879	0.00	211.559	201.406	-18.635
400	4.268	36.339	-504	211.946	197.876	-18.615
500	4.268	36.448	1.003	212.298	194.319	-18.637
600	4.268	40.353	1.500	212.623	190.691	-18.659
700	4.268	41.119	1.894	212.722	187.012	-18.686
800	4.268	42.382	2.990	213.424	173.546	-18.508
900	4.268	42.368	3.687	211.999	175.946	-18.453
1000	4.268	42.591	3.984	211.691	172.350	-18.299
1100	4.268	43.365	4.850	211.657	168.799	-18.743
1200	4.268	43.757	5.674	181.247	162.080	-25.302
1300	4.268	44.563	5.974	182.244	160.658	-25.408
1400	4.268	44.905	6.467	182.740	159.201	-21.746
1500	4.268	45.226	6.951	185.224	151.492	-15.766
1600	4.268	45.527	7.442	185.721	148.877	-14.889
1700	4.268	46.000	7.958	185.714	148.575	-13.987
1800	4.268	46.335	8.485	187.210	144.690	-12.666
1900	4.268	46.577	9.051	185.224	151.492	-15.766
2000	4.268	46.508	9.551	185.721	148.877	-14.889
2100	4.268	47.260	10.442	185.714	148.575	-13.987
2200	4.268	47.443	10.939	187.210	144.690	-12.666
2300	4.268	47.638	11.435	187.705	143.194	-12.036
2400	4.268	48.062	11.932	188.200	141.691	-11.401
2500	4.268	48.190	12.426	189.184	137.970	-10.398
2600	4.268	48.349	13.423	189.680	136.193	-9.922
2700	4.268	48.512	13.919	190.170	134.402	-9.475
2800	4.268	48.822	14.915	191.685	132.775	-8.056
2900	4.268	49.115	15.007	191.629	128.941	-6.268
3000	4.268	49.434	15.410	192.110	127.085	-5.936
3100	4.268	49.778	15.891	194.449	117.637	-6.427
3200	4.268	50.255	16.403	192.585	125.225	-7.602
3300	4.268	50.523	16.997	193.028	123.185	-7.266
3400	4.268	50.584	17.494	193.092	119.552	-6.699
3500	4.268	50.652	17.994	194.449	117.637	-6.427
3600	4.268	50.724	18.391	194.449	115.709	-6.168
3700	4.268	50.801	18.888	194.449	113.774	-5.920
3800	4.268	50.878	19.385	194.449	111.840	-5.672
3900	4.268	50.954	19.882	194.449	109.906	-5.424
4000	4.268	51.029	20.379	194.449	107.971	-5.176
4100	4.268	51.104	20.876	194.449	106.036	-4.928
4200	4.268	51.179	21.373	194.449	104.101	-4.680
4300	4.268	51.254	21.870	194.449	102.166	-4.432
4400	4.268	51.329	22.367	194.449	100.231	-4.184
4500	4.268	51.404	22.864	194.449	98.296	-3.936
4600	4.268	51.479	23.361	194.449	96.361	-3.688
4700	4.268	51.554	23.858	194.449	94.426	-3.440
4800	4.268	51.629	24.355	194.449	92.491	-3.192
4900	4.268	51.704	24.852	194.449	90.556	-2.944
5000	4.268	51.779	25.349	194.449	88.621	-2.696
5100	4.268	51.854	25.846	194.449	86.686	-2.448
5200	4.268	51.929	26.343	194.449	84.751	-2.200
5300	4.268	52.004	26.840	194.449	82.816	-1.952
5400	4.268	52.079	27.337	194.449	80.881	-1.704
5500	4.268	52.154	27.834	194.449	78.946	-1.456
5600	4.268	52.229	28.331	194.449	77.011	-1.208
5700	4.268	52.304	28.828	194.449	75.076	-0.960
5800	4.268	52.379	29.325	194.449	73.141	-0.712
5900	4.268	52.454	29.822	194.449	71.206	-0.464
6000	4.268	52.529	30.319	194.449	69.271	-0.216

Dec. 31, 1967

MAGNESIUM UNIPOSITIVE ION(Mg⁺)

(IDEAL GAS)

GFW = 24.31145

Ground State Configuration 1S₀
 $\Delta H_{f,0}^{\circ} = 211.3 \pm 0.1$ kcal/mol
 $\Delta H_{f,298.15}^{\circ} = 211.6 \pm 0.1$ kcal/mol
 $S_{298.15}^{\circ} = 36.879$ gibbs/mol

Electronic Levels and Quantum Weights			
ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0.0	2	106979.10	76
35730.45	6	112273.83	44
71209.84	12	114385.15	44
80641.13	6	115847.07	32
94271.23	32	117578.72	96

Heat of Formation

We derive the heat of formation at 0°K from the reaction $Mg(g) + Mg^{+}(g) \rightarrow Mg^{+}(g)$ using the JANAF auxiliary value for $Mg(g)$ and an ionization potential of 178.278 kcal/mol from C. E. Moore, U. S. Natl. Bur. Std. Circ. 487, Vol. I, 1949.

Heat Capacity and Entropy

We take the electronic levels and quantum weights from C. E. Moore, loc. cit. $H_0^{\circ} - H_{298}^{\circ} = -1.481$ kcal/mol at 0°K.

Mg⁺

Monomagnesium Mononitride (MgN)

(Ideal Gas) Mol. Wt. = 38.328

MOL. WT. = 38.328

(IDEAL GAS)

MONOMAGNESIUM MONONITRIDE (MgN)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ cal. mole ⁻¹	ΔH _f ⁰ cal. mole ⁻¹	ΔF _f ⁰ cal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	6.968	45.789	60.321	-1.453	69.084	INFINITE
200	7.311	50.696	54.412	-0.743	66.084	-146.064
300	7.623	53.713	49.412	-0.000	64.345	-70.309
400	7.832	55.713	45.412	0.014	62.138	-45.547
500	8.208	56.070	42.025	0.181	62.096	-45.235
600	8.449	57.929	38.462	0.818	59.819	-32.682
700	8.607	59.484	35.310	2.505	57.584	-25.169
800	8.716	60.520	32.371	6.836	55.360	-20.171
900	8.854	63.028	27.139	13.503	53.503	-15.603
1000	8.901	63.964	21.046	18.617	51.603	-11.686
1100	8.939	64.814	15.533	6.909	48.949	-10.282
1200	8.959	65.593	10.589	65.115	45.224	-8.985
1300	8.969	66.327	6.705	68.793	43.429	-7.908
1400	9.023	66.980	3.472	70.642	41.429	-7.008
1500	9.046	67.603	0.0120	33.470	40.408	-6.308
1600	9.066	68.188	61.054	33.461	40.889	-5.957
1700	9.085	68.738	61.490	33.452	41.371	-5.651
1800	9.103	69.250	62.321	33.441	41.855	-5.381
1900	9.119	69.730	62.307	33.418	42.322	-5.142
2000	9.136	70.219	62.691	33.404	43.307	-4.732
2100	9.151	70.665	63.061	33.491	43.791	-4.557
2200	9.166	71.091	63.416	33.577	44.279	-4.398
2300	9.181	71.495	63.750	33.660	44.761	-4.253
2400	9.195	71.890	64.069	33.742	45.242	-4.121
2500	9.209	72.265	64.409	33.825	45.739	-4.008
2600	9.223	72.627	64.718	33.918	46.229	-3.886
2700	9.236	72.975	65.017	33.403	46.718	-3.781
2800	9.248	73.310	65.300	33.485	47.200	-3.685
2900	9.263	73.636	65.589	33.572	47.698	-3.594
3000	9.276	73.950	65.863	33.455	48.189	-3.510
3100	9.288	74.255	66.129	33.437	48.680	-3.432
3200	9.301	74.550	66.387	33.417	49.171	-3.358
3300	9.316	74.836	66.634	33.396	49.660	-3.284
3400	9.326	75.114	66.884	33.373	50.150	-3.224
3500	9.339	75.385	67.123	33.347	50.650	-3.163
3600	9.351	75.648	67.356	33.318	51.147	-3.105
3700	9.364	75.904	67.584	33.286	51.644	-3.050
3800	9.376	76.156	67.806	33.250	52.140	-2.999
3900	9.389	76.404	68.024	33.211	52.636	-2.949
4000	9.401	76.636	68.236	33.164	53.135	-2.903
4100	9.413	76.868	68.443	33.113	53.635	-2.859
4200	9.425	77.095	68.647	33.056	54.135	-2.817
4300	9.437	77.317	68.846	32.992	54.638	-2.777
4400	9.449	77.534	69.041	32.924	55.140	-2.737
4500	9.462	77.747	69.232	32.842	55.650	-2.703
4600	9.474	77.955	69.419	32.755	56.159	-2.668
4700	9.486	78.159	69.603	32.660	56.667	-2.635
4800	9.498	78.356	69.783	32.554	57.181	-2.603
4900	9.510	78.548	69.959	32.434	57.694	-2.571
5000	9.522	78.747	70.134	32.315	58.212	-2.544
5100	9.534	78.935	70.305	32.179	58.725	-2.516
5200	9.546	79.121	70.473	32.032	59.251	-2.490
5300	9.558	79.306	70.638	31.873	59.780	-2.465
5400	9.569	79.491	70.800	31.702	60.310	-2.440
5500	9.581	79.657	70.959	31.518	60.836	-2.417
5600	9.593	79.830	71.116	31.320	61.369	-2.395
5700	9.605	80.000	71.270	31.110	61.912	-2.374
5800	9.617	80.166	71.422	30.885	62.459	-2.353
5900	9.629	80.331	71.571	30.644	63.000	-2.333
6000	9.641	80.493	71.719	30.490	63.545	-2.315

Mar. 31, 1964

Ground State Configuration $[^2\pi]$

$\Delta H_f^0 = [69 \pm 6] \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = [53.713] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^0 298.15 = [69 \pm 6] \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\frac{E_i, \text{ cm.}^{-1}}{0}$

$\mu_e = [700] \text{ cm.}^{-1}$

$\mu_e^X = [4.8] \text{ cm.}^{-1}$

$B_e = [0.5542] \text{ cm.}^{-1}$

$\alpha_e = [0.0052]$

$r_e = [1.85] \text{ \AA}$

Heat of Formation.

The $\Delta H_f^0 298.15$ for MgN was estimated from bond strengths using MgO and comparison with analogous pairs of compounds such as, PN and PO, and also the bond strengths of C-N and C-O in organic compounds.

Heat Capacity and Entropy.

The r_e value for MgN was estimated from MgO by comparison with similar pairs PO and PN, SiO and SiN, and AlO and AlN. Using Guggenheimer's Relation, Proc. Phys. Soc. (London) 59, 456 (1946), μ for MgO was found to lie between the single and multiple bonding cases. Magnesium nitride was assumed to be similar to MgO and giving $\mu_e^X = 4.8 \text{ cm.}^{-1}$. B_e was calculated from r_e . The α_e value was calculated from B_e , μ_e and μ_e^X .

Magnesium Oxide (MgO)

(Crystal)

Mol. Wt. = 40.3114

MgO

MOL. WT. = 40.3114

(CRYSTAL)

MAGNESIUM OXIDE (MgO)

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	1.000	INFINITE	1.235	-142.701	-142.701	-142.701	INFINITE	INFINITE
100	1.866	6.008	12.465	-143.163	-143.163	-140.920	307.066	3.07-066
200	6.370	3.369	7.177	-143.640	-143.640	-138.584	151.431	1.51-431
298	8.882	6.440	8.000	-143.700	-143.700	-135.985	99.675	0.99-675
300	8.915	6.495	8.016	-143.701	-143.701	-135.937	99.025	0.99-025
400	10.169	9.251	6.807	-143.709	-143.709	-133.346	72.025	0.72-025
500	10.848	11.598	7.537	-143.664	-143.664	-130.759	57.152	0.57-152
600	11.285	13.616	8.386	-143.603	-143.603	-128.185	46.689	0.46-689
1000	11.604	15.381	9.262	-143.540	-143.540	-125.620	39.218	0.39-218
1200	12.057	16.355	9.876	-143.486	-143.486	-123.052	31.518	0.31-518
1400	12.664	18.355	10.966	-143.463	-143.463	-120.512	25.740	0.25-740
1600	12.821	20.808	12.537	-143.571	-143.571	-115.003	22.848	0.22-848
1800	12.970	22.970	14.492	-145.577	-145.577	-112.224	20.438	0.20-438
2000	13.027	27.755	17.053	-145.577	-145.577	-109.181	18.398	0.18-398
2200	13.136	28.427	18.127	-173.548	-173.548	-101.203	14.745	0.14-745
2400	13.214	29.070	18.633	-173.548	-173.548	-96.251	13.147	0.13-147
2600	13.267	31.933	20.024	-171.634	-171.634	-91.317	11.739	0.11-739
2800	13.306	32.947	21.747	-171.634	-171.634	-86.514	10.374	0.10-374
3000	13.321	33.902	22.526	-170.429	-170.429	-81.514	9.375	0.09-375
3200	13.359	34.359	22.900	-169.605	-169.605	-76.642	8.471	0.08-471
3400	13.379	34.905	23.765	-168.187	-168.187	-71.788	7.471	0.07-471
3600	13.393	36.462	24.642	-167.484	-167.484	-66.948	6.650	0.06-500
3800	13.407	36.877	24.967	-167.053	-167.053	-62.348	5.930	0.05-930
4000	13.429	37.643	25.588	-166.589	-166.589	-57.540	4.569	0.04-569
4200	13.450	38.400	26.051	-166.107	-166.107	-52.540	4.015	0.04-015
4400	13.459	38.014	25.904	-165.750	-165.750	-47.768	3.461	0.03-461
4600	13.467	37.643	25.588	-165.484	-165.484	-43.012	2.928	0.02-928
4800	13.474	37.290	25.290	-165.226	-165.226	-38.269	2.410	0.02-410
5000	13.480	36.947	25.000	-164.970	-164.970	-33.541	1.901	0.01-901
5200	13.485	36.604	24.714	-164.714	-164.714	-28.829	1.391	0.01-391
5400	13.490	36.261	24.429	-164.457	-164.457	-24.127	0.881	0.00-881
5600	13.494	35.918	24.143	-164.200	-164.200	-19.443	0.371	0.00-371
5800	13.498	35.575	23.857	-163.943	-163.943	-14.768	0.000	0.00-000
6000	13.502	35.232	23.571	-163.686	-163.686	-9.900	0.000	0.00-000
6200	13.506	34.889	23.285	-163.429	-163.429	-5.032	0.000	0.00-000
6400	13.510	34.546	23.000	-163.172	-163.172	-0.164	0.000	0.00-000
6600	13.514	34.203	22.714	-162.915	-162.915	4.704	0.000	0.00-000
6800	13.518	33.860	22.429	-162.658	-162.658	9.596	0.000	0.00-000
7000	13.522	33.517	22.143	-162.401	-162.401	14.488	0.000	0.00-000
7200	13.526	33.174	21.857	-162.144	-162.144	19.380	0.000	0.00-000
7400	13.530	32.831	21.571	-161.887	-161.887	24.272	0.000	0.00-000
7600	13.534	32.488	21.286	-161.630	-161.630	29.164	0.000	0.00-000
7800	13.538	32.145	21.000	-161.373	-161.373	34.056	0.000	0.00-000
8000	13.542	31.802	20.714	-161.116	-161.116	38.948	0.000	0.00-000
8200	13.546	31.459	20.429	-160.859	-160.859	43.840	0.000	0.00-000
8400	13.550	31.116	20.143	-160.602	-160.602	48.732	0.000	0.00-000
8600	13.554	30.773	19.857	-160.345	-160.345	53.624	0.000	0.00-000
8800	13.558	30.430	19.571	-160.088	-160.088	58.516	0.000	0.00-000
9000	13.562	30.087	19.286	-159.831	-159.831	63.408	0.000	0.00-000
9200	13.566	29.744	19.000	-159.574	-159.574	68.300	0.000	0.00-000
9400	13.570	29.401	18.714	-159.317	-159.317	73.192	0.000	0.00-000
9600	13.574	29.058	18.429	-159.060	-159.060	78.084	0.000	0.00-000
9800	13.578	28.715	18.143	-158.803	-158.803	82.976	0.000	0.00-000
10000	13.582	28.372	17.857	-158.546	-158.546	87.868	0.000	0.00-000

The samples of (1) and (2) were finely divided magnesia and the other samples were periclase. Periclase is taken to be the standard state. The high temperature heat content data of (6) and (7) were joined by a Shomate plot with the low temperature C_p data of (4). The heat capacity was extrapolated linearly above 1800°K to a value of 14 cal. mole⁻¹ deg.⁻¹ at 3100°K. $S_{298.15}^o = 6.44$ cal. deg.⁻¹ mole⁻¹ is from (4).

Melting Data.

T_m (MgO, c) = 3088 ± 20°K by R. N. McNally, F. I. Peters, and F. H. Ribbe, J. Am. Ceram. Soc. **44**, 491 (1961) was adopted. Their value is 41°K higher than the earlier measurements of C. W. Knoll, J. Wash. Acad. Sci. **3**, 315 (1913). K. K. Kelley, Bur. Mines Bull. 395 (1956) calculated ΔH_m (MgO, c) = 18.5 ± 1.5 kcal./mole from melting point measurements in the MgO - ZnO system.

Sublimation Data.

T_b is the temperature at which the free energy change of the reaction $MgO(c) = MgO(g)$ approaches zero. The difference between ΔH_f^o 298.15 for MgO(c) and MgO(g) is ΔH_g^o 298.15.

MAGNESIUM OXIDE (MgO)

(LIQUID)

MOL. WT. = 40.3114

$\Delta H_f^0 298.15 = [12.033] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_m^0 298.15 = [-126.137] \text{ kcal. mole}^{-1}$
 $\Delta H_m^0 = [18.5 \pm 1.5] \text{ kcal. mole}^{-1}$
 $\Delta H_v^0 = [113.4] \text{ kcal. mole}^{-1}$
 $T_m = 3098^\circ \text{K.}$
 $T_B = [3533]^\circ \text{K.}$

Heat of Formation.

$\Delta H_f^0 298.15(1)$ was calculated from $\Delta H_f^0 298.15(c)$ by adding ΔH_m^0 and the difference between H_m^0 and liquid.

Heat Capacity and Entropy.

A glass transition is assumed at 2066°K. $C_p(1)$ below 2066°K. were assumed to be equal to those of $\text{MgO}(c)$. At and above 2066°K. the heat capacities were assumed to be constant at $7.25 \text{ cal. deg.}^{-1} \text{ g. atom}^{-1}$. The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgO(c) table for details.

Vaporization Data.

W. R. Mott, Tran. Am. Electrochem. Soc. 34, 255 (1918) estimated the boiling point at 3873°K. by comparing crater distances of arc energy deposits with reference compounds. $T_B = 3533^\circ \text{K.}$ is the temperature at which the free energy change of the reaction $\text{MgO}(l) = \text{MgO}(g)$ approaches zero. The difference between $\Delta H_f^0 3533$ for $\text{MgO}(g)$ and $\text{MgO}(l)$ is ΔH_v^0 .

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	cal. mole ⁻¹	Log K _p
0						
100	8.882	12.033	12.033	-126.137	-120.090	88.024
200						
298						
300	8.915	12.038	12.033	-126.138	-120.052	87.454
400	10.169	12.400	12.400	-126.146	-118.021	84.480
500	10.848	13.130	13.130	-126.101	-115.993	80.698
600	11.285	13.979	13.979	-126.040	-113.978	76.514
700	11.604	14.855	14.855	-125.977	-111.972	71.970
800	11.856	15.719	15.719	-125.927	-109.975	67.044
900	12.057	16.548	16.548	-125.880	-107.982	61.704
1000	12.232	17.361	17.361	-125.810	-105.981	55.981
1100	12.382	18.160	18.160	-125.728	-103.992	49.824
1200	12.507	18.944	18.944	-125.635	-101.972	43.182
1300	12.596	19.712	19.712	-125.532	-99.915	36.168
1400	12.664	20.464	20.464	-125.418	-97.825	28.795
1500	12.713	21.200	21.200	-125.295	-95.705	21.068
1600	12.831	21.925	21.925	-125.162	-93.558	13.090
1700	12.900	22.640	22.640	-125.020	-91.388	4.868
1800	12.978	23.348	23.348	-124.868	-89.198	-4.828
1900	13.057	24.050	24.050	-124.708	-86.992	-14.808
2000	13.136	24.750	24.750	-124.540	-84.772	-24.808
2100	14.500	25.450	25.450	-124.365	-82.538	-34.828
2200	14.500	26.150	26.150	-124.185	-80.292	-44.868
2300	14.500	26.850	26.850	-124.000	-78.032	-54.928
2400	14.500	27.550	27.550	-123.810	-75.762	-64.988
2500	14.500	28.250	28.250	-123.615	-73.488	-75.048
2600	14.500	28.950	28.950	-123.415	-71.212	-85.108
2700	14.500	29.650	29.650	-123.210	-68.932	-95.168
2800	14.500	30.350	30.350	-123.000	-66.648	-105.228
2900	14.500	31.050	31.050	-122.785	-64.358	-115.288
3000	14.500	31.750	31.750	-122.565	-62.062	-125.348
3100	14.500	32.450	32.450	-122.340	-59.762	-135.408
3200	14.500	33.150	33.150	-122.110	-57.458	-145.468
3300	14.500	33.850	33.850	-121.875	-55.152	-155.528
3400	14.500	34.550	34.550	-121.635	-52.842	-165.588
3500	14.500	35.250	35.250	-121.390	-50.528	-175.648
3600	14.500	35.950	35.950	-121.140	-48.212	-185.708
3700	14.500	36.650	36.650	-120.885	-45.892	-195.768
3800	14.500	37.350	37.350	-120.625	-43.568	-205.828
3900	14.500	38.050	38.050	-120.360	-41.242	-215.888
4000	14.500	38.750	38.750	-120.090	-38.912	-225.948
4100	14.500	39.450	39.450	-119.815	-36.582	-236.008
4200	14.500	40.150	40.150	-119.535	-34.248	-246.068
4300	14.500	40.850	40.850	-119.250	-31.912	-256.128
4400	14.500	41.550	41.550	-118.960	-29.572	-266.188
4500	14.500	42.250	42.250	-118.665	-27.228	-276.248
4600	14.500	42.950	42.950	-118.365	-24.882	-286.308
4700	14.500	43.650	43.650	-118.060	-22.532	-296.368
4800	14.500	44.350	44.350	-117.750	-20.178	-306.428
4900	14.500	45.050	45.050	-117.435	-17.822	-316.488
5000	14.500	45.750	45.750	-117.115	-15.468	-326.548

Magnesium Oxide (MgO)

(Ideal Gas) Mol. Wt. = 40.3114

MgO

MAGNESIUM OXIDE (MgO) (IDEAL GAS) MOL. WT. = 40.3114

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ ^o)/T	H° - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	6.909	INFINITE	2.411	1.122	1.122	INFINITE
100	6.939	46.139	50.295	1.403	1.403	INFINITE
200	7.104	49.983	53.562	1.615	1.615	3.655
298	7.498	52.889	56.889	1.900	1.900	3.768
300	7.506	52.936	56.936	1.906	1.906	3.768
400	8.189	55.151	59.166	2.189	2.189	3.401
500	8.682	56.946	60.961	2.473	2.473	3.099
600	8.996	58.459	62.474	2.747	2.747	2.827
700	9.135	59.765	63.780	3.021	3.021	2.574
800	9.224	60.813	64.828	3.295	3.295	2.339
900	9.283	61.677	65.692	3.569	3.569	2.116
1000	9.316	62.399	66.414	3.843	3.843	1.900
1100	9.339	62.999	66.999	4.117	4.117	1.684
1200	9.354	63.500	67.500	4.391	4.391	1.468
1300	9.366	63.918	67.918	4.665	4.665	1.252
1400	9.374	64.262	68.262	4.939	4.939	1.036
1500	9.379	64.542	68.542	5.213	5.213	0.820
1600	9.381	64.775	68.775	5.487	5.487	0.604
1700	9.381	64.970	68.970	5.761	5.761	0.388
1800	9.379	65.128	69.128	6.035	6.035	0.172
1900	9.374	65.258	69.258	6.309	6.309	-0.044
2000	9.366	65.360	69.360	6.583	6.583	-0.260
2100	9.354	65.436	69.436	6.857	6.857	-0.476
2200	9.339	65.488	69.488	7.131	7.131	-0.692
2300	9.321	65.518	69.518	7.405	7.405	-0.908
2400	9.299	65.526	69.526	7.679	7.679	-1.124
2500	9.274	65.512	69.512	7.953	7.953	-1.340
2600	9.246	65.478	69.478	8.227	8.227	-1.556
2700	9.214	65.425	69.425	8.501	8.501	-1.772
2800	9.178	65.354	69.354	8.775	8.775	-1.988
2900	9.138	65.268	69.268	9.049	9.049	-2.204
3000	9.094	65.168	69.168	9.323	9.323	-2.420
3100	9.046	65.056	69.056	9.597	9.597	-2.636
3200	8.994	64.934	68.934	9.871	9.871	-2.852
3300	8.938	64.802	68.802	10.145	10.145	-3.068
3400	8.878	64.660	68.660	10.419	10.419	-3.284
3500	8.814	64.508	68.508	10.693	10.693	-3.499
3600	8.746	64.347	68.347	10.967	10.967	-3.715
3700	8.674	64.177	68.177	11.241	11.241	-3.931
3800	8.598	64.000	68.000	11.515	11.515	-4.147
3900	8.518	63.816	67.816	11.789	11.789	-4.363
4000	8.434	63.626	67.626	12.063	12.063	-4.579
4100	8.346	63.430	67.430	12.337	12.337	-4.795
4200	8.254	63.228	67.228	12.611	12.611	-5.011
4300	8.158	63.020	67.020	12.885	12.885	-5.227
4400	8.058	62.806	66.806	13.159	13.159	-5.443
4500	7.954	62.587	66.587	13.433	13.433	-5.659
4600	7.846	62.363	66.363	13.707	13.707	-5.875
4700	7.734	62.134	66.134	13.981	13.981	-6.091
4800	7.618	61.900	65.900	14.255	14.255	-6.307
4900	7.498	61.661	65.661	14.529	14.529	-6.523
5000	7.374	61.418	65.418	14.803	14.803	-6.739
5100	7.246	61.171	65.171	15.077	15.077	-6.955
5200	7.114	60.920	64.920	15.351	15.351	-7.171
5300	6.978	60.665	64.665	15.625	15.625	-7.387
5400	6.838	60.406	64.406	15.899	15.899	-7.603
5500	6.694	60.143	64.143	16.173	16.173	-7.819
5600	6.546	59.876	63.876	16.447	16.447	-8.035
5700	6.394	59.605	63.605	16.721	16.721	-8.251
5800	6.238	59.330	63.330	16.995	16.995	-8.467
5900	6.078	59.051	63.051	17.269	17.269	-8.683
6000	5.914	58.768	62.768	17.543	17.543	-8.899

Dec. 31, 1960; Dec. 31, 1965

Ground State Configuration 3Σ
 $S_{298.15}^{\circ} = 52.889$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^{\circ} 298.15 = 1.0 \pm 20$ kcal. mole⁻¹
 $\Delta H_f^{\circ} 298.15 = 1.0 \pm 20$ kcal. mole⁻¹

Electronic Levels and Quantum Weights

ϵ_1 , cm.⁻¹ ϵ_2
 0 3
 $\omega_e = 902$ cm.⁻¹ $\omega_e x_e = 13.0$ cm.⁻¹ $\omega_e = 1$
 $B_e = [0.625]$ cm.⁻¹ $A_e = [0.0094]$ cm.⁻¹ $r_e = [1.672]$ Å

Heat of Formation.

There is considerable discordance in the heat of formation results even though results were adjusted to a common 3Σ ground state where necessary. A mean $\Delta H_f^{\circ} 298$ (MgO, g) = 1.0 ± 20 kcal. mole⁻¹ was selected.

R. L. Altman, J. Phys. Chem. 67, 366 (1963) made a Knudsen effusion and oxygen transpiration study of the vaporization of MgO. The predominant vapor species over MgO(c) were shown to be Mg(g) and O₂(g). MgO transpiration results with oxygen at 1 atm yielded a 3rd law heat of sublimation $\Delta H_{sub}^{\circ} 298$ (MgO, g) = 162.3 kcal. mole⁻¹ and $\Delta H_f^{\circ} 298$ (MgO, g) = 18.6 kcal. mole⁻¹.

J. Drowart, G. Exsteen and G. Verhaegen, Trans. Far. Soc. 50, 1920 (1954) used the Knudsen effusion-mass spectrometer technique to determine relative ion intensities and enthalpies for the reaction $MgO(g) + O(g) \rightarrow Mg(g) + O_2(g)$. After adjusting their values for a 3Σ ground state we calculated $\Delta H_f^{\circ} 298$ (MgO, g) = 11.9 kcal. mole⁻¹. Similar calculations for their data on $MgO(g) + WO_2(g) \rightarrow Mg(g) + WO_3(g)$ yielded $\Delta H_f^{\circ} 298$ = 10.5 kcal. mole⁻¹. The agreement is fortuitous, however, since uncertainties in the JANAF values for $WO_2(g)$ and $WO_3(g)$ are on the order of 7 kcal. each.

R. F. Porter, W. A. Chupka and M. O. Inghram, J. Chem. Phys. 23, 1347 (1955) mass spectrometrically determined an upper limit for the vapor pressure of MgO(g) over MgO(c) at 1950°K. Their results reduce to a lower limit of 148.6 kcal. mole⁻¹ for $\Delta H_f^{\circ} 298.15$ (MgO, c) or a lower limit of 4.9 kcal. mole⁻¹ for $\Delta H_f^{\circ} 298$ (MgO, g).

E. Bulewicz and T. Sugden, Trans. Far. Soc. 55, 720 (1959), using a flame photometric technique, reported $D_0^{\circ} = 98 \pm 2$ kcal. mole⁻¹ for MgO. $\Delta H_f^{\circ} 298$ (MgO, g) = -4.1 kcal. mole⁻¹ was calculated.

I. Veita and K. Gurvich, Optika and Spektroskopiya 2, 22 (1956) used a flame technique to obtain $D_0^{\circ} = 100$ kcal. mole⁻¹. A 4 kcal. mole⁻¹ adjustment for 1Σ to 3Σ yields $\Delta H_f^{\circ} 298$ (MgO, g) = -2.1 kcal. mole⁻¹.

The flame method data of L. Huldt and A. Lagerquist, Arkiv Fysik 2, 335 (1950) yielded a 3Σ adjusted $D_0^{\circ} = 115$ kcal. mole⁻¹. $\Delta H_f^{\circ} 298$ (MgO, g) = -21.1 kcal. mole⁻¹ was calculated.

L. Brewer and R. F. Porter, J. Chem. Phys. 22, 1876 (1954) have shown by vapor pressure measurements on MgO(c) that the solid vaporizes mainly into molecular species. They gave spectroscopic evidence that the 3Σ electronic state of MgO(g) is not the principal vaporizing species. Using their vapor pressures for the reaction $MgO(c) = MgO(g)$ and a 3Σ ground state we calculated 2nd and 3rd law heat of sublimation at 298°K. of 120.0 and 129.1 kcal. mole⁻¹. The 3rd law value yields $\Delta H_f^{\circ} 298$ (MgO, g) = -14.6 kcal. mole⁻¹.

Heat Capacity and Entropy.

The fundamental frequency and anharmonicity correction were reported by L. Brewer and R. Porter, J. Chem. Phys. 22, 1876 (1954) and are based on a 3Σ ground state. The rotational constants were estimated by H. L. Schick 35 al. AVCO Corp. RAD-SR-82-251, 15 Dec. 1962. Although the ground state and spectroscopic constants are in doubt, the free energies are probably within RT in 3 of true values.

MgO

Magnesium Metasilicate (MgSiO₃)

GFW = 100.3962

(Crystal)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	2.695	-368.018	-368.018	INFINITE
100	5.715	2.637	29.737	2.708	-369.090	-362.827	792.958
200	14.235	9.424	17.634	1.682	-369.951	-369.338	769.353
298	19.281	16.197	16.197	1.000	-370.200	-369.442	756.148
300	19.653	16.318	16.197	0.936	-370.203	-369.314	754.475
400	22.513	22.404	17.008	2.158	-370.269	-362.337	187.084
500	24.262	27.627	18.622	4.502	-370.207	-335.357	146.584
600	25.573	32.170	20.510	6.996	-370.081	-326.400	119.619
800	27.672	39.825	22.468	9.910	-369.918	-312.464	100.365
1000	28.762	43.139	26.314	12.328	-369.718	-314.528	85.913
				15.142	-369.498	-307.675	74.714
				18.176	-371.245	-300.652	65.707
1100	28.762	49.087	29.947	21.054	-371.045	-293.404	58.334
1300	28.762	54.218	33.282	27.218	-370.832	-286.569	52.191
1500	28.762	58.406	36.359	30.144	-400.718	-272.089	42.475
1700	28.762	62.068	39.173	38.923	-400.270	-265.916	38.307
1800	28.762	64.721	40.492	41.849	-411.423	-253.774	34.664
1900	28.762	66.824	42.473	47.701	-410.560	-244.551	31.439
2000	28.762	68.252	44.193	50.427	-409.489	-205.480	21.385
2100	28.762	69.277	45.270	51.554	-409.277	-195.765	19.447
2300	29.262	70.914	46.357	56.480	-408.872	-186.069	17.681
2400	29.262	72.159	47.407	59.406	-408.476	-176.389	16.062
2500	29.262	73.354	48.421	62.332	-408.090	-166.731	14.576

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967

S°_{298.15} = 18.197 ± 0.2 gibbs/molT₁ = 903 °KT₂ = 1258 °K

Tm = 1850 ± 2 °K

Heat of Formation

Torgeson et al. (1) report a $\Delta H_{298}^\circ = -8.69 \pm 0.15$ kcal/mol for reaction (a). They used a hydrofluoric acid solution calorimeter and measured the heats of solution of each component. They appear to have made the water-absorption correction to the heat of solution of SiO₂(c) in the wrong direction. We reverse the correction so that the new ΔH_{298}° almost overlaps the range observed by King (11). We derive ΔH_{298}° (MgSiO₃, c) = -370.20 ± 1.0 kcal/mol using the ΔH_{298}° of MgO(c) and SiO₂ (c, low quartz) from the JANAF tables.

Reesman et al. (2) calculated a $\Delta G_{298}^\circ = 23.72$ kcal/mol for reaction (b) using aqueous solubility data. We use the ΔG_{298}° of H₂O(l) and OH⁻(aq) from source 3, ΔG_{298}° of H₄SiO₄(aq) from source 4 and ΔG_{298}° of Mg⁺⁺(aq) from source 5 and we obtain a ΔG_{298}° (MgSiO₃, c) = -332.534 kcal/mol. We derive a ΔH_{298}° (MgSiO₃, c) = -373.253 kcal/mol using the above ΔG_{298}° of MgSiO₃(c) and the entropies of Mg(c), Si(c) and O₂(g) from the JANAF tables.

We choose the heat of formation derived from the Torgeson et al. (1) which is considered to be better since it relates directly to the oxides. Also the ΔG_{298}° (MgSiO₃, c) thus calculated is in very good agreement with that derived from the activities of SiO₂ and MgO (in the SiO₂-MgO system) measured by Rein et al. (9). The ΔH_{298}° (MgSiO₃, c) derived from the work of Reesman et al. is less accurate and involves uncertainties in the auxiliary data used to calculate the value.

Source	Method	Reaction	ΔH_{298}° kcal/mol	ΔG_{298}° kcal/mol
Torgeson et al.	HF solution calorimeter	(a) MgO(c)+SiO ₂ (c) = MgSiO ₃ (c)		ΔH_{298}°
Reesman et al.	Aqueous solubility	(b) MgSiO ₃ (c)+H ₂ O(l) = Mg ⁺⁺ (aq) + H ₄ SiO ₄ (aq)+2OH ⁻ (aq)	-8.740.16	-370.20
			23.72	-373.3

Source

1. D. R. Torgeson and Th. G. Sahara, J. Am. Chem. Soc. 70, 2156 (1948).
2. A. L. Reesman and W. D. Keller, Am. Mineralogist 50, 1779-39 (1965).
3. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
4. U. S. Natl. Bur. Std. Tech. Note 270-2, 1966.
5. U. S. Natl. Bur. Std. Circ. 500, 1962.
6. R. H. Rein and J. Chipman, Trans. AIME 233, 415-425 (1965).
7. K. X. Kelley, J. Am. Chem. Soc. 65, 339-41 (1943).
8. H. Wagner, Z. Anorg. Allgem. Chem. 208, 1-22 (1932).
9. F. R. Boyd and J. L. England, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 117-120 (1965).
10. L. Atlas, J. Geol. 60, 125-47 (1952).
11. D. A. Stephenson, C. B. Sclar and J. V. Smith, Mineral. Mag. 35, 839-48 (1966).
12. J. V. Smith, Acta Cryst. 12, 515 (1959).
13. F. R. Boyd, J. L. England and B. T. C. Davis, J. Geophys. Res. 69 (10), 2101 (1964).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (53 - 295°K) of Kelley (2). Wagner (9) measured the average heat capacities in the temperature range 580 - 1570°K. Using his data we derive the high temperature heat capacities which are joined smoothly with the low temperature values by a constrained fitting technique. The Cp values at 903 - 1258°K and above 1258°K are derived as 28.762 and 29.262 gibbs/mol, respectively, by assuming that the data of Wagner (9) pertain to the stable phase in these regions. The entropy is based on S°₀ = 0.49 eu.

Transition Data

T₁ = 903°K is obtained from Boyd et al. (9). The authors determined the phase diagram boundary at high pressures and extrapolated to one atmosphere. T₂ = 1258°K is taken from Atlas (10). Below 903°K the phase is known as clinonastatite. Between 903° and 1258°K it is rhombic enstatite and above 1258°K it is protonastatite. We calculate ΔH_{298}° and ΔH_{298}° from dT/dP (slopes of the isotherms) = 2.6°/kbar and 84°/kbar reported by Boyd et al. (9, 11) and from the densities of clinonastatite (3.210 gm/cc) and rhombic enstatite (3.208 gm/cc) reported by Stephenson et al. (11) and the density of protonastatite (3.10 gm/cc) reported by Smith (12).

Melting Data

See liquid table.

Magnesium Metasilicate (MgSiO_3)

(Liquid) GFW = 100.3962

T, °K	Cp*	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
100							
200							
298	19.581	22.112	22.112	.000	-357.281	-338.287	247.971
300	19.653	22.233	22.112	.036	-357.284	-338.169	246.356
400	22.513	28.319	22.923	2.158	-357.350	-331.278	181.278
500	24.262	33.542	24.537	4.502	-357.286	-325.396	142.230
600	25.373	38.085	26.425	6.996	-357.144	-319.030	116.006
700	27.472	42.628	28.911	9.491	-357.199	-312.085	93.629
800	29.672	45.740	30.330	12.328	-356.799	-306.371	83.697
900	31.000	49.054	32.229	15.142	-356.579	-300.079	72.869
1000	35.000	52.741	34.099	18.642	-357.862	-293.664	64.190
1100	35.000	56.077	35.948	22.142	-357.058	-287.287	57.079
1200	35.000	59.753	37.754	25.642	-356.848	-280.276	50.773
1300	35.000	61.924	39.507	29.142	-355.595	-273.729	46.186
1400	35.000	64.518	41.202	32.642	-348.300	-268.055	41.845
1500	35.000	66.933	42.838	36.142	-384.279	-259.715	37.860
1600	35.000	69.192	44.415	39.642	-383.276	-251.445	34.346
1700	35.000	71.314	47.401	46.642	-383.268	-231.268	28.444
1800	35.000	73.318	48.816	50.142	-392.255	-235.861	25.934
1900	35.000	75.206	50.180	53.642	-391.250	-216.709	23.681
2000	35.000	77.002	51.899	57.142	-390.255	-208.006	21.688
2100	35.000	78.709	51.899	60.642	-389.255	-199.351	19.694
2200	35.000	80.137	54.773	64.142	-388.291	-190.741	18.124
2300	35.000	81.893	54.005	67.642	-387.321	-182.170	16.589
2400	35.000	83.383	55.198	71.142	-386.361	-173.647	15.160
2500	35.000	84.812	56.355	74.642	-385.407	-165.156	13.882
2600	35.000	86.188	57.676	78.142	-384.454	-156.703	12.604
2700	35.000	87.554	59.054	81.642	-383.526	-148.283	11.574
2800	35.000	88.778	59.650	85.142	-382.598	-139.895	10.543
2900	35.000	90.006	60.647	88.642	-381.680	-131.543	9.593
3000	35.000	91.193	61.645				

MAGNESIUM METASILICATE (MgSiO_3) (LIQUID)

S°_{298.15} = 122.112 J/gibbs/mol

T₁ = 903 °K

T₂ = 1258 °K

T_m = 1850 ± 2 °K

Heat of Formation

The heat of formation is obtained from ΔHf°₂₉₈(c) by adding ΔHm° and the difference between H°_m - H°₂₉₈ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 900°K. Below 900°K the heat capacity is obtained from the heat capacity of the crystal.

Above 900°K the heat capacity is assumed constant and estimated as 35 gibbs/mol or 7 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Transition Data

See crystal table.

Melting Data

T_m is taken from M. L. Bowen and O. Andersen, Am. J. Sci. 27, 487 (1914). MgSiO_3 (c) melts incongruently in the temperature range 1830 - 1850°K at atmospheric pressure. ΔHm° is estimated from the phase diagrams of the MgSiO_3 - TiO_2 system reported by

I. D. MacGregor, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 135-9 (1965). The phase diagrams were determined at 10 and 20 kbars pressure where MgSiO_3 (c) melts congruently.

MgO_3Si

GFW = 100.3962

ΔHf°_{298.15} = [-357.281 ± 5] kcal/mol

ΔHf°₁ = 0.16 kcal/mol

ΔHf°₂ = 0.39 kcal/mol

ΔHm° = [18 ± 5] kcal/mol

MgO_3Si

MAGNESIUM METATITANATE (MgTiO₃) (CRYSTAL) GFW = 120.2102

T, °K	C _p ^a	gibbs/mol S ^b - (C _p ^a - H ^c)/T	H ^c - H ¹⁰⁰⁰	kcal/mol ΔH ^c	ΔG ^d	Log K _p
0	.000	INFINITE	3.240	-373.630	-373.630	INFINITE
100	6.397	2.595	3.125	-374.772	-374.772	189.331
200	16.222	10.157	1.942	-375.851	-375.851	185.281
298	21.980	17.320	.000	-375.850	-375.734	260.027
300	22.037	17.956	.041	-375.851	-374.603	258.328
400	28.154	28.763	2.414	-375.776	-375.523	189.879
500	27.337	30.593	5.030	-375.544	-370.487	148.027
600	24.311	35.442	7.491	-375.281	-331.505	121.879
700	20.243	40.079	10.681	-374.907	-326.574	101.961
800	20.267	44.033	13.643	-374.577	-319.693	87.336
900	30.556	47.597	16.670	-374.268	-312.930	75.970
1000	31.256	50.843	19.751	-373.110	-305.959	66.845
1100	31.495	53.424	22.879	-375.832	-298.569	59.376
1200	31.491	56.582	26.049	-376.513	-291.425	53.149
1300	32.259	59.149	29.254	-376.158	-284.782	47.876
1400	32.606	61.553	32.500	-406.184	-277.288	43.287
1500	32.940	63.814	35.777	-405.455	-269.106	39.063
1600	33.246	65.950	39.087	-404.720	-259.973	35.374
1700	33.598	67.976	42.430	-403.980	-249.885	32.125
1800	33.910	69.905	45.805	-403.241	-240.842	29.242
1900	34.233	71.747	49.212	-402.499	-231.850	26.668
2000	34.559	73.511	52.652	-401.755	-222.725	24.338
2100	34.890	75.206	56.124	-400.937	-213.570	22.227
2200	35.228	76.836	59.630	-400.066	-204.451	20.310
2300	35.572	78.410	63.170	-400.827	-195.370	18.564
2400	35.925	79.931	66.745	-402.982	-186.322	16.967
2500	36.287	81.405	70.355	-402.112	-177.317	15.501
2600	36.659	82.836	74.002	-401.211	-168.342	14.150
2700	37.040	84.226	77.687	-400.282	-159.401	12.903
2800	37.432	85.560	81.411	-399.322	-150.498	11.747
2900	37.835	86.801	85.174	-398.331	-141.585	10.673
3000	38.250	88.190	88.978	-397.308	-132.790	9.674

$$\Delta H_f^\circ = -373.63 \pm 1.5 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -375.85 \pm 1.5 \text{ kcal/mol}$$

$$\Delta H_m^\circ = [21.6] \text{ kcal/mol}$$

$$S_{298.15}^\circ = 17.82 \pm 0.1 \text{ gibbs/mol}$$

$$T_m = 1953 \pm 20^\circ \text{K}$$

Heat of Formation

The adopted heat of formation is calculated from $\Delta H_f^\circ = -6.35 \pm 0.25 \text{ kcal/mol}$ for the reaction

$\text{MgO(c)} + \text{TiO}_2(\text{rutile}) + \text{MgTiO}_3(\text{c})$ measured by K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954, using a solution calorimetric method. For the same reaction a value of $\Delta H_f^\circ = -5.5 \pm 0.1 \text{ kcal/mol}$ was obtained with a calorimetric bomb method by B. I. Ronfilov and N. N. Feodos'ev, Russ. J. Inorg. Chem. (English Transl.) 3, 1452 (1964). These authors used the oxidation of lampblack in order to initiate the formation of the titanate from the oxides. Unfortunately the desired heat of reaction was only 1.2 to 1.5 percent of the total measured heat, and consequently this result appears to be more uncertain than that measured by the solution calorimetric method.

Heat Capacity and Entropy

Low temperature heat capacities are from the data ($52 - 298^\circ \text{K}$) of C. H. Shonate, J. Am. Chem. Soc. 67, 964 (1946). High temperature enthalpies have been measured ($402 - 1720^\circ \text{K}$) by B. F. Naylor and O. A. Cook, J. Am. Chem. Soc. 68, 1003 (1946). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S_2^\circ = 0.45 \text{ eu}$.

Melting Data

See liquid table.



GFW = 120.2102

(LIQUID)

MAGNESIUM METATITANATE (MgTiO₃)

$$\Delta H_f^{298.15} = [-357.842 \pm 1.5] \text{ kcal/mol}$$

$$\Delta H_m^* = [21.6] \text{ kcal/mol}$$

$$S_{298.15}^* = [26.549] \text{ gibbs/mol}$$

$$T_m = 1953 \pm 20^\circ\text{K}$$

Heat of Formation

ΔH_f^{298} is obtained from $\Delta H_f^{298}(c)$ by adding ΔH_m^* and the difference between H_{298}^* and H_{298} for crystal and liquid.

Heat Capacity and Entropy

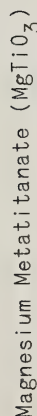
A glass transition is assumed at 1300°K. The heat capacity below 1300°K is obtained from the heat capacity of the crystal. Above 1300°K the heat capacity is assumed constant and estimated as 39 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The incongruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) indicates congruent melting point at 1903°K. The ΔH_m^* is estimated from those of Na₂O·2TiO₂ and Na₂O·TiO₂ observed by Naylor (3) and CaO·TiO₂·SiO₂ observed by King (4).

Reference

1. F. Massazza and E. Sirochia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. Depressse, J. Res. Natl. Bur. Std. 51, 87 (1953).
3. B. F. Naylor, J. Am. Chem. Soc. 67, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. 76, 4320 (1954).



(Liquid) Mol. Wt. = 120.2102

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f	ΔG _f	Log K _p
0							
100							
200	21.960	26.549	26.549	.000	-357.942	-339.428	248.007
300	22.037	26.685	26.549	.041	-357.943	-339.313	247.189
400	22.154	26.892	26.549	2.418	-357.845	-333.109	182.002
500	27.337	39.322	29.261	5.030	-357.636	-326.943	142.907
600	28.311	44.371	31.366	7.801	-357.333	-320.838	116.966
700	28.311	44.371	31.366	10.691	-356.989	-314.776	98.277
800	29.267	52.762	35.708	13.693	-356.669	-308.778	84.352
900	30.556	56.326	37.404	16.670	-356.360	-302.798	73.529
1000	31.056	59.372	39.421	19.751	-356.202	-296.680	64.839
1100	31.495	62.553	41.754	22.879	-357.028	-290.583	57.726
1200	31.800	65.878	44.371	26.061	-357.845	-284.502	51.795
1300	32.000	67.478	45.373	29.256	-358.250	-278.292	46.773
1400	32.000	70.768	47.095	33.156	-358.619	-271.624	42.402
1500	32.000	73.459	48.755	37.056	-358.268	-263.356	38.375
1600	32.000	75.376	50.376	40.956	-358.043	-255.238	34.944
1700	32.000	77.481	52.956	44.856	-357.845	-247.269	31.776
1800	32.000	80.570	55.483	48.756	-357.636	-239.150	29.040
1900	32.000	82.678	58.964	52.656	-357.427	-231.257	26.601
2000	32.000	84.678	62.400	56.556	-357.218	-223.243	24.393
2100	32.000	86.581	65.723	60.456	-357.009	-215.218	22.398
2200	32.000	88.481	69.046	64.356	-356.800	-207.218	20.588
2300	32.000	90.129	72.369	68.256	-356.591	-199.243	18.941
2400	32.000	91.789	75.692	72.156	-356.382	-191.462	17.435
2500	32.000	93.381	79.015	76.056	-356.173	-183.688	16.054
2600	32.000	94.911	82.338	79.956	-355.964	-175.935	14.784
2700	32.000	96.401	85.661	83.856	-355.755	-168.208	13.611
2800	32.000	97.851	88.984	87.756	-355.546	-160.504	12.525
2900	32.000	99.170	92.307	91.656	-355.337	-152.815	11.516
3000	32.000	100.492	95.630	95.556	-355.128	-145.210	10.579
3100	32.000	101.771	98.898	99.456	-354.919	-137.640	9.704
3200	32.000	103.009	102.121	103.356	-354.710	-130.083	8.894
3300	32.000	104.209	104.366	107.256	-354.501	-122.613	8.120
3400	32.000	105.373	106.530	111.156	-354.292	-115.143	7.401
3500	32.000	106.504	107.650	115.056	-354.083	-107.716	6.726
3600	32.000	107.602	108.722	118.956	-353.874	-100.243	6.073
3700	32.000	108.711	109.756	122.856	-353.665	-92.773	5.440
3800	32.000	109.781	110.781	126.756	-353.456	-85.302	4.822
3900	32.000	110.724	111.722	130.656	-353.247	-77.831	4.216
4000	32.000	111.711	112.711	134.556	-353.038	-70.360	3.624



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S ⁰ -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	- 3.678	- 288.853	- 288.853	INFINITE
100	8.679	38.312	- 3.354	- 300.273	- 281.022	637.695
200	21.521	23.751	- 2.008	- 301.242	- 283.258	209.540
298	23.000	21.844	0.000	- 301.574	- 274.251	201.038
300	23.050	21.987	0.043	- 301.578	- 274.092	199.675
400	26.290	29.085	2.518	- 302.238	- 264.885	144.726
500	28.540	35.199	5.262	- 302.536	- 255.506	111.662
600	30.500	40.581	8.217	- 302.617	- 246.090	89.438
700	32.100	45.404	11.348	- 302.535	- 236.648	75.689
800	33.580	49.788	14.653	- 315.396	- 228.519	62.428
900	34.950	53.823	18.060	- 314.796	- 217.693	52.863
1000	36.250	57.574	21.621	- 316.249	- 206.756	45.187
1100	37.450	61.086	25.306	- 315.487	- 195.848	38.911
1200	38.560	64.394	29.100	- 314.651	- 185.006	33.494
1300	39.620	67.520	33.016	- 313.756	- 174.237	28.292
1400	40.601	70.578	37.008	- 313.183	- 163.061	23.455
1500	40.953	73.282	41.072	- 341.806	- 150.244	21.691
1600	41.536	75.944	45.107	- 340.380	- 137.519	18.784
1700	42.040	78.478	49.376	- 338.911	- 124.884	15.955
1800	42.490	80.894	53.603	- 337.459	- 112.359	13.440
1900	42.896	83.202	57.873	- 335.875	- 99.874	11.468
2000	43.268	85.412	62.161	- 334.315	- 87.497	9.961
2100	43.611	87.531	66.525	- 332.730	- 75.194	7.826
2200	43.931	89.567	70.903	- 331.125	- 62.965	6.255
2300	44.232	91.527	75.311	- 329.499	- 50.815	4.829
2400	44.517	93.415	79.748	- 327.856	- 38.730	3.527
2500	44.788	95.238	84.214	- 326.197	- 26.722	2.336

$\Delta H_f^0 = -298.8 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 \text{ 298.15} = -301.6 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 3.5 \text{ kcal. mole}^{-1}$

$S_{298.15}^0 = 21.844 \pm 0.2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1400^\circ \text{K.}$

Heat of Formation.

The adopted $\Delta H_f^0 \text{ 298.15} = -301.6 \pm 5 \text{ kcal. mole}^{-1}$ was calculated from the $\Delta H_f^0 \text{ 298.15} = 63.3 \pm 5 \text{ kcal. mole}^{-1}$ for the reaction $\text{MgO(c)} + \text{SO}_3(\text{g}) = \text{MgSO}_4(\text{c})$. The value of $\Delta H_f^0 \text{ 298.15}$ was calculated by the third law method using the equilibrium data obtained from a transpiration study by Knopf and Staude.¹ In addition Marchal² measured the total pressure of $\text{SO}_3(\text{g})$, $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$ above $\text{MgSO}_4(\text{c})$ and partial pressures were obtained by application of the $\text{SO}_2\text{-SO}_3$ equilibrium data. Another value of $\Delta H_f^0 \text{ 298.15}$ (MgSO_4 , c) may be derived from the measured heat of solution of $\text{MgSO}_4(\text{c})$ by Thomsen^{3a} and the measured heats of mixing of $\text{MgCl}_2(200 \text{ H}_2\text{O})$ with $\text{H}_2\text{SO}_4(200 \text{ H}_2\text{O})$ and $\text{MgSO}_4(200 \text{ H}_2\text{O})$ with $2\text{HCl}(100 \text{ H}_2\text{O})$ by Thomsen^{3b}.

References	Reaction	T, °K. range	Third Law drift, e.u.	$\Delta H_f^0 \text{ 298.15}$ kcal. mole ⁻¹	$\Delta H_f^0 \text{ 298.15}$ kcal. mole ⁻¹
1	$\text{MgO(c)} + \text{SO}_3(\text{g}) = \text{MgSO}_4(\text{c})$	1144-1313	0.514	63.284	-301.574
2	$\text{MgO(c)} + \text{SO}_3(\text{g}) = \text{MgSO}_4(\text{c})$	1223-1428	0.525	72.394	-310.867
3a	$\text{MgSO}_4(\text{c}) \rightarrow \text{MgSO}_4(200 \text{ H}_2\text{O})$	298.15		-20.84	
3b	$\text{MgCl}_2(200 \text{ H}_2\text{O}) + \text{H}_2\text{SO}_4(200 \text{ H}_2\text{O}) \rightarrow \text{MgSO}_4(200 \text{ H}_2\text{O}) + 2\text{HCl}(100 \text{ H}_2\text{O})$	298.15		- 3.52	-305.1*

*Combination of the reactions 3a and 3b with the following $\Delta H_f^0 \text{ 298.15}$: $\text{H}_2\text{SO}_4(200 \text{ H}_2\text{O}) = -212.587$, $\text{HCl}(100 \text{ H}_2\text{O}) = -39.74$ and $\text{MgCl}_2(200 \text{ H}_2\text{O}) = -189.5 \text{ kcal. mole}^{-1}$.

References

- 1 H. J. Knopf and H. Staude, Z. physik. Chem. (Leipzig) **204**, 265-275 (1955).
- 2 G. Marchal, J. Chim. Phys. **22**, 493 (1925).
- 3a and 3b J. Thomsen, "Thermochemische Untersuchungen," vols I-IV, Barth, Leipzig (1892-1896).

Heat Capacity and Entropy.

The low temperature heat capacities $53.3\text{-}295.4^\circ \text{K.}$ were measured by G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **64**, 2949 (1942). The heat capacities in the temperature range $298\text{-}1400^\circ \text{K.}$ were estimated from the equation $\text{MgSO}_4(\text{c}) = \text{CaSO}_4(\text{c}) + \text{MgO(c)} - \text{CaO(c)}$. $\text{CaSO}_4(\text{c})$ and CaO(c) C_p were calculated using the equations $C_p = 16.78 + 23.60 \times 10^{-3} T$ and $C_p = 11.67 + 1.08 \times 10^{-3} T - 1.56 \times 10^{-6} T^2$ respectively, K. K. Kelley, U. S. Bur. Mines Bull. **584** (1960). The heat capacity of MgO(c) was calculated from the correlation of the low temperature heat capacities and high temperature heat content using the Shomate functions to back calculate the heat capacities. The values from the two sources join smoothly at 298°K. Above the melting point (1400°K.) the heat capacity was graphically extrapolated. The entropy was calculated at 50.12°K. using the Debye and Einstein function $D(\frac{298}{50.12}) + 2E(\frac{298}{50.12}) + E(\frac{298}{50.12})$ given by G. E. Moore and K. K. Kelley loc. cit. The value of $S_{50.12}^0 = 1.08 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m and ΔH_m from K. K. Kelley, U. S. Bur. Mines Bull. **393** (1956).

Magnesium Sulfate (MgSO₄)

(Liquid) Mol. Wt. = 120.3736

MgO₄S

T, °K.	C _p	S° - (F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100								
200								
298	23.000	24.464	24.464	-	0.000	-297.864	-271.332	198.892
300								
350	23.050	24.606	24.606		0.053	-297.868	-271.167	197.545
400	23.290	31.705	25.010		2.518	-298.528	-262.223	143.272
500	28.540	37.818	27.295		5.262	-298.826	-253.106	110.632
600	30.500	43.201	29.506		8.217	-298.907	-243.952	88.659
700	32.100	48.024	31.613		11.348	-298.825	-234.672	73.689
800	33.450	52.148	33.625		14.479	-298.585	-225.381	61.689
900	34.590	55.427	35.376		18.006	-311.100	-216.341	52.535
1000	35.600	58.028	36.877		21.676	-312.484	-205.665	44.948
1100	36.000	60.248	38.573					
1200	36.000	63.870	40.710		25.476	-311.607	-195.031	38.749
1300	36.000	67.176	42.780		29.276	-310.774	-184.468	33.596
1400	36.000	70.132	44.502		32.876	-309.985	-173.061	28.585
1500	36.000	72.656	45.939		36.205	-309.235	-160.861	23.655
1600	36.000	74.818	47.108		40.676	-308.492	-150.491	21.927
1700	36.000	76.512	48.142		44.476	-307.761	-137.993	18.849
1800	36.000	77.839	49.015		48.276	-306.931	-125.563	15.142
1900	36.000	78.839	49.630		51.876	-306.000	-113.133	11.605
2000	36.000	79.598	50.030		55.230	-304.976	-100.892	9.687
2100	36.000	80.000	50.311		58.476	-303.761	-88.644	7.956
2200	36.000	80.210	50.630		63.476	-302.069	-76.447	6.387
2300	36.000	80.210	50.630		67.276	-301.042	-64.257	5.087
2400	36.000	80.210	50.630		74.876	-300.018	-52.068	3.655
2500	36.000	80.210	50.630		81.476	-300.018	-40.135	2.459
2600	36.000	80.210	50.630		86.976	-300.018	-28.123	

MAGNESIUM SULFATE (MgSO₄) (LIQUID)

MOL. WT. = 120.3736

ΔH_f^o 298.15 = -297.9 ± 5 kcal. mole⁻¹

ΔH_m^o = 3.5 kcal. mole⁻¹

S_{298.15}^o = 24.464 ± 0.2 cal. deg.⁻¹ mole⁻¹

T_m = 1400°K.

Heat of Formation.

The ΔH_f^o 298.15 was obtained from ΔH_f^o 298.15(c) by adding ΔH_m^o and the difference between H_m^o - H_{298.15}^o for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 1000°K. The heat capacity below 1000°K. was obtained from the heat capacity of the crystal. Above 1000°K. the heat capacity was assumed constant and estimated as 38.0 cal. deg.⁻¹ mole⁻¹ by comparison with those for MgCl₂(l), KCl(l) and K₂SO₄(l). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See MgSO₄(c) table.

MgO₄S

MAGNESIUM TUNGSTATE (MgWO₄)

(CRYSTAL)

GFW = 272.1596

$\Delta H_f^\circ = -359.9 \pm 8$ kcal/mol
 $\Delta H_f^\circ = -382.3 \pm 8$ kcal/mol
 $\Delta H_f^\circ = \text{Unknown}$

$S_{298.15}^\circ = 24.18 \pm 0.2$ gibbs/mol
 $T_m = \text{Unknown}$

Heat of Formation.

T. N. Rezukhina and V. A. Levitskii¹ measured the emf, $E = 0.2453 - 0.001264T$, for the cell reaction $\text{MgO}(c) + \text{W}(c) + 3\text{FeO}_{0.95}\text{O}(c) \rightarrow \text{MgWO}_4(c) + 2.85 \text{Fe}(c)$, in the temperature range $1220^\circ - 1370^\circ \text{K}$. Incorporating the results with auxiliary thermal data, the authors obtained $\Delta H_f^\circ = -224,370 + 65.67T$ (cal/mol) for $\text{MgO}(c) + \text{W}(c) + 3/2\text{O}_2(g) \rightarrow \text{MgWO}_4(c)$. Third law analysis of the ΔH_f° equation gives $\Delta H_f^\circ = -218.6$ kcal/mol, from which the adopted $\Delta H_f^\circ(298 \text{ MgWO}_4, c)$, -362.3 kcal/mol, is calculated. The second law analysis gives $\Delta H_f^\circ(298 \text{ MgWO}_4, c) = -372.7$ kcal/mol. The drift in the third law analysis is 8.0 eu.

T. N. Rezukhina, Ya. I. Gerasimov and Yu. P. Simanov² determined the Gibbs energy changes $\Delta G_r^\circ = 51,300 - 27.67T$ (cal/mol) for the reaction $\text{MgWO}_4(c) + 3\text{H}_2(g) \rightarrow \text{MgO}(c) + \text{W}(c) + 3\text{H}_2\text{O}(g)$ in the temperature range $1073^\circ \text{K} - 1273^\circ \text{K}$ by a circulation method. This leads to heats of formation of -366.1 kcal/mol by the third law method and -377.2 kcal/mol by the second law method. Both determinations were performed by Rezukhina and his co-workers, but they considered the data obtained by the emf method to be more reliable than that derived from heterogeneous equilibria.

Heat Capacity and Entropy.

Low temperature heat capacities, $52.92^\circ - 296.09^\circ \text{K}$, were measured calorimetrically by E. G. King and W. W. Weller³. The heat capacities above 300°K are estimated by comparison with those of $\text{CaWO}_4(c)$ ⁴, $\text{CaO}(c)$ ⁵, and $\text{MgO}(c)$ ⁶. These two sets of data are joined smoothly at 298°K by a graphical method.

The entropy, $S_{298}^\circ = 21.184$ eu, is taken from King and Weller³, based on an extrapolation of $S_{517}^\circ = 1.27$ eu. No spin-magnetic entropy is predicted below 51°K based on the diamagnetism observed by Ya. I. Gerasimov⁷.

References.

1. T. N. Rezukhina and V. A. Levitskii, Russ. J. Phys. Chem. (English Transl.) **37**, 1277 (1963).
2. T. N. Rezukhina, Ya. I. Gerasimov and Yu. P. Simanov, Vestnik Moskov. Univ. **4**, No. 6, 103 (1949).
3. E. G. King and W. W. Weller, U. S. Bur. Mines Rept. Invest. 5791 (1961).
4. R. A. Yakovleva and T. N. Rezukhina, Russ. J. Phys. Chem. (English Transl.) **34**, 390 (1960).
5. K. K. Kelley, U. S. Bur. Mines Bull. 564 (1960).
6. JANAP MgO table (Dec. 31, 1965).
7. Ya. I. Gerasimov, Papers Presented to Section on Inorganic Chemistry, 16th Intern. Congress Pure and Applied Chem. Paris (1957), pp. 227-35, Butterworths Scientific Publications, London, 1958.

Magnesium Dtitatanate (MgTi₂O₅)
(Crystal) GFW = 200.109

T, °K	Cp ^a	gibbs/mol S ^b - (C ^a - H ²⁹⁸)/T	h ^c - H ²⁹⁸ /T	ΔH ^c	ΔG ^f	Log K ^p
0						
100	11.200	5.000	INFINITE	-594.825	-594.825	INFINITE
200	26.818	19.078	57.246	-596.213	-597.774	1284.576
298	35.100	32.410	32.410	-599.500	-574.872	630.376
300	35.214	32.627	32.411	-599.750	-566.189	615.028
400	39.516	43.424	43.424	-599.515	-565.981	612.317
500	42.824	52.563	52.563	-599.275	-565.731	609.587
600	44.996	60.434	60.434	-598.844	-565.450	606.845
700	45.604	67.348	67.348	-598.367	-565.140	604.095
800	44.911	73.225	73.225	-597.880	-564.804	601.352
900	44.997	79.120	79.120	-597.397	-564.453	598.609
1000	44.204	84.245	84.245	-596.906	-564.098	595.866
1100	50.259	88.984	88.984	-596.415	-563.743	593.123
1200	51.276	93.401	93.401	-595.924	-563.388	590.380
1300	52.266	97.545	97.545	-595.433	-563.033	587.637
1400	53.236	101.454	101.454	-594.942	-562.678	584.894
1500	54.190	105.159	105.159	-594.451	-562.323	582.151
1600	55.132	108.687	108.687	-593.960	-561.968	579.408
1700	56.064	112.057	112.057	-593.469	-561.613	576.665
1800	56.984	115.288	115.288	-592.978	-561.258	573.922
1900	57.900	118.389	118.389	-592.487	-560.903	571.179
2000	58.819	121.387	121.387	-591.996	-560.548	568.436
2100	59.728	124.279	124.279	-591.505	-560.193	565.693
2200	60.633	127.078	127.078	-591.014	-559.838	562.950
2300	61.534	129.793	129.793	-590.523	-559.483	560.207
2400	62.433	132.431	132.431	-590.032	-559.128	557.464
2500	63.330	134.996	134.996	-589.541	-558.773	554.721
2600	64.224	137.499	137.499	-589.050	-558.418	551.978
2700	65.117	139.940	139.940	-588.559	-558.063	549.235
2800	66.008	142.324	142.324	-588.068	-557.708	546.492
2900	66.998	144.656	144.656	-587.577	-557.353	543.749
3000	67.787	146.939	146.939	-587.086	-557.000	541.006

MAGNESIUM DITITANATE (MgTi₂O₅) (CRYSTAL)

GFW = 200.109

$$\Delta H_f^\circ = -596.43 \pm 2.5 \text{ kcal/mol}$$

$$\Delta H_f^\circ = -599.75 \pm 2.5 \text{ kcal/mol}$$

$$\Delta H_m^\circ = [35] \text{ kcal/mol}$$

$$S_{298.15}^\circ = 32.41 \pm 1.5 \text{ gibbs/mol}$$

$$T_m = 1963 \pm 20^\circ\text{K}$$

Heat of Formation

ΔH_f° is calculated from $\Delta H_{298}^\circ = -4.45 \pm 0.45 \text{ kcal/mol}$ for the reaction $\text{MgO}(c) + 2\text{TiO}_2(\text{rutile}) = \text{MgTi}_2\text{O}_5(c)$ measured by K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954, using a solution calorimetric method. The uncertainty of $\pm 2.5 \text{ kcal/mol}$ assigned to the heat of formation is due primarily to $\text{TiO}_2(\text{rutile})$.

Heat Capacity and Entropy

Low temperature heat capacities are from the data ($52 - 298^\circ\text{K}$) of S. S. Todd, J. Am. Chem. Soc. **74**, 4689 (1952). High temperature enthalpies have been measured ($397 - 1812^\circ\text{K}$) by R. L. Orr and J. P. Coughlin, J. Am. Chem. Soc. **74**, 3186 (1952). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S_{51}^\circ - S_0^\circ = 1.11 \text{ eu}$.

Kelley et al., loc. cit., suggested that there may be a zero-point entropy due to randomness of the cations. The authors estimated S_0° from the following alternative assumptions: (a) all the Mg and Ti ions are randomly distributed among the lattice sites giving 3.79 eu and (b) all the Mg and one-half of the Ti ions are randomly distributed giving 2.75 eu . These assumptions were proposed in order to make MgTi_2O_5 stable relative to MgTiO_3 at high temperatures. Phase data of F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958, indicate that MgTi_2O_5 melts congruently at $1963 \pm 20^\circ\text{K}$ and that there is a eutectic with MgTiO_3 at $1873 \pm 20^\circ\text{K}$. These data require that $\Delta G^\circ < 0$ for $\text{MgTiO}_3(c) + \text{TiO}_2(\text{rutile}) \rightarrow \text{MgTi}_2\text{O}_5(c)$ in this temperature range. To make $\Delta G^\circ < 0$ would require that $S_{298.15}^\circ > 32.035 \text{ eu}$. We adopt a compromise zero-point entropy of 2 eu between the upper (3.79 eu) and the lower (0.35 eu) limits.

Melting Data

See liquid table.

Magnesium D titanate (MgTi₂O₅)
(Liquid) GFw = 200.109

MgO₅Ti₂

T, °K	Cp ^a	S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH ^c	ΔG ^c	Log Kp
0							
100							
200							
298	35.100	47.270	47.270	.000	- 569.385	- 540.255	396.017
300	35.216	47.487	47.271	.045	- 569.385	- 540.078	393.883
400	38.514	50.284	48.711	3.429	- 569.249	- 530.316	299.751
500	42.224	52.823	51.565	7.929	- 568.915	- 520.519	227.562
600	46.394	55.294	54.979	12.240	- 568.479	- 511.001	186.132
700	49.604	57.208	56.330	16.736	- 567.902	- 501.457	156.562
800	52.331	58.941	57.618	21.481	- 567.202	- 491.874	132.012
900	54.931	60.593	58.831	26.414	- 566.382	- 482.274	117.185
1000	57.204	62.165	60.125	30.980	- 565.461	- 473.033	103.381
1100	59.259	63.644	61.160	35.953	- 564.465	- 463.492	92.087
1200	61.076	65.061	62.069	41.030	- 563.399	- 453.621	82.670
1300	62.640	66.437	62.861	46.261	- 562.269	- 443.428	74.806
1400	63.961	67.771	63.551	51.688	- 561.082	- 432.926	68.202
1500	65.040	69.063	64.144	57.261	- 559.842	- 422.149	61.595
1600	65.880	70.316	64.642	62.928	- 558.555	- 411.109	56.182
1700	66.490	71.531	65.051	68.642	- 557.222	- 399.994	51.423
1800	66.880	72.711	65.371	74.351	- 555.842	- 388.792	47.206
1900	67.060	73.861	65.611	80.001	- 554.411	- 377.511	43.482
2000	67.130	74.981	65.781	85.551	- 552.931	- 366.151	40.103
2100	67.100	76.071	65.891	91.001	- 551.401	- 354.711	36.947
2200	66.970	77.131	65.951	96.351	- 549.821	- 343.191	33.146
2300	66.740	78.161	65.971	101.601	- 548.191	- 331.591	29.747
2400	66.410	79.161	65.951	106.751	- 546.511	- 319.911	26.710
2500	65.980	80.131	65.891	111.801	- 544.781	- 308.141	23.982
2600	65.450	81.071	65.791	116.751	- 543.001	- 296.281	21.512
2700	64.820	81.981	65.651	121.601	- 541.171	- 284.331	19.262
2800	64.090	82.861	65.471	126.351	- 539.291	- 272.291	17.202
2900	63.260	83.711	65.251	131.001	- 537.361	- 260.161	15.302
3000	62.330	84.531	65.001	135.551	- 535.381	- 247.941	13.542
3100	61.300	85.321	64.711	140.001	- 533.351	- 235.661	11.912
3200	60.170	86.081	64.391	144.351	- 531.271	- 223.321	10.402
3300	58.940	86.811	64.031	148.601	- 529.141	- 210.931	9.002
3400	57.610	87.511	63.641	152.751	- 526.961	- 198.491	7.712
3500	56.180	88.181	63.211	156.801	- 524.731	- 186.001	6.522
3600	54.650	88.821	62.751	160.751	- 522.451	- 173.461	5.432
3700	53.020	89.431	62.261	164.601	- 520.121	- 160.881	4.442
3800	51.290	90.011	61.741	168.351	- 517.741	- 148.261	3.552
3900	49.460	90.561	61.191	172.001	- 515.211	- 135.601	2.762
4000	47.530	91.081	60.611	175.551	- 512.531	- 122.911	2.072

June 30, 1961; June 30, 1967

MAGNESIUM DITITANATE (MgTi₂O₅)

(LIQUID)

GFw = 200.109

S_{298.15} = [47.27] gibbs/mol

ΔH^c_{298.15} = [-569.385 ± 2] kcal/mol

ΔH^m = [35] kcal/mol

T_m = 1963 ± 20°K

Heat of Formation

The heat of formation is obtained from ΔH^c₂₉₈(c) by adding ΔH^m and the difference between H^c₂₉₈ and H^c₂₉₈ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300°K. Below 1300°K the heat capacity is obtained from the heat capacity of the crystal. Above 1300°K the heat capacity is assumed constant and estimated as 62/4 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The congruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) indicates congruent melting at 1925°K. The ΔH^m is estimated from those of Na₂O·2TiO₂ and Na₂O·TiO₂ observed by Naylor (3) and CaO·TiO₂·SiO₂ observed by King (4).

References

1. F. Massazza and E. Sirochia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProsse, J. Res. Natl. Bur. Stds. **51**, 87 (1953).
3. B. V. Naylor, J. Am. Chem. Soc. **67**, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. **76**, 4320 (1954).

MgO₅Ti₂

Magnesium Sulfide (MgS)

(Solid) Mol. Wt. = 56.39

INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _f
0						
100						
200						
298	10.000	11.000	.000	- 81.000	- 81.072	59.864
300	10.000	11.062	.019	- 83.003	- 81.663	59.889
400	10.250	13.961	1.027	- 83.703	- 81.172	44.348
500	10.500	16.275	2.064	- 84.281	- 80.478	35.175
600	10.750	18.212	3.127	- 84.606	- 79.680	29.022
700	11.000	20.000	4.200	- 84.600	- 78.799	24.600
800	11.250	21.373	5.277	- 84.536	- 77.128	21.616
900	11.500	22.712	6.464	- 84.598	- 76.698	18.624
1000	11.750	23.937	7.627	- 100.796	- 74.083	16.190
1100	12.000	25.068	8.814	- 100.853	- 71.811	14.187
1200	12.250	26.114	10.019	- 100.972	- 66.085	11.103
1300	12.500	27.114	11.266	- 100.972	- 62.892	9.817
1400	12.750	28.049	12.527	- 131.464	- 58.008	8.451
1500	13.000	28.937	13.814	- 131.122	- 53.145	7.259
1600	13.250	29.764	15.127	- 130.754	- 43.492	6.280
1700	13.500	30.537	16.464	- 129.966	- 38.669	5.451
1800	13.750	31.278	17.827	- 129.506	- 33.932	4.708
1900	14.000	32.124	19.214	- 129.041	- 29.191	4.038
2000	14.250	32.848	20.627	- 128.553	- 24.879	3.428
2100	14.500	33.550	22.064	- 127.502	- 15.101	2.875
2200	14.750	34.237	23.535	- 126.636	- 10.454	2.375
2300	15.000	34.931	24.937	- 126.353	- 5.831	1.914
2400	15.250	35.535	26.442	- 125.742	- 1.490	1.490
2500	15.500	36.163	27.960	- 124.609	- 3.563	1.069
2600	15.750	36.775	29.627	- 123.767	- 7.898	.595
2700	16.000	37.361	31.464	- 123.061	- 12.428	.105
2800	16.250	37.924	32.627			
2900	16.500	38.535	34.464			
3000	16.750	39.099	36.127			

MgS

Magnesium Sulfide (MgS)

(Solid)

Mol. Wt. = 56.39

ΔH°_f 298.15 = -83 kcal. mole⁻¹

S°_{298.15} = [11] cal. deg.⁻¹ mole⁻¹

ΔH°_f 298.15 from National Bureau of Standards Circular 500. Other data estimated.

MgS

INTERIM TABLE

Mol. Wt. = 56.39

T, °K.	C_p°	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF°	Log K_p
0	0.000	INFINITE	INFINITE	2.206	33.243	33.243	INFINITE
100	7.019	49.187	64.287	1.510	33.243	29.227	63.873
200	7.650	54.226	70.123	1.779	33.243	24.867	27.172
298	8.226	57.367	73.367	2.000	33.243	20.698	15.171
300	8.231	57.438	73.367	2.000	33.194	20.671	15.021
400	8.453	59.638	77.713	2.850	32.320	16.500	9.015
500	8.611	61.742	81.335	3.704	31.599	12.628	5.519
600	8.705	63.321	84.038	4.570	30.947	8.897	3.241
700	8.764	64.464	85.748	5.444	30.330	5.296	1.653
800	8.804	65.241	86.438	6.322	29.759	1.893	0.493
900	8.832	65.880	87.097	7.204	29.227	-1.509	-0.366
1000	8.853	66.411	87.723	8.088	28.735	-2.896	-1.270
1100	8.868	66.856	88.314	8.974	28.276	-4.267	-2.193
1200	8.879	67.221	88.877	9.862	27.847	-5.621	-3.131
1300	8.889	67.514	89.413	10.752	27.446	-6.959	-4.073
1400	8.896	67.738	89.923	11.644	27.062	-8.281	-5.019
1500	8.902	67.912	90.407	12.538	26.694	-9.588	-5.963
1600	8.907	68.047	90.866	13.434	26.342	-10.871	-6.904
1700	8.911	68.152	91.297	14.331	26.006	-12.131	-7.841
1800	8.914	68.236	91.702	15.229	25.684	-13.374	-8.773
1900	8.917	68.301	92.083	16.128	25.375	-14.601	-9.700
2000	8.920	68.348	92.440	17.028	25.078	-15.813	-10.621
2100	8.922	68.381	92.774	17.928	24.792	-17.010	-11.536
2200	8.924	68.400	93.087	18.828	24.516	-18.193	-12.445
2300	8.925	68.408	93.380	19.728	24.250	-19.362	-13.348
2400	8.927	68.403	93.654	20.628	24.000	-20.517	-14.245
2500	8.928	68.397	93.910	21.528	23.764	-21.658	-15.136
2600	8.929	68.381	94.148	22.428	23.542	-22.785	-16.021
2700	8.930	68.354	94.367	23.328	23.334	-23.900	-16.899
2800	8.931	68.317	94.567	24.228	23.140	-25.003	-17.771
2900	8.932	68.270	94.748	25.128	22.960	-26.094	-18.638
3000	8.932	68.214	94.900	26.028	22.794	-27.173	-19.491
3100	8.933	68.148	95.034	26.928	22.642	-28.241	-20.329
3200	8.934	68.072	95.150	27.828	22.504	-29.298	-21.154
3300	8.934	68.000	95.248	28.728	22.380	-30.344	-21.966
3400	8.935	67.914	95.328	29.628	22.260	-31.380	-22.764
3500	8.935	67.814	95.390	30.528	22.154	-32.406	-23.549
3600	8.936	67.700	95.434	31.428	22.060	-33.422	-24.321
3700	8.936	67.567	95.463	32.328	21.976	-34.429	-25.080
3800	8.936	67.414	95.478	33.228	21.900	-35.427	-25.826
3900	8.937	67.248	95.478	34.128	21.830	-36.416	-26.559
4000	8.937	67.067	95.463	35.028	21.766	-37.396	-27.280
4100	8.937	66.872	95.434	35.928	21.708	-38.367	-27.988
4200	8.937	66.667	95.390	36.828	21.654	-39.330	-28.682
4300	8.937	66.442	95.332	37.728	21.604	-40.285	-29.363
4400	8.936	66.200	95.260	38.628	21.558	-41.232	-30.030
4500	8.936	65.942	95.174	39.528	21.516	-42.171	-30.683
4600	8.936	65.667	95.074	40.428	21.478	-43.102	-31.323
4700	8.936	65.377	94.960	41.328	21.444	-44.026	-31.950
4800	8.936	65.072	94.832	42.228	21.414	-44.943	-32.564
4900	8.936	64.750	94.689	43.128	21.388	-45.853	-33.164
5000	8.936	64.414	94.532	44.028	21.366	-46.756	-33.750
5100	8.936	64.067	94.361	44.928	21.348	-47.652	-34.323
5200	8.936	63.700	94.176	45.828	21.334	-48.542	-34.883
5300	8.936	63.314	93.978	46.728	21.324	-49.426	-35.429
5400	8.936	62.914	93.767	47.628	21.318	-50.304	-35.962
5500	8.936	62.500	93.542	48.528	21.316	-51.176	-36.481
5600	8.936	62.072	93.307	49.428	21.318	-52.042	-36.986
5700	8.936	61.630	93.060	50.328	21.324	-52.902	-37.477
5800	8.936	61.174	92.802	51.228	21.334	-53.756	-37.954
5900	8.936	60.700	92.532	52.128	21.348	-54.604	-38.417
6000	8.936	60.214	92.250	53.028	21.366	-55.446	-38.866

December 31, 1960.

Magnesium Sulfide (MgS)

(Ideal Gas)

Mol. Wt. = 56.39

 ΔH_f° 298.15 = 33.2 kcal. mole⁻¹ $S_{298.15}^\circ$ = 57.367 cal. deg.⁻¹ mole⁻¹

C_p° , D_0 , and other data from R. Altman, Rocketdyne Engineering, Canoga Park, Calif., "Thermodynamic Properties of Propellant Combustion Products", July, 1959. ΔH_f° 298.15 calculated from D_0 .



Magnesium Orthosilicate (Mg₂SiO₄)
(Crystal)

GFW = 140.7076

T, °K	C _p ^a	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔH°	ΔG°	Log K _p
0	0.000	INFINITE	INFINITE	0.130	-517.118	-517.118	INFINITE	INFINITE
100	7.724	3.958	25.110	2.433	-516.268	-516.268	510.151	1114.933
200	20.589	12.945	22.739	0.000	-516.979	-516.979	501.310	547.806
298	28.367	22.739	22.739	0.000	-520.300	-520.300	491.858	360.541
300	28.477	22.915	22.740	0.053	-520.304	-520.304	491.882	358.100
400	32.877	31.749	23.917	3.141	-520.373	-520.373	482.124	293.420
500	35.539	39.411	26.270	6.570	-520.234	-520.234	472.571	206.561
600	37.388	46.062	29.026	10.221	-519.999	-519.999	463.063	168.670
700	38.783	51.945	31.666	14.033	-519.714	-519.714	453.593	141.618
800	40.081	57.052	34.182	17.912	-519.422	-519.422	443.780	120.576
900	41.300	61.481	36.582	21.913	-519.142	-519.142	433.780	105.576
1000	41.732	66.305	40.159	26.145	-523.126	-523.126	425.056	92.866
1100	42.488	70.318	42.721	30.357	-522.831	-522.831	415.268	82.506
1200	43.180	74.045	45.176	34.641	-522.542	-522.542	405.503	73.852
1300	43.810	77.594	47.534	38.904	-522.252	-522.252	395.753	65.733
1400	44.380	80.977	49.734	43.140	-521.962	-521.962	386.080	58.044
1500	45.007	83.882	51.965	47.876	-521.674	-521.674	376.597	50.854
1600	45.559	86.805	54.052	52.405	-520.578	-520.578	356.990	48.763
1700	46.091	89.583	56.061	56.987	-520.442	-520.442	342.942	44.068
1800	46.606	92.232	57.897	61.622	-520.275	-520.275	328.359	39.668
1900	47.100	94.766	59.566	66.306	-520.078	-520.078	314.242	35.468
2000	47.601	97.194	61.672	71.044	-520.683	-520.683	299.399	32.717
2100	48.082	99.528	63.420	75.828	-520.351	-520.351	285.019	29.662
2200	48.555	101.776	65.112	80.660	-520.989	-520.989	270.699	26.861
2300	49.029	103.963	66.597	85.534	-520.589	-520.589	256.366	24.366
2400	49.499	106.100	68.000	90.434	-520.189	-520.189	242.025	22.025
2500	49.932	108.070	69.896	95.434	-520.681	-520.681	228.125	19.943
2600	50.380	110.037	71.402	100.450	-520.175	-520.175	214.046	17.992
2700	50.824	111.946	72.869	105.510	-520.639	-520.639	200.034	16.192
2800	51.261	113.801	74.287	110.613	-520.068	-520.068	186.178	14.578
2900	51.701	115.609	75.661	115.758	-520.578	-520.578	172.481	13.048
3000	52.133	117.369	77.051	120.955	-520.834	-520.834	158.131	11.534

MAGNESIUM ORTHOSILICATE (Mg₂SiO₄)

(CRYSTAL)

GFW = 140.7076

ΔH_f⁰ = -517.12 ± 1.0 kcal/mol

ΔH_f^{298.15} = -520.30 ± 1.0 kcal/mol

ΔH_m⁰ = [17 ± 5] kcal/mol

Heat of Formation

Torgeson et al. (1) have reported a ΔH_f²⁹⁸ = -15.1 ± 0.2 kcal/mol for reaction (a). They used an HF solution calorimeter and measured the heats of solution of each component. We derive ΔH_f²⁹⁸(Mg₂SiO₄, c) = -520.30 ± 1.0 kcal/mol using the ΔH_f²⁹⁸ of MgO(c) and SiO₂(c, low quartz) from JANAF tables.

Kapustinikii et al. (2) used the same method but measured only ΔH_f²⁹⁸ = 95.00 ± 0.47 kcal/mol for reaction (b). We calculate ΔH_f²⁹⁸(Mg₂SiO₄, c) = -522.27 kcal/mol using the ΔH_f²⁹⁸ of H₂SiF₆(aq) from source 3 and the ΔH_f²⁹⁸ of H₂O(l) and HF(aq) from source 4.

Reesman et al. (3) calculated a ΔG_f²⁹⁸ = 42.46 kcal/mol for reaction (c) using aqueous solubility data. We use the ΔG_f²⁹⁸ of H₂O(l) and OH⁻(aq) from source 4, ΔG_f²⁹⁸ of H₂SiO₄(aq) from source 3 and ΔG_f²⁹⁸ of Mg²⁺(aq) from source 6 and we obtain a ΔG_f²⁹⁸(Mg₂SiO₄, c) = -498.784 kcal/mol. We derive a ΔH_f²⁹⁸(Mg₂SiO₄, c) = -524.848 kcal/mol using the above ΔG_f²⁹⁸ of Mg₂SiO₄(c) and the entropies of Mg(c), Si(c) and O₂(g) from the JANAF tables.

The adopted value is from the work of Torgeson et al. (1) which is considered to be the most reliable since it relates directly to the oxides. The other reported values are less accurate and involve uncertainties in the auxiliary data used to derive the heat of formation.

Source	Method	Reaction	ΔH _f ²⁹⁸ kcal/mol	ΔG _f ²⁹⁸ kcal/mol
Torgeson et al.	Hydrofluoric acid solution calorimeter	(a) 2MgO(c) + SiO ₂ (c) = Mg ₂ SiO ₄ (c)	-15.10 ± 0.2	-520.3
Kapustinikii et al.	Hydrofluoric acid solution calorimeter	(b) Mg ₂ SiO ₄ (c) + 10HF(4.44H ₂ O) = 2MgF ₂ (c) + H ₂ SiF ₆ (714HF·3220H ₂ O) + 4H ₂ O(l)	95.0 ± 0.47	-522.27
Reesman et al.	Aqueous solubility	(c) Mg ₂ SiO ₄ (c) + 4H ₂ O(l) = 2Mg ²⁺ (aq) + H ₄ SiO ₄ (aq) + 4OH ⁻ (aq)	42.46	-524.848

Source

1. D. R. Torgeson and Th. G. Sahara, J. Am. Chem. Soc. **70**, 2156 (1948).
2. A. F. Kapustinikii and K. K. Samplavskaya, Russ. J. Inorg. Chem. (Engl. transl.) **6**, 1141 (1961).
3. U. S. Natl. Bur. Std. Tech. Note 270-2, 1966.
4. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
5. A. L. Reesman and W. D. Keller, Am. Mineralogist **50**, 1729-39 (1965).
6. U. S. Natl. Bur. Std. Circ. 500, 1952.
7. K. K. Kelley, J. Am. Chem. Soc. **65**, 339-41 (1943).
8. R. L. Orr, J. Am. Chem. Soc. **75**, 528-9 (1953).
9. B. T. C. Davis and J. L. England, J. Geophys. Res. **69**, 1113-1116 (1964).
10. I. D. MacGregor, Ann. Rept. Director of the Geophysical Laboratory, No. 1455, 135-3 (1965).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (53-235°K) of Kelley (7). High temperature enthalpies have been measured (398-1808°K) by Orr (8). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on S₀⁰ = 0.60 eu.

Melting Data

T_m is obtained from Davis et al. (9). ΔH_m⁰ is estimated from MacGregor's (10) phase diagrams of the Mg₂SiO₄ - TiO₂ system. The phase diagrams were determined at 10 and 20 kbars pressure.



Magnesium Orthosilicate (Mg_2SiO_4)

(Liquid) GFW = 140.7076



GFW = 140.7076

(LIQUID)

MAGNESIUM ORTHOSILICATE (Mg_2SiO_4)

$\Delta H_f^{298.15} = [-505.229 \pm 5] \text{ kcal/mol}$

$\Delta H_m^* = [17 \pm 5] \text{ kcal/mol}$

$S_{298.15}^* = [29.407] \text{ gibbs/mol}$

$T_m = 2171 \pm 11^\circ K$

Heat of Formation

The heat of formation is obtained from $\Delta H_f^{298}(c)$ by adding ΔH_m^* and the difference between H_{lm}^* and H_{298}^* for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at $1400^\circ K$. Below $1400^\circ K$ the heat capacity is obtained from the heat capacity of the crystal. Above $1400^\circ K$ the heat capacity is assumed constant and estimated as 49 gibbs/mol or 7 gibbs/g-atom . The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See crystal table.

T, °K	C_p^*	$\frac{\text{gibbs/mol}}{S^*}$	$-(G^* - H^*)_{298}/T$	$H^* - H^*_{298}$	$\frac{\text{kcal/mol}}{\Delta H^*}$	ΔG^*	Log Kp
0							
100	28.387	29.407	29.407	.000	- 505.229	- 476.775	350.951
200	28.477	29.583	29.408	.053	- 505.233	- 476.811	348.668
300	28.677	30.585	30.585	3.141	- 505.302	- 469.721	256.643
400	35.539	36.079	32.938	6.570	- 505.163	- 460.834	201.430
500	37.388	52.730	35.654	10.221	- 504.928	- 451.993	164.438
600	38.793	63.660	38.556	14.033	- 504.643	- 441.190	138.370
700	39.929	68.650	41.396	17.971	- 504.351	- 434.435	118.692
800	40.891	72.973	44.161	22.013	- 504.071	- 428.710	103.377
900	41.732	76.986	46.827	26.145	- 504.055	- 418.553	91.059
1000	42.488	80.584	49.389	30.357	- 503.760	- 407.531	80.948
1100	43.060	83.824	51.864	34.691	- 503.194	- 396.331	72.565
1200	43.482	86.195	54.202	39.191	- 501.196	- 389.357	65.457
1300	43.824	87.465	56.462	43.404	- 507.664	- 379.344	59.218
1400	49.000	90.846	58.643	48.304	- 566.175	- 365.944	53.318
1500	49.000	94.008	60.755	53.204	- 564.708	- 352.482	48.169
1600	49.000	96.979	62.800	58.104	- 575.254	- 338.927	43.423
1700	49.000	99.779	64.777	63.004	- 573.776	- 325.492	39.550
1800	49.000	102.429	66.690	67.904	- 572.308	- 311.739	35.858
1900	49.000	104.942	68.540	72.804	- 570.852	- 298.064	32.571
2000	49.000	107.333	70.331	77.704	- 569.406	- 284.681	28.408
2100	49.000	109.623	72.065	82.604	- 567.977	- 271.521	24.694
2200	49.000	111.790	73.745	87.504	- 566.550	- 257.954	24.464
2300	49.000	113.876	75.374	92.404	- 565.138	- 244.044	22.223
2400	49.000	115.876	76.954	97.304	- 563.740	- 230.700	20.168
2500	49.000	117.798	78.489	102.204	- 562.350	- 217.000	18.274
2600	49.000	119.647	79.979	107.104	- 560.974	- 204.161	16.526
2700	49.000	121.429	81.428	112.004	- 559.608	- 190.971	14.906
2800	49.000	123.149	82.837	116.904	- 558.254	- 177.825	13.401
2900	49.000	124.810	84.208	121.804	- 556.914	- 164.732	12.001
3000	49.000	126.417	85.544	126.704	- 555.584	- 151.680	10.493
3100	49.000	127.972	86.844	131.604	- 554.268	- 138.675	9.471
3200	49.000	129.480	88.115	136.504	- 552.964	- 125.710	8.325
3300	49.000	130.943	89.353	141.404	- 551.676	- 112.776	7.249
3400	49.000	132.363	90.562	146.304	- 550.400	- 99.895	6.238

Dec. 31, 1960; Sept. 30, 1964; Dec. 31, 1967





Magnesium Orthotitanate (Mg_2TiO_4)
(Crystal) GFW = 160.5216

T, K	C_p°	gibbs/mol S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	4.200	-0.000	INFINITE	-	514.108	-514.108	INFINITE
100	8.219	6.391	48.821	-4.502	-515.679	-507.384	1108.684
200	22.543	16.811	30.091	-2.656	-517.066	-498.714	544.969
298	36.730	27.510	27.510	0.000	-517.300	-489.438	358.767
300	30.936	27.700	27.511	.057	-517.302	-489.265	356.429
400	34.963	37.198	28.777	3.368	-517.259	-479.919	282.216
500	37.383	45.277	31.291	6.993	-517.026	-470.606	205.702
600	39.122	52.253	34.216	10.822	-516.711	-461.354	168.048
700	40.756	58.383	36.923	14.650	-516.395	-452.102	131.025
800	42.156	63.870	39.343	18.422	-516.079	-442.850	105.367
900	43.368	68.870	41.413	22.154	-515.649	-433.605	92.769
1000	44.426	73.440	43.147	25.947	-515.166	-424.477	82.451
1100	45.360	77.671	44.641	29.703	-514.639	-415.489	74.451
1200	46.195	81.513	45.916	33.428	-514.064	-406.564	67.510
1300	46.975	85.019	46.995	37.124	-513.443	-397.699	61.510
1400	47.584	88.133	47.922	40.800	-512.776	-388.894	56.410
1500	48.066	90.912	48.799	44.467	-512.064	-380.148	52.066
1600	48.426	93.400	49.563	48.124	-511.307	-371.462	48.407
1700	48.675	95.645	50.236	51.771	-510.505	-362.835	45.278
1800	48.836	97.688	50.826	55.409	-509.658	-354.267	42.610
1900	48.915	99.466	51.336	59.039	-508.766	-345.758	40.350
2000	48.915	101.000	51.777	62.661	-507.829	-337.310	38.510
2100	48.836	102.326	52.156	66.276	-506.847	-328.924	37.066
2200	48.675	103.496	52.488	69.886	-505.820	-320.600	36.016
2300	48.426	104.536	52.771	73.491	-504.758	-312.346	35.356
2400	48.195	105.466	53.011	77.091	-503.661	-304.161	35.066
2500	47.975	106.300	53.200	80.686	-502.529	-296.046	35.116
2600	47.675	106.946	53.356	84.276	-501.361	-288.001	35.516
2700	47.300	107.411	53.488	87.861	-500.158	-280.028	36.266
2800	46.866	107.700	53.591	91.441	-498.920	-272.120	37.466
2900	46.386	107.836	53.666	95.011	-497.646	-264.276	39.016
3000	45.866	107.836	53.711	98.576	-496.336	-256.496	41.016
3100	45.300	107.700	53.736	102.141	-494.991	-248.776	43.466
3200	44.691	107.411	53.746	105.701	-493.611	-241.121	46.366
3300	44.046	106.946	53.746	109.256	-492.196	-233.546	49.716
3400	43.366	106.300	53.736	112.811	-490.746	-226.066	53.466
3500	42.656	105.466	53.711	116.366	-489.266	-218.666	57.616
3600	41.911	104.536	53.666	119.921	-487.746	-211.321	62.166
3700	41.136	103.496	53.591	123.481	-486.186	-204.046	67.116
3800	40.336	102.326	53.488	127.041	-484.591	-196.841	72.466
3900	39.511	101.000	53.356	130.601	-482.961	-189.701	78.216
4000	38.656	99.466	53.200	134.161	-481.301	-182.626	84.366
4100	37.776	97.688	53.011	137.721	-479.611	-175.611	90.916
4200	36.866	95.645	52.771	141.281	-477.886	-168.666	97.866
4300	35.926	93.400	52.488	144.841	-476.126	-161.786	105.216
4400	34.966	90.912	52.156	148.401	-474.331	-154.966	112.966
4500	33.986	88.133	51.777	151.961	-472.501	-148.206	121.216
4600	32.986	85.019	51.336	155.521	-470.636	-141.506	129.966
4700	31.966	81.513	50.826	159.081	-468.741	-134.866	139.216
4800	30.926	77.671	50.236	162.641	-466.816	-128.286	148.966
4900	29.866	73.440	49.563	166.201	-464.861	-121.766	159.216
5000	28.786	68.870	48.799	169.761	-462.886	-115.306	170.066
5100	27.686	63.870	47.922	173.321	-460.886	-108.906	181.516
5200	26.566	58.383	46.995	176.881	-458.861	-102.566	193.566
5300	25.426	52.253	45.916	180.441	-456.811	-96.286	206.216
5400	24.266	45.277	44.641	184.001	-454.736	-90.066	219.466
5500	23.086	37.198	43.147	187.561	-452.636	-83.906	233.316
5600	21.886	28.777	41.413	191.121	-450.511	-77.806	247.766
5700	20.666	20.091	39.343	194.681	-448.361	-71.766	262.816
5800	19.426	11.821	36.923	198.241	-446.186	-65.786	278.466
5900	18.166	3.921	34.216	201.801	-444.001	-59.866	294.716
6000	16.886	-4.000	31.291	205.361	-441.796	-54.006	311.566
6100	15.586	-11.821	28.777	208.921	-439.566	-48.306	329.016
6200	14.266	-19.426	26.566	212.481	-437.311	-42.766	347.166
6300	12.926	-26.886	24.266	216.041	-435.036	-37.306	366.016
6400	11.566	-34.136	21.886	219.601	-432.741	-31.906	385.566
6500	10.186	-41.186	19.426	223.161	-430.426	-26.566	405.816
6600	8.786	-48.000	16.886	226.721	-428.086	-21.306	426.766
6700	7.366	-54.586	14.266	230.281	-425.731	-16.106	448.416
6800	5.926	-60.966	11.566	233.841	-423.361	-11.066	470.766
6900	4.466	-67.146	8.786	237.401	-420.976	-6.186	493.816
7000	2.986	-73.146	5.926	240.961	-418.576	-1.466	517.566
7100	1.486	-78.966	2.986	244.521	-416.161	3.146	542.016
7200	0.000	-84.600	0.000	248.081	-413.736	7.806	567.266
7300	-1.486	-90.046	-2.986	251.641	-411.301	12.506	593.316
7400	-2.986	-95.306	-5.926	255.201	-408.856	17.246	620.066
7500	-4.466	-100.386	-8.786	258.761	-406.401	22.026	647.516
7600	-5.926	-105.286	-11.566	262.321	-403.936	26.846	675.766
7700	-7.366	-110.000	-14.266	265.881	-401.461	31.706	704.816
7800	-8.786	-114.536	-16.886	269.441	-398.976	36.606	734.766
7900	-10.186	-118.906	-19.426	273.001	-396.481	41.546	765.616
8000	-11.566	-123.106	-21.886	276.561	-393.976	46.526	797.366
8100	-12.926	-127.146	-24.266	280.121	-391.461	51.546	830.016
8200	-14.266	-131.046	-26.566	283.681	-388.936	56.606	863.566
8300	-15.586	-134.806	-28.777	287.241	-386.401	61.706	898.016
8400	-16.886	-138.426	-30.926	290.801	-383.856	66.846	933.366
8500	-18.166	-141.906	-32.986	294.361	-381.301	72.026	969.616
8600	-19.426	-145.246	-34.966	297.921	-378.736	77.246	1006.766
8700	-20.666	-148.466	-36.866	301.481	-376.161	82.506	1044.816
8800	-21.886	-151.566	-38.686	305.041	-373.576	87.806	1083.766
8900	-23.086	-154.546	-40.426	308.601	-370.981	93.146	1123.616
9000	-24.266	-157.406	-42.186	312.161	-368.376	98.526	1164.366
9100	-25.426	-160.146	-43.886	315.721	-365.761	103.946	1206.016
9200	-26.566	-162.766	-45.526	319.281	-363.136	109.406	1248.566
9300	-27.686	-165.266	-47.106	322.841	-360.501	114.906	1292.016
9400	-28.786	-167.646	-48.626	326.401	-357.856	120.446	1336.366
9500	-29.866	-169.906	-50.086	329.961	-355.201	126.026	1381.616
9600	-30.926	-172.046	-51.486	333.521	-352.536	131.646	1427.766
9700	-31.966	-174.066	-52.826	337.081	-349.861	137.306	1474.816
9800	-32.986	-175.966	-54.106	340.641	-347.176	143.006	1522.766
9900	-33.986	-177.746	-55.326	344.201	-344.481	148.746	1571.616
10000	-34.966	-179.406	-56.486	347.761	-341.776	154.526	1621.366

MAGNESIUM ORTHOTITANATE (Mg_2TiO_4) (CRYSTAL)

GFW = 160.5216

$$\Delta H_f^\circ = -514.11 \pm 1.5 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = -517.3 \pm 1.5 \text{ kcal/mol}$$

$$\Delta H_m^\circ = [31] \text{ kcal/mol}$$

$$S^\circ_{298.15} = 27.51 \pm 1.5 \text{ gibbs/mol}$$

$$T_m = 2013 \pm 20^\circ \text{K}$$

Heat of Formation

The heat of formation is calculated from $\Delta H^\circ_{298} = -4.1 \pm 0.25 \text{ kcal/mol}$ for the reaction $2 \text{ MgO(c)} + \text{TiO}_2(\text{rutile}) \rightarrow \text{Mg}_2\text{TiO}_4(\text{c})$ measured by Kelley (1), using a solution calorimetric method. The uncertainty of $\pm 1.5 \text{ kcal/mol}$ assigned to the heat of formation is due primarily to $\text{TiO}_2(\text{rutile})$.

Heat Capacity and Entropy

Low temperature heat capacities are from the data ($52 - 298^\circ \text{K}$) of Todd (2).

High temperature enthalpies have been measured ($392 - 1817^\circ \text{K}$) by Orr (3). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values.

The entropy is based on $S^\circ_0 = 0.66 + 2.75 = 3.41 \text{ eu}$, where the first term is a lattice contribution and the second term is a zero-point entropy of $2R \ln 2$ corresponding to random distribution of Ti and Mg on the octahedral sites of the spinel lattice. The adopted value is $S^\circ_{298} = 27.51 \pm 1.5 \text{ eu}$ instead of $24.76 \pm 0.15 \text{ eu}$ as given by Todd.

Barth (4) showed from intensities of the X-ray diffraction lines that Mg_2TiO_4 is a spinel of the inverse (or variate) class. Thus, half of the Mg ions occupy the tetrahedral interstices in the oxygen lattice, while the remaining Mg ions and the Ti ions are (presumably) randomly located in the octahedral interstices. This conclusion was confirmed by Romeijn (5).

King and Kelley (6) suggested that the degree of structural randomness is not established and that it may vary with the sample of Mg_2TiO_4 ; thus, they recommended an intermediate value of $R \ln 2$ for the zero-point entropy. In a previous review, however, Kelley (1) used the theoretical value of $2R \ln 2$ in order to make Mg_2TiO_4 stable relative to MgTiO_3 at high temperatures. We choose to adopt $2R \ln 2$, although the evidence is not conclusive. Recent studies of solid state reactions by Bartsch and Werner (7) indicate that ΔG° is negative for $\text{MgTiO}_3(\text{c}) + \text{MgO(c)} \rightarrow \text{Mg}_2\text{TiO}_4(\text{c})$ at temperatures of 1673°K and above. Both $R \ln 2$ and $2R \ln 2$ are consistent with this evidence.

Melting Data

See liquid table.

References

1. K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, 1954.
2. S. S. Todd, J. Am. Chem. Soc. **74**, 4669 (1952).
3. R. L. Orr and J. P. Coughlin, J. Am. Chem. Soc. **74**, 3186 (1952).
4. T. F. W. Barth and E. Posnjak, Z. Krist. **82**, 325 (1932).
5. F. C. Romeijn, Philips Res. Rep. **8**, 304 (1953).
6. E. G. King and K. K. Kelley, U. S. Bur. Mines RI 5502, 1959.
7. H. J. Bartsch and I. Werner, Silikat Tech. **14**, 203 (1963).



Heat of Formation

ΔH_f° is obtained from $\Delta H_f^\circ(298.15^\circ K)$ by adding ΔH_m° and the difference between H_m° and H_{298}° for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1400°K. Below 1400°K the heat capacity is obtained from the heat capacity of the crystal. Above 1400°K the heat capacity is assumed constant and estimated as 54.6 gibbs/mol or 7.8 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The incongruent melting point is obtained from Massazza (1). Previous work by Coughanour (2) suggested congruent melting at 2005°K. The ΔH_m° is estimated from those of $Na_2O \cdot 2TiO_2$ and $Na_2O \cdot TiO_2$ observed by Naylor (3) and $CaO \cdot TiO_2 \cdot SiO_2$ observed by King (4).

Reference

1. F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp. 161-8, Butterworths Scientific Publications, London, 1958.
2. L. W. Coughanour and V. A. DeProse, J. Res. Natl. Bur. Stds. **53**, 87 (1953).
3. B. F. Naylor, J. Am. Chem. Soc. **67**, 2120 (1945).
4. E. G. King, R. L. Orr and K. R. Bonnickson, J. Am. Chem. Soc. **76**, 4320 (1954).

T, °K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log Kp
0							
100							
200							
298	30.730	41.208	41.208	.000	-489.084	-465.306	341.076
300	30.338	41.398	41.209	.057	-489.086	-465.158	338.867
400	34.263	50.496	42.475	3.364	-489.043	-457.162	249.793
500	37.383	58.275	44.959	5.993	-488.810	-449.239	196.362
600	40.122	65.951	47.916	8.822	-488.495	-441.354	140.764
700	42.531	72.991	50.938	14.807	-488.138	-433.526	135.353
800	44.756	77.585	53.932	18.922	-487.779	-425.752	116.310
900	47.568	82.568	56.841	23.154	-487.433	-418.019	101.509
1000	48.202	87.138	59.645	27.493	-491.350	-409.959	89.596
1100	44.880	91.350	62.330	31.823	-490.981	-401.841	79.838
1200	44.815	95.318	64.922	36.468	-491.589	-393.716	71.705
1300	44.715	99.017	67.406	41.095	-491.055	-385.583	64.822
1400	54.600	102.511	69.790	45.810	-551.285	-376.530	58.779
1500	54.600	106.278	72.098	51.270	-540.305	-364.116	53.052
1600	54.600	109.402	74.344	56.730	-547.357	-351.836	48.058
1700	54.600	113.112	76.530	62.190	-545.438	-339.672	43.668
1800	54.600	116.233	78.650	67.650	-543.555	-327.624	39.779
1900	54.600	119.185	80.706	73.110	-541.704	-315.678	36.311
2000	54.600	121.986	82.701	78.570	-544.335	-303.674	33.184
2100	54.600	124.550	84.512	84.030	-542.520	-291.489	30.357
2200	54.600	127.190	86.212	89.490	-540.738	-279.785	27.794
2300	54.600	129.617	88.336	94.950	-538.954	-267.984	25.462
2400	54.600	131.940	90.103	100.410	-537.182	-256.217	23.332
2500	54.600	134.169	91.821	105.870	-535.424	-244.552	21.379
2600	54.600	136.311	93.492	111.330	-533.678	-232.908	19.581
2700	54.600	138.371	95.112	116.790	-531.938	-221.414	17.922
2800	54.600	140.357	96.696	122.250	-530.212	-209.948	16.387
2900	54.600	142.273	98.235	127.710	-528.498	-198.533	14.962
3000	54.600	144.124	99.734	133.170	-526.799	-187.186	13.637
3100	54.600	145.916	101.195	138.630	-525.108	-175.890	12.400
3200	54.600	147.448	102.628	144.090	-523.432	-164.661	11.244
3300	54.600	149.328	104.010	149.550	-521.768	-153.475	10.164
3400	54.600	150.958	105.367	155.010	-520.120	-142.333	9.149
3500	54.600	152.541	106.692	160.470	-518.484	-131.235	8.196
3600	54.600	154.070	107.997	165.930	-516.850	-119.244	7.282
3700	54.600	155.575	109.293	171.390	-515.225	-107.118	6.268
3800	54.600	157.031	110.491	176.850	-513.615	-95.335	5.310
3900	54.600	158.449	111.703	182.310	-513.677	-84.405	4.405
4000	54.600	159.831	112.889	187.770	-512.134	-74.698	3.546

Dimagnesium Silicide (Mg_2Si)

INTERIM TABLE

(Crystal) Mol. Wt. = 76.73

Mg_2Si

T, °K	C_p^0	$\frac{cal. mole^{-1} deg^{-1}}{S^0}$	$-(F^0-H_{298}^0)/T$	$H^0-H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0							
100							
200							
298	16.220	19.500	19.500	.000	18.400	18.428	13.507
300	16.251	19.600	19.500	.030	18.401	18.426	13.423
400	17.600	22.400	21.400	1.000	18.631	18.422	10.922
500	19.470	28.512	21.435	3.538	18.685	18.296	7.997
600	19.080	31.934	22.907	5.416	18.662	18.223	6.637
700	19.600	34.916	24.414	7.351	18.699	18.146	5.665
800	20.050	37.563	25.895	9.334	18.766	18.063	4.934
900	20.480	39.949	27.326	11.360	18.876	17.968	4.363
1000	20.890	42.176	28.699	13.429	18.972	17.865	3.926
1100	21.290	44.138	30.013	15.538	19.057	17.753	3.592
1200	21.670	46.007	31.268	17.686	19.121	17.638	3.302
1300	22.040	47.756	32.470	19.872	19.172	17.521	3.043
1400	22.400	49.404	33.621	22.096	19.211	17.404	2.812
1500	22.760	50.963	34.726	24.356	19.240	17.287	2.603
1600	23.130	52.445	35.788	26.651	19.260	17.170	2.413
1700	23.470	53.857	36.809	28.981	19.271	17.053	2.241
1800	23.800	55.206	37.794	31.345	19.274	16.936	2.086
1900	24.120	56.493	38.741	33.741	19.269	16.820	1.947
2000	24.430	57.748	39.664	36.169	19.257	16.704	1.822
2100	24.730	58.948	40.554	38.627	19.238	16.589	1.711
2200	25.020	60.105	41.417	41.114	19.214	16.474	1.611
2300	25.300	61.223	42.254	43.630	19.186	16.359	1.521
2400	25.580	62.306	43.067	46.174	19.154	16.244	1.441
2500	25.830	63.355	43.857	48.744	19.118	16.129	1.371

DIMAGNESIUM SILICIDE (Mg_2Si) (crystal)

Mol. Wt. = 76.73

ΔH_f^0 298.15 = -18.6 kcal. mole⁻¹

$S_{298.15}^0$ = [19.5] cal. deg.⁻¹ mole⁻¹

T_m = 1375°K

ΔH_m = [15.33] kcal. mole⁻¹

Heat of Formation. ΔH_f^0 298.15 was found in the National Bureau of Standards Circular 500 (1952).

Heat Capacity and Entropy. C_p taken from Kubaschewski and Evans, "Metallurgical Thermochemistry," 3rd Edition, Pergamon Press Ltd., New York, (1958). $S_{298.15}$ was estimated.

Melting Data. T_m was taken from NBS Circular 500 (1952). ΔH_m was found in Wilson, Beahm, and Cooper, "Determination and Analysis of the Potentials of Thermal Energy Storage Materials," Gallery Chemical Co., Gallery, Pa., June 30, 1961.

Mg_2Si

INTERIM TABLE

(Liquid) Mol. Wt. = 76.73



T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF°	Log K _p
0						
100						
200						
240	24,500	29,561	0.000	.792	-3.619	2.653
2500	24,500	29,561	.042	.781	-3.637	2.649
300	22,500	16,173	2.292	.260	-4.670	2.551
400	22,500	11,194	4.542	.167	-5.625	2.546
500	22,500	45,296	31,977	6.792	-7.056	2.570
600	22,500	48,764	35,448	9.042	-8.342	2.604
700	22,500	51,769	37,658	11.292	-9.663	2.640
800	22,500	54,819	39,373	13.542	-11.002	2.672
900	22,500	56,790	40,960	15.792	-11.996	2.622
1000	22,500	58,934	42,533	18.042	-12.869	2.560
1100	22,500	60,892	43,982	20.292	-13.127	2.509
1200	22,500	62,693	45,353	22.542	-13.776	2.509
1300	22,500	64,360	46,652	24.792	-14.561	2.480
1400	22,500	65,913	47,883	27.042	-15.063	2.465
1500	22,500	67,365	49,057	29.292	-15.601	2.453
1600	22,500	68,729	50,175	31.542	-16.174	2.442
1700	22,500	70,015	51,242	33.792	-16.782	2.431
1800	22,500	71,231	52,262	36.042	-17.422	2.420
1900	22,500	72,385	53,240	38.292	-18.092	2.409
2000	22,500	73,483	54,178	40.542	-18.792	2.398
2100	22,500	74,530	55,079	42.792	-19.522	2.387
2200	22,500	75,530	55,947	45.042	-20.282	2.376
2300	22,500	76,486	56,783	47.292	-21.072	2.365
2400	22,500	77,406	57,589	49.542	-21.892	2.354
2500	22,500	78,289	58,369	51.792	-22.742	2.343
2600	22,500	79,138	59,122	54.042	-23.622	2.332
2700	22,500	79,956	59,852	56.292	-24.532	2.321
2800	22,500	80,745	60,559	58.542	-25.472	2.310
2900	22,500	81,508	61,244	60.792	-26.442	2.299
3000	22,500	82,246	61,910	63.042	-27.442	2.288
3100	22,500	82,960	62,557	65.292	-28.472	2.277
3200	22,500	83,653	63,186	67.542	-29.532	2.266
3300	22,500	84,324	63,797	69.792	-30.622	2.255
3400	22,500	84,977	64,393	72.042	-31.742	2.244
3500	22,500	85,610	64,974	74.292	-32.892	2.233
3600	22,500	86,227	65,540	76.542	-34.072	2.222
3700	22,500	86,827	66,092	78.792	-35.282	2.211
3800	22,500	87,411	66,632	81.042	-36.522	2.200
3900	22,500	87,981	67,158	83.292	-37.792	2.189
4000	22,500					

December 31, 1960.

DIMAGNESIUM SILICIDE (Mg₂Si)

(Liquid)

Mol. Wt. = 76.73

ΔH°_f 298.15 = -3.749 kcal. mole⁻¹S°_{298.15} = [30.2] cal. deg.⁻¹ mole⁻¹T_m = 1375°KΔH_m = [15.33] kcal. mole⁻¹Heat of Formation. ΔH°_f 298.15 was based on ΔH°_f 298.15 of the crystal and the heat of melting.Heat Capacity and Entropy. C_p was estimated. A glass transition was assumed at 916°K. S°_{298.15} was calculated from the entropy of the crystal and the entropy of melting.

Trimagnesium Dinitride (Mg_3N_2)
(Solid) Mol. Wt. = 100.98

INTERIM TABLE

T, °K.	C_p°	$S^\circ - (F^\circ - H_{298}^\circ)/T$	ΔH_{298}°	ΔF_{298}°	ΔF_{298}°	Log K_p
		cal. mole ⁻¹ deg ⁻¹	kcal. mole ⁻¹			
0						
100						
200						
298	24.980	21.000	.000	110.200	95.820	70.234
300	25.000	21.000	.000	110.200	95.730	69.736
400	26.187	21.990	2.583	110.190	90.907	49.667
500	26.646	23.682	5.192	110.195	86.091	37.628
600	27.190	26.031	7.874	110.209	81.266	29.600
700	27.990	30.215	10.658	110.250	76.440	21.584
800	28.990	34.400	13.658	110.340	71.614	13.568
900	29.600	38.600	16.618	110.222	66.774	5.552
1000	29.600	42.824	19.578	116.797	61.404	13.419
1100	29.540	47.088	22.796	116.770	55.864	11.009
1200	29.540	51.352	26.000	116.770	50.324	8.599
1300	29.540	55.616	29.200	116.770	44.784	6.189
1400	29.540	59.880	32.400	116.770	39.244	3.779
1500	29.540	64.144	35.600	116.770	33.704	1.369
1600	29.540	68.408	38.800	116.770	28.164	-1.041
1700	29.540	72.672	42.000	116.770	22.624	-3.451
1800	29.540	76.936	45.200	116.770	17.084	-5.861
1900	29.540	81.200	48.400	116.770	11.544	-8.271
2000	29.540	85.464	51.600	116.770	6.004	-10.681
2100	29.540	89.728	54.800	116.770	0.464	-13.091
2200	29.540	93.992	58.000	116.770	-5.076	-15.501
2300	29.540	98.256	61.200	116.770	-10.536	-17.911
2400	29.540	102.520	64.400	116.770	-15.996	-20.321
2500	29.540	106.784	67.600	116.770	-21.456	-22.731
2600	29.540	111.048	70.800	116.770	-26.916	-25.141
2700	29.540	115.312	74.000	116.770	-32.376	-27.551
2800	29.540	119.576	77.200	116.770	-37.836	-29.961
2900	29.540	123.840	80.400	116.770	-43.296	-32.371
3000	29.540	128.104	83.600	116.770	-48.756	-34.781
3100	29.540	132.368	86.800	116.770	-54.216	-37.191
3200	29.540	136.632	90.000	116.770	-59.676	-39.601
3300	29.540	140.896	93.200	116.770	-65.136	-42.011
3400	29.540	145.160	96.400	116.770	-70.596	-44.421
3500	29.540	149.424	99.600	116.770	-76.056	-46.831
3600	29.540	153.688	102.800	116.770	-81.516	-49.241
3700	29.540	157.952	106.000	116.770	-86.976	-51.651
3800	29.540	162.216	109.200	116.770	-92.436	-54.061
3900	29.540	166.480	112.400	116.770	-97.896	-56.471
4000	29.540	170.744	115.600	116.770	-103.356	-58.881
4100	29.540	175.008	118.800	116.770	-108.816	-61.291
4200	29.540	179.272	122.000	116.770	-114.276	-63.701
4300	29.540	183.536	125.200	116.770	-119.736	-66.111
4400	29.540	187.800	128.400	116.770	-125.196	-68.521
4500	29.540	192.064	131.600	116.770	-130.656	-70.931
4600	29.540	196.328	134.800	116.770	-136.116	-73.341
4700	29.540	200.592	138.000	116.770	-141.576	-75.751
4800	29.540	204.856	141.200	116.770	-147.036	-78.161
4900	29.540	209.120	144.400	116.770	-152.496	-80.571
5000	29.540	213.384	147.600	116.770	-157.956	-82.981

TRIMAGNESIUM DINITRIDE (Mg_3N_2) (Solid)

Mol. Wt. = 100.98

$\Delta H_f^\circ 298.15 = -110.2 \pm 1$ kcal. mole⁻¹

$S_{298.15}^\circ = [21 \pm 2]$ cal. deg⁻¹ mole⁻¹

Data from National Bureau of Standards Report No. 6928, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element Compounds", July, 1960.

Mg_3N_2



Magnesium Orthophosphate ($\text{Mg}_3\text{P}_2\text{O}_8$)

(Crystal) Mol. Wt. = 262.91

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0									
100	45.000	45.000	45.000	0.000	-895.100	-839.836	615.586		
200	51.000	45.315	45.001	0.094	-895.109	-839.492	611.540		
300	57.400	40.943	47.088	5.242	-892.413	-820.800	448.498		
400	62.700	74.332	51.228	11.552	-895.395	-802.264	350.652		
500	67.450	86.101	56.085	18.064	-895.112	-783.664	285.436		
600	72.000	100.000	61.164	25.000	-894.700	-757.302	206.875		
700	76.000	116.082	67.207	32.000	-893.264	-735.209	178.524		
800	80.300	124.735	71.207	48.528	-893.992	-712.742	155.762		
900	84.200	132.844	80.901	57.038	-896.126	-690.313	137.146		
1000	87.400	140.395	85.631	75.717	-894.239	-668.949	108.689		
1100	90.320	144.135	94.455	83.551	-1021.325	-622.565	97.182		
1200	90.800	160.384	98.644	92.610	-1018.133	-594.192	86.569		
1300	91.000	165.222	102.688	101.702	-1014.934	-566.038	77.314		
1400	91.200	171.074	106.591	110.810	-1011.461	-538.304	61.916		
1500	91.200	181.917	113.086	129.050	-1005.410	-482.708	55.521		
1600	91.200	186.595	117.510	138.170	-1002.281	-455.286	49.749		
1700	91.200	191.045	120.907	147.290	-999.172	-428.010	44.543		
1800	91.200	195.458	127.372	156.430	-995.030	-373.897	35.527		
1900	91.200	203.223	130.452	174.650	-989.093	-347.043	31.601		
2000	91.200	206.946	133.438	183.770	-986.981	-320.321	28.001		
2100	91.200	210.523	136.334	192.890	-983.989	-293.707	24.687		
2200	91.200	213.285	139.146	202.010	-979.079	-260.435	18.797		
2300	91.200	220.482	144.543	220.250	-975.157	-214.547	16.168		
2400	91.200	223.573	147.117	229.370	-972.263	-188.370	13.722		

Dec. 31, 1960; Mar. 31, 1963

MAGNESIUM ORTHOPHOSPHATE ($\text{Mg}_3\text{P}_2\text{O}_8$)

(CRYSTAL)

MOL. WT. = 262.91

ΔH_f⁰ = Unknown

ΔH_f⁰ 298.15 = -895.1 ± 2.5 kcal. mole⁻¹

ΔH_m⁰ = [29 ± 10] kcal. mole⁻¹

S_{298.15}⁰ = [45] cal. deg. ⁻¹ mole⁻¹

T_m = 1621°K.

Heat of Formation.

The selected ΔH_f⁰ 298.15 is a weighted average of a revised calorimetric determination and a third law calculation using equilibrium data.

A calorimetric determination of the heat of formation reported by C. G. Stevens and E. T. Turkdogan, Trans. Faraday Soc. 50, 370 (1954) was revised three ways:

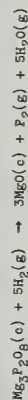
1. The heat of reaction for the reaction $3\text{MgO}(c) + \text{P}_2\text{O}_5(\text{orthorhombic}) \rightarrow \text{Mg}_3\text{P}_2\text{O}_8(c)$ had been evaluated at 348°K. A small temperature correction to 298.15 was made with thermal data not available to Stevens and Turkdogan (loc. cit.) on MgO (W. F. Glauque, J. Am. Chem. Soc. 71, 5192 (1949)), P_2O_5 (JANAP Table, Dec. 31, 1962) and $\text{Mg}_3\text{P}_2\text{O}_8$ (this table).

2. A new ΔH_f⁰ 298.15 for $\text{P}_2\text{O}_5(\text{hexagonal})$ as reported by W. S. Holmes, Trans. Faraday Soc. 58, 1916 (1962) was combined with the heat of reaction, -6.85 ± 1.0 kcal. mole⁻¹, for the reaction: $\text{P}_2\text{O}_5(\text{hexagonal}) \rightarrow \text{P}_2\text{O}_5(\text{orthorhombic})$ as reported by W. L. Hill, G. T. Faust, and S. B. Hendricks, J. Am. Chem. Soc. 65, 734 (1943).

3. A correction of +0.35 kcal. mole⁻¹ was made for the change in phosphorus reference state from white (α) to red (V). (The correction is +0.35 kcal./mole of $\text{Mg}_3\text{P}_2\text{O}_8$ or +4.173 kcal. mole⁻¹ of P.)

This revised ΔH_f⁰ 298.15, -897.60 ± 2.0 kcal. mole⁻¹, would appear to be more reliable than the original value reported by Stevens and Turkdogan (loc. cit.).

For the reaction



the third law treatment of the equilibrium data of J. B. Bookey, J. Iron Steel Institute (London) 172, 68 (1952) and the JANAP Table free energy functions gave a ΔH_f⁰ 298.15 = -893.11 kcal. mole⁻¹.

The quantity, -895.10 ± 2.50 kcal. mole⁻¹, is taken as the most probable value for the heat of formation of magnesium orthophosphate.

Heat Capacity and Entropy.

The entropy at 298.15 was estimated by considering the additive entropy constants of K. K. Kelley, private communication, June 1960, and E. L. Evans and O. Kubaschewski, "Metallurgical Thermochemistry, 1958. The heat capacity was estimated in a similar manner by considering the heat capacities of the constituent elements and related compounds such as Mg, O₂, MgO, P, P₂O₅, Ca₃P₂O₇, and Ca₃P₂O₈.

Melting Data.

The melting point, 1621°K, as reported by Stevens and Turkdogan (loc. cit.) was selected. There is disagreement on the melting point in the literature. From the work of H. Winter, Diss. Universitäts zu Leipzig 1913, K. K. Kelley, U. S. Bureau of Mines Bulletin 393, (1956) has quoted a melting point of 1457°K and has calculated a "rather uncertain value" of 11,300 kcal./mole for the heat of fusion. J. B. Bookey (loc. cit.) has found a melting point of 1703°K. J. Berak, Roczniki Chm. 32, 17 (1955) gives 1630°K as the melting point.



Magnesium Orthophosphate ($Mg_3P_2O_8$)

(Liquid) Mol. Wt. = 262.91



MOL. WT. = 262.91

MAGNESIUM ORTHOPHOSPHATE ($Mg_3P_2O_8$)

(LIQUID)

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0								
100								
200								
298	50.850	54.764	54.764	0.000	-876.897	-824.544	604.378	
300	51.000	55.079	54.764	5.094	-876.906	-824.218	600.414	
400	57.000	61.000	57.000	11.613	-877.131	-788.955	344.635	
500	62.700	66.243	61.017	18.123	-876.850	-771.346	280.949	
600	67.450	69.098	65.894	25.097	-876.333	-753.787	235.335	
700	72.000	106.840	70.987	32.536	-916.427	-746.967	204.052	
800	76.530	116.767	76.096	40.661	-919.676	-742.394	155.938	
900	80.000	124.840	80.000					
1000	84.020	134.703	84.062					
1100	103.550	143.074	90.658	57.438	-917.523	-682.963	135.686	
1200	105.072	152.131	95.591	67.849	-913.871	-661.802	120.525	
1300	109.100	160.884	100.271	80.556	-910.059	-640.965	107.748	
1400	112.500	169.562	109.405	100.737	-901.893	-592.129	86.269	
1500								
1600	113.291	183.852	113.832	112.031	-986.402	-565.665	77.263	
1700	113.600	190.730	118.155	123.377	-980.971	-559.528	69.358	
1800	113.842	197.430	122.369	134.750	-975.541	-513.719	62.371	
1900	114.048	204.043	126.473	146.157	-968.691	-489.510	56.194	
2000	114.206	209.243	130.468	157.557	-961.691	-462.594	50.391	
2100	114.327	214.820	134.351	168.984	-959.275	-438.040	45.585	
2200	114.408	220.140	138.131	180.421	-953.879	-413.342	41.060	
2300	114.448	225.227	141.808	191.864	-948.493	-388.896	36.952	
2400	114.458	230.083	145.385	203.317	-943.124	-364.693	33.202	
2500	114.408	234.769	148.868	214.753	-937.775	-340.693	29.762	
2600	114.327	239.255	152.259	226.190	-932.486	-316.907	26.637	
2700	114.206	243.567	155.561	237.617	-927.214	-293.334	23.743	
2800	114.044	247.718	158.779	249.039	-921.977	-269.955	21.070	
2900	113.842	251.723	161.903	260.454	-916.783	-246.754	18.595	
3000	113.600	255.572	164.973	271.857	-911.633	-223.736	16.250	
3100	113.600	259.297	167.956	283.157	-906.518	-200.887	14.162	
3200	113.600	262.904	170.867	294.517	-901.431	-178.217	12.171	
3300	113.600	266.399	173.709	305.877	-896.384	-155.696	10.311	
3400	113.600	269.787	176.484	317.237	-891.374	-133.309	8.590	
3500	113.600	273.083	179.199	328.597	-886.315	-111.109	6.998	
3600	113.600	276.284	181.851	339.957	-881.330	-89.023	5.404	
3700	113.600	279.396	184.446	351.317	-876.373	-67.080	3.962	
3800	113.600	282.426	186.984	362.677	-871.440	-45.265	2.603	
3900	113.600	285.376	189.467	374.037	-866.536	-23.603	1.323	
4000	113.600	288.252	191.903	385.397	-861.666	-2.056	0.112	
4100	113.600	291.057	194.288	396.757	-856.829	19.380	-1.033	
4200	113.600	293.795	196.624	408.117	-852.020	40.680	-2.117	
4300	113.600	296.468	198.915	419.477	-847.247	61.893	-3.146	
4400	113.600	299.083	201.157	430.837	-842.507	83.106	-4.122	
4500	113.600	301.632	203.367	442.197	-837.804	104.397	-5.049	
4600	113.600	304.129	205.530	453.557	-833.134	124.852	-5.932	
4700	113.600	306.572	207.654	464.917	-828.505	145.625	-6.771	
4800	113.600	308.964	209.740	476.277	-823.915	166.311	-7.572	
4900	113.600	311.306	211.796	487.637	-819.364	186.997	-8.335	
5000	113.600	313.601	213.802	498.997	-814.850	207.368	-9.064	
5100	113.600	315.851	215.761	510.357	-810.385	227.767	-9.760	
5200	113.600	318.057	217.727	521.717	-805.958	248.068	-10.425	
5300	113.600	320.221	219.640	533.077	-801.573	268.324	-11.064	
5400	113.600	322.344	221.507	544.437	-797.134	288.527	-11.676	
5500	113.600	324.428	223.374	555.797	-792.639	308.577	-12.259	
5600	113.600	326.475	225.197	567.157	-788.699	328.499	-12.820	
5700	113.600	328.486	226.992	578.517	-784.501	348.420	-13.358	
5800	113.600	330.462	228.759	589.877	-780.352	368.259	-13.876	
5900	113.600	332.397	230.487	601.237	-776.154	388.030	-14.373	
6000	113.600	334.313	232.213	612.597	-772.009	407.726	-14.851	

Dec. 31, 1960; Mar. 31, 1963

Heat of Formation.
The ΔH_f^o 298.15 was calculated from the estimated ΔH_m and the ΔH_f^o 298.15 of the crystal.

Heat Capacity and Entropy.

The heat capacity was estimated as 13/11 of the corresponding heat capacity of $Ca_3P_2O_8$, as given in K. K. Kelley.

Kelley, U. S. Bur. Mines Bull. 5841 (1960).

Melting Data.

The heat of melting was estimated by taking 13/11 of the ΔH_m of $Ca_3P_2O_8$, as given in K. K. Kelley (loc. cit.)



Molybdenum (Mo)
(Reference State)

GF_W = 95.94

T, °K	C _p ^a	gibbs/mol S ^b	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH ^c	ΔG ^c	Log K _p
0	+0.00	+0.00	INFINITE	-	-	-	-
100	3.232	1.679	11.469	-1.096	+0.00	+0.00	+0.00
200	5.131	4.655	7.345	+0.979	+0.00	+0.00	+0.00
298	5.729	6.837	6.837	+0.538	+0.00	+0.00	+0.00
300	5.737	6.873	6.838	-0.11	+0.00	+0.00	+0.00
400	6.050	8.569	7.087	+0.601	+0.00	+0.00	+0.00
500	6.246	9.942	7.509	1.217	+0.00	+0.00	+0.00
600	6.380	11.083	8.013	1.888	+0.00	+0.00	+0.00
700	6.469	12.084	8.441	2.441	+0.00	+0.00	+0.00
800	6.522	12.954	8.793	2.900	+0.00	+0.00	+0.00
900	6.562	13.730	9.056	3.401	+0.00	+0.00	+0.00
1000	6.598	14.431	9.264	4.067	+0.00	+0.00	+0.00
1100	6.794	15.074	10.400	5.141	+0.00	+0.00	+0.00
1200	6.927	15.670	10.814	5.827	+0.00	+0.00	+0.00
1300	7.006	16.223	11.303	6.480	+0.00	+0.00	+0.00
1400	7.024	16.743	11.757	7.286	+0.00	+0.00	+0.00
1500	7.473	17.272	11.950	7.983	+0.00	+0.00	+0.00
1600	7.684	17.761	12.298	8.741	+0.00	+0.00	+0.00
1700	7.906	18.223	12.693	10.520	+0.00	+0.00	+0.00
1800	8.147	18.664	13.047	11.440	+0.00	+0.00	+0.00
1900	8.377	19.136	13.270	11.188	+0.00	+0.00	+0.00
2000	8.630	19.574	13.575	11.999	+0.00	+0.00	+0.00
2100	8.897	20.001	13.871	12.875	+0.00	+0.00	+0.00
2200	9.190	20.422	14.159	13.779	+0.00	+0.00	+0.00
2300	9.500	20.837	14.437	14.680	+0.00	+0.00	+0.00
2400	9.820	21.231	14.715	15.684	+0.00	+0.00	+0.00
2500	10.463	21.666	14.985	16.703	+0.00	+0.00	+0.00
2600	11.090	22.089	15.250	17.760	+0.00	+0.00	+0.00
2700	11.816	22.520	15.511	18.924	+0.00	+0.00	+0.00
2800	12.542	22.951	15.768	20.180	+0.00	+0.00	+0.00
2900	13.268	23.382	16.022	21.527	+0.00	+0.00	+0.00
3000	14.000	23.813	16.280	22.975	+0.00	+0.00	+0.00
3100	14.732	24.244	16.538	24.522	+0.00	+0.00	+0.00
3200	15.464	24.675	16.796	26.168	+0.00	+0.00	+0.00
3300	16.196	25.106	17.054	27.915	+0.00	+0.00	+0.00
3400	16.928	25.537	17.312	29.762	+0.00	+0.00	+0.00
3500	17.660	25.968	17.570	31.710	+0.00	+0.00	+0.00
3600	18.392	26.399	17.828	33.758	+0.00	+0.00	+0.00
3700	19.124	26.830	18.086	35.905	+0.00	+0.00	+0.00
3800	19.856	27.261	18.344	38.152	+0.00	+0.00	+0.00
3900	20.588	27.692	18.602	40.499	+0.00	+0.00	+0.00
4000	21.320	28.123	18.860	42.946	+0.00	+0.00	+0.00
4100	22.052	28.554	19.118	45.493	+0.00	+0.00	+0.00
4200	22.784	28.985	19.376	48.140	+0.00	+0.00	+0.00
4300	23.516	29.416	19.634	50.887	+0.00	+0.00	+0.00
4400	24.248	29.847	19.892	53.734	+0.00	+0.00	+0.00
4500	24.980	30.278	20.150	56.681	+0.00	+0.00	+0.00
4600	25.712	30.709	20.408	59.728	+0.00	+0.00	+0.00
4700	26.444	31.140	20.666	62.875	+0.00	+0.00	+0.00
4800	27.176	31.571	20.924	66.122	+0.00	+0.00	+0.00
4900	27.908	32.002	21.182	69.469	+0.00	+0.00	+0.00
5000	28.640	32.433	21.440	72.916	+0.00	+0.00	+0.00
5100	29.372	32.864	21.698	76.463	+0.00	+0.00	+0.00
5200	30.104	33.295	21.956	80.110	+0.00	+0.00	+0.00
5300	30.836	33.726	22.214	83.857	+0.00	+0.00	+0.00
5400	31.568	34.157	22.472	87.704	+0.00	+0.00	+0.00
5500	32.300	34.588	22.730	91.651	+0.00	+0.00	+0.00
5600	33.032	35.019	22.988	95.698	+0.00	+0.00	+0.00
5700	33.764	35.450	23.246	99.845	+0.00	+0.00	+0.00
5800	34.496	35.881	23.504	104.092	+0.00	+0.00	+0.00
5900	35.228	36.312	23.762	108.439	+0.00	+0.00	+0.00
6000	35.960	36.743	24.020	112.886	+0.00	+0.00	+0.00

Dec. 31, 1966

See crystal, liquid and monatomic gas tables for details.

(REFERENCE STATE)

0 - 2892°K Crystal
2892 - 4919°K Liquid
4919 - 6000°K Ideal Monatomic gas

MOLYBDENUM (Mo)

GF_W = 95.94

Molybdenum (Mo)
(Crystal)

GFW = 95.94

Mo

QFW = 95.94

(CRYSTAL)

MOLYBDENUM (Mo)

T, °K	Cp	gibbs/mol S ^o - (G ^o - H ^o)/T	H ^o - H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0	•000	INFINITE	- 1.096	•000	•000	•000
100	3.131	1.096	•000	•000	•000	•000
200	4.655	1.096	•538	•000	•000	•000
298	5.729	6.837	•000	•000	•000	•000
300	5.737	6.873	•011	•000	•000	•000
400	6.050	8.569	1.501	•000	•000	•000
500	6.246	9.342	1.421	•000	•000	•000
600	6.380	11.093	8.013	•000	•000	•000
700	6.476	12.084	8.525	•000	•000	•000
800	6.552	12.954	9.026	•000	•000	•000
900	6.622	13.730	9.506	•000	•000	•000
1000	6.698	14.431	9.964	•000	•000	•000
1100	6.794	15.074	10.400	•000	•000	•000
1200	6.827	15.670	10.814	•000	•000	•000
1300	7.090	16.231	11.210	•000	•000	•000
1400	7.274	15.763	11.587	•000	•000	•000
1500	7.473	17.272	11.950	•000	•000	•000
1600	7.684	17.761	12.298	•000	•000	•000
1700	7.806	18.233	12.633	•000	•000	•000
1800	8.140	18.692	12.957	•000	•000	•000
1900	8.377	18.138	13.270	•000	•000	•000
2000	8.630	18.574	13.575	•000	•000	•000
2100	8.897	20.001	13.871	•000	•000	•000
2200	9.190	20.422	14.159	•000	•000	•000
2300	9.520	20.837	14.440	•000	•000	•000
2400	9.820	21.231	14.715	•000	•000	•000
2500	10.463	21.666	14.985	•000	•000	•000
2600	11.090	22.089	15.250	•000	•000	•000
2700	11.616	22.520	15.511	•000	•000	•000
2800	12.618	22.964	15.770	•000	•000	•000
2900	13.590	23.422	16.026	•000	•000	•000
3000	14.460	23.897	16.280	•000	•000	•000
3100	15.400	24.386	16.534	•000	•000	•000
3200	16.320	24.890	16.787	•000	•000	•000
3300	17.240	25.406	17.040	•000	•000	•000
3400	18.160	25.934	17.294	•000	•000	•000
3500	19.080	26.474	17.548	•000	•000	•000
3600	20.000	27.025	17.804	•000	•000	•000
3700	20.920	27.585	18.061	•000	•000	•000
3800	21.840	28.155	18.319	•000	•000	•000
3900	22.760	28.734	18.579	•000	•000	•000
4000	23.680	29.322	18.840	•000	•000	•000

$\Delta H_{298}^{\circ} = 0$ kcal/mol

$S_{298}^{\circ} = 6.837 \pm 0.01$ gibbs/mol

$\Delta H_{298}^{\circ} = 0$ kcal/mol

$\Delta H_{298}^{\circ} = 6.837 \pm 0.01$ gibbs/mol

$T_m = 2892 \pm 10^{\circ}K$

$\Delta H_{298}^{\circ} = 6.837 \pm 0.01$ gibbs/mol

$\Delta H_{298}^{\circ} = 157.3 \pm 0.5$ kcal/mol

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Below 20°K several investigators 1,2,3,4,5,6 have determined the heat capacity, and an average of these determinations was used to obtain a Debye theta = 440 and an electronic gamma = 4.7×10^{-4} gibbs/mol-deg. From these the entropy at 20°K was calculated as 0.024 gibbs/mol and the enthalpy as 0.265 cal. Between 20°K and 271°K the data of Clusius and Franzosini⁷ are the adopted heat capacities. The data of Simon and Zeidler⁸ are as much as 2.5% high below 78°K and as much as 1% low above this.

Both the high temperature enthalpies and heat capacity have been measured by several investigators and there is generally good agreement in the 1000-2000°K range. A smooth curve was drawn through the high temperature enthalpy data of several investigators 7,8,9,10,11,12 which was also joined smoothly to the integrated low temperature data of Clusius and Franzosini. The heat capacity was obtained by fitting the smoothed enthalpy data with a polynomial and differentiating. The heat capacity obtained agreed satisfactorily with that reported in several investigations 13,14,15,16,17,18,19.

References:

1. C. A. Bryant and P. H. Keesom, J. Chem. Phys. **35**, 1149 (1961). Cp 1°-4.5°K.
2. K. Clusius and P. Franzosini, Z. Naturforsch. **14a**, 99 (1959). Cp 13°-270°K.
3. M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953). Cp 1.3°-10.4°K.
4. P. J. Morin and J. P. Meite, Phys. Rev. **129**, 1115 (1963). Cp 1.5°-20°K.
5. F. Simon and W. Zeidler, Z. Phys. Chem. **125**, 383 (1926). Cp 15°-238°K.
6. D. C. Rohrer, D. G. Orr and H. Meyer, Phys. Rev. **139**, A1661, (1965). Cp 0.4°-4°K.
7. P. M. Jaeger and M. A. Veenstra, Rec. Trav. Chim. **53**, 677 (1934). H_m-H_{273} 670°-1827°K.
8. V. A. Kirillin, A. E. Sheindlin and V. Ye. Chekhovskoi, Inter. J. Heat Mass Transfer **5**, 1 (1962). H_m-H_{273} 973°-2610°K.
9. C. W. Kothan, Ph.D. Dissertation, Ohio State University (1952). H_m-H_{298} 1103°-2623°K.
10. L. S. Lazareva, P. B. Kantor and V. V. Kandyba, Phys. Metals and Metallog. **11**, 133 (1961). H_m-H_{298} 1154°-2462°K.
11. T. A. Redfield and J. H. Hill, U.S. At. Energy Comm., ORNL-1087 (1951). H_m-H_{273} 481°-1359°K.
12. F. Wust, A. Meuthen and R. Durrer, Forsch. Gebiete Ingenieurw. **204**, 3 (1916). H_m-H_{273} 375-775°K.
13. H. L. Bronson, H. M. Chisholm and S. M. Dockett, Can. J. Res. **8**, 282 (1933). Cp 254-774°K.
14. D. Cooper and G. O. Longstroth, Phys. Rev. **33**, 243 (1929). Cp 233°-563°K.
15. G. C. Lowenthal, Australian J. Phys. **16**, 47 (1963). Cp 1200° - 2100°K.
16. N. S. Rasor and J. D. McClelland, J. Phys. Chem. Solids **15**, 17 (1959). Cp 1400°-2860°K.
17. R. L. Rudkin, W. J. Parker and R. J. Jenkins, "Temperature, Its Measurement and Control in Science and Industry," Ed. A. I. Dahl Vol. 3, Part 2, Reinhold Publishing Corp., New York, 1962.
18. T. E. Stern, Phys. Rev. **32**, 298 (1928). Cp 273°-718°K.
19. R. E. Taylor and R. A. Finch, J. Less-Common Metals **6**, 283 (1964). Cp 200-2860°K.

Sublimation Data.

See Mo(g) for details.

T, °K	Cp°	S° gibbs/mol	-(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° kcal/mol	ΔG°	Log Kp
0							
100							
200	5.729	9.261	9.261	.000	7.076	6.353	-4.657
298							
300	5.737	9.296	9.261	.011	7.076	6.349	-4.625
400	6.050	10.993	9.490	.601	7.076	6.106	-3.336
500	6.246	12.366	9.932	1.217	7.076	5.864	-2.563
600	6.380	13.517	10.436	1.808	7.076	5.622	-2.048
700	6.476	14.508	10.919	2.491	7.076	5.379	-1.679
800	6.552	15.377	11.449	3.143	7.076	5.137	-1.403
900	6.622	16.153	11.930	3.801	7.076	4.896	-1.189
1000	6.690	16.855	12.368	4.467	7.076	4.652	-1.017
1100	6.794	17.497	12.823	5.141	7.076	4.411	-.876
1200	6.927	18.094	13.238	5.827	7.076	4.167	-.759
1300	7.090	18.655	13.633	6.528	7.076	3.925	-.660
1400	7.274	19.187	14.011	7.246	7.076	3.682	-.575
1500	7.473	19.695	14.373	7.983	7.076	3.442	-.501
1600	7.684	20.184	14.721	8.741	7.076	3.199	-.437
1700	7.906	20.657	15.056	9.520	7.076	2.956	-.380
1800	8.140	21.115	15.380	10.323	7.076	2.714	-.330
1900	8.377	21.562	15.694	11.148	7.076	2.471	-.284
2000	10.000	21.998	15.998	11.999	7.076	2.228	-.243
2100	10.000	22.486	16.296	12.999	7.200	1.981	-.206
2200	10.000	22.951	16.588	13.999	7.296	1.732	-.172
2300	10.000	23.395	16.874	14.999	7.361	1.477	-.140
2400	10.000	23.821	17.155	15.999	7.391	1.223	-.111
2500	10.000	24.229	17.430	16.999	7.372	.964	-.084
2600	10.000	24.621	17.699	17.999	7.295	.711	-.060
2700	10.000	24.999	17.962	18.999	7.151	.457	-.037
2800	10.000	25.362	18.220	19.999	6.930	.215	-.017
2900	10.000	25.713	18.472	20.999	.000	.000	.000
3000	10.000	26.052	18.719	21.999	.000	.000	.000
3100	10.000	26.380	18.961	22.999	.000	.000	.000
3200	10.000	26.698	19.198	23.999	.000	.000	.000
3300	10.000	27.005	19.430	24.999	.000	.000	.000
3400	10.000	27.304	19.657	25.999	.000	.000	.000
3500	10.000	27.594	19.880	26.999	.000	.000	.000
3600	10.000	27.876	20.098	27.999	.000	.000	.000
3700	10.000	28.150	20.312	28.999	.000	.000	.000
3800	10.000	28.416	20.522	29.999	.000	.000	.000
3900	10.000	28.676	20.728	30.999	.000	.000	.000
4000	10.000	28.929	20.929	31.999	.000	.000	.000
4100	10.000	29.176	21.128	32.999	.000	.000	.000
4200	10.000	29.417	21.322	33.999	.000	.000	.000
4300	10.000	29.652	21.513	34.999	.000	.000	.000
4400	10.000	29.882	21.701	35.999	.000	.000	.000
4500	10.000	30.107	21.885	36.999	.000	.000	.000
4600	10.000	30.327	22.076	37.999	.000	.000	.000
4700	10.000	30.542	22.264	38.999	.000	.000	.000
4800	10.000	30.752	22.449	39.999	.000	.000	.000
4900	10.000	30.959	22.631	40.999	.000	.000	.000
5000	10.000	31.161	22.811	41.999	.000	.000	.000
5100	10.000	31.359	22.927	42.999	-141.613	2.327	-.102
5200	10.000	31.553	23.091	43.999	-141.287	5.200	-.223
5300	10.000	31.743	23.253	44.999	-141.589	8.072	-.339
5400	10.000	31.930	23.412	45.999	-141.816	10.957	-.452
5500	10.000	32.114	23.568	46.999	-142.269	13.845	-.560
5600	10.000	32.294	23.723	47.999	-142.684	16.735	-.665
5700	10.000	32.471	23.875	48.999	-143.040	19.640	-.766
5800	10.000	32.645	24.024	49.999	-143.456	22.545	-.864
5900	10.000	32.816	24.172	50.999	-143.888	25.466	-.960
6000	10.000	32.984	24.317	51.999	-144.336	28.386	-1.051
					-144.797	31.321	-1.141

Dec. 31, 1966

OPW = 95.94

(LIQUID)

MOLYBDENUM (Mo)

$$\Delta H_{298.15}^{\circ} = [7.076] \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = [6652 \pm 600] \text{ kcal/mol}$$

$$\Delta H_v^{\circ} = [140.812] \text{ kcal/mol}$$

$S_{298.15}^{\circ} = [9.261] \text{ gibbs/mol}$
 $T_m = 2892 \pm 10^{\circ}\text{K}$
 $T_b = [491.9^{\circ}\text{K}]$

Heat of Formation.

The ΔH_{298}° was obtained from that of the crystal plus ΔH_m° and the difference between $H_{2892}^{\circ} - H_{298}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity was estimated as 10 gibbs/mol in the real range in order to be comparable with the value in the crystal below the melting point. Below the melting point the heat capacity was assumed constant to a glass transition, assumed to be 2000°K, below which the heat capacity was that of the crystal. The entropy was obtained in a manner analogous to the heat of formation.

Melting Data.

The heat of melting was obtained from an entropy of melting of 2.3 eu assumed by comparison with Fe, Cu, Mg and Al. The melting point was reported by E. Rudy and S. Windisch, Aerojet-General Corporation, Report No. AFML-TR-65-2, Part 1, Vol. III, July 1965. A. G. Worthing, Phys. Rev. 25, 846 (1925), reports a melting point of 2895°K which, corrected to the 1948 International Temperature Scale, is 2882°K.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

QFW = 95.94

(IDEAL GAS)

MOLYBDENUM (Mo)

GFW = 95.94

Molybdenum (Mo)
(Ideal Gas)

T, °K	Cp°	$\frac{\text{gibbs/mol}}{T}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0	4.968	0.000	INFINITE	156.915	INFINITE	
100	4.968	39.033	47.677	156.915	156.915	
200	4.968	41.477	43.915	156.915	156.915	
298	4.968	43.460	43.460	156.915	156.915	
300	4.968	43.460	43.460	156.915	156.915	
400	4.968	43.460	43.460	156.915	156.915	
500	4.968	43.460	43.460	156.915	156.915	
600	4.968	43.460	43.460	156.915	156.915	
700	4.968	43.460	43.460	156.915	156.915	
800	4.968	43.460	43.460	156.915	156.915	
900	4.968	43.460	43.460	156.915	156.915	
1000	4.968	43.460	43.460	156.915	156.915	
1100	4.969	49.946	46.324	156.915	156.915	
1200	4.970	50.378	46.845	156.915	156.915	
1300	4.972	50.810	47.366	156.915	156.915	
1400	4.974	51.242	47.887	156.915	156.915	
1500	4.976	51.674	48.408	156.915	156.915	
1600	4.978	52.106	48.929	156.915	156.915	
1700	4.980	52.538	49.450	156.915	156.915	
1800	4.982	52.970	49.971	156.915	156.915	
1900	4.984	53.402	50.492	156.915	156.915	
2000	4.986	53.834	51.013	156.915	156.915	
2100	5.183	53.188	48.899	153.432	83.739	6.715
2200	5.254	53.431	49.099	153.432	83.739	6.715
2300	5.340	53.674	49.299	153.432	83.739	6.715
2400	5.430	53.917	49.499	153.432	83.739	6.715
2500	5.556	54.120	49.661	153.432	83.739	6.715
2600	5.689	54.340	49.837	153.432	83.739	6.715
2700	5.838	54.558	50.008	153.432	83.739	6.715
2800	6.005	54.773	50.174	153.432	83.739	6.715
2900	6.191	54.984	50.337	153.432	83.739	6.715
3000	6.391	55.200	50.495	153.432	83.739	6.715
3100	6.610	55.413	50.650	153.432	83.739	6.715
3200	6.847	55.627	50.802	153.432	83.739	6.715
3300	7.099	55.841	50.952	153.432	83.739	6.715
3400	7.366	56.055	51.103	153.432	83.739	6.715
3500	7.652	56.275	51.243	153.432	83.739	6.715
3600	7.949	56.494	51.386	153.432	83.739	6.715
3700	8.259	56.716	51.527	153.432	83.739	6.715
3800	8.580	56.941	51.667	153.432	83.739	6.715
3900	8.911	57.166	51.807	153.432	83.739	6.715
4000	9.248	57.398	51.942	153.432	83.739	6.715
4100	9.591	57.630	52.078	153.432	83.739	6.715
4200	9.938	57.866	52.213	153.432	83.739	6.715
4300	10.285	58.104	52.347	153.432	83.739	6.715
4400	10.632	58.342	52.481	153.432	83.739	6.715
4500	10.980	58.587	52.614	153.432	83.739	6.715
4600	11.320	58.832	52.746	153.432	83.739	6.715
4700	11.653	59.079	52.878	153.432	83.739	6.715
4800	11.978	59.328	53.010	153.432	83.739	6.715
4900	12.302	59.573	53.142	153.432	83.739	6.715
5000	12.592	59.820	53.273	153.432	83.739	6.715
5100	12.879	60.062	53.404	153.432	83.739	6.715
5200	13.150	60.334	53.535	153.432	83.739	6.715
5300	13.405	60.567	53.666	153.432	83.739	6.715
5400	13.647	60.800	53.797	153.432	83.739	6.715
5500	13.881	61.032	53.928	153.432	83.739	6.715
5600	14.061	61.344	54.056	153.432	83.739	6.715
5700	14.242	61.594	54.186	153.432	83.739	6.715
5800	14.403	61.844	54.316	153.432	83.739	6.715
5900	14.559	62.094	54.446	153.432	83.739	6.715
6000	14.669	62.337	54.576	153.432	83.739	6.715

DEC. 31, 1966

Ground State Configuration $7s_3$
 $S^\circ_{298.15} = 43.46 \text{ gibbs/mol}$
 $\Delta H^\circ_{298.15} = 157.3 \pm 0.5 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	$\epsilon_1, \text{cm}^{-1}$	$\epsilon_1, \text{cm}^{-1}$	$\epsilon_1, \text{cm}^{-1}$	$\epsilon_1, \text{cm}^{-1}$	$\epsilon_1, \text{cm}^{-1}$
0	7	21206.5	42	42864.0	138
10768.3	5	23571.2	21	44803.0	188
10966.0	1	24504.7	34	45765.0	119
11142.8	3	25990.1	152	46766.0	163
11454.4	5	27548.0	52	47784.5	194
11858.5	7	29551.1	133	48787.6	167
12346.5	9	31809.1	105	49856.1	211
16746.8	45	34546.4	109	50825.0	201
18321.8	15	37024.7	169	52783.0	330
20240.5	26	39820.1	168	54945.0	180
22639.0	8	40876.3	124	56851.0	58

Heat of Formation

The heat of formation is simply the heat of sublimation at 298°K; this is obtained by second and third law analysis of several vapor pressure sets. A comparison of the results is tabulated below.

Reference	Method	Points	Range °K	2nd law $\Delta H^\circ_{298} \text{ kcal/mol}$	3rd law $\Delta H^\circ_{298} \text{ kcal/mol}$	Drift in 3rd law
1. Vozella	Langmuir	12	2140-2535	156.4 ± 2.9	157.6 ± 0.9	0.2 ± 1.3 eu
2. Edwards	Langmuir	9	2150-2460	146.7 ± 1.5	158.2 ± 1.2	5.0 ± 0.6 eu
3. Fries	Langmuir	12	2086-2489	156.5 ± 1.6	156.7 ± 0.7	0.1 ± 0.7 eu
4. Jones	Langmuir	9*	2113-2496	161.6 ± 3.8	156.0 ± 1.4	-2.6 ± 1.6 eu
5. Norris	Langmuir	Equn.	2000-2600*	131.1	148.6 ± 4.3	8.8 eu
6. Zwikker	Langmuir	Equn.	1200-2500*	159.1	156.2 ± 0.8	-0.8 eu
7. Babeliewsky	Mass Spec.		2220-2603*	149.6 ± 2.2		

* One point rejected due to failure of statistical test

The data of references 1 and 3 show no drift and thus indicate that the accommodation coefficient is essentially unity. A median value of the 3rd law heat is adopted as $157.3 \pm 0.5 \text{ kcal/mol}$.

References:

1. P. A. Vozella, A. D. Miller and M. A. DeCrescente, *J. Chem. Phys.* **41**, 589 (1964).
2. J. W. Edwards, H. L. Johnston and P. E. Blackburn, *J. Am. Chem. Soc.* **74**, 1559 (1952).
3. R. J. Fries, *ASAC Accession No. 13053*, Rept. No. LA-3423, January 1966.
4. H. A. Jones, I. Langmuir and G. M. J. Mackay, *Phys. Rev.* **30**, 201 (1927).
5. L. Norris and A. G. Worthing, *Phys. Rev.* **44**, 323 (1935).
6. C. Zwikker, *Physica* **7**, 71 (1927).
7. T. P. J. H. Babeliewsky, *Physica* **28**, 1180 (1962).

** Temperatures adjusted to 1946 IFTS according to R. J. Corruccini, *J. Natl. Bur. Std.* **42**, 133 (1949).

Heat Capacity and Entropy

The electronic energy levels are those listed by C. E. Moore, U. S. Natl. Bur. Std. Circular 467, Washington D. C. (1959). Several individual lines missing from given terms were estimated by analogy with the observed lines in the term. In addition, an estimate of the values of completely missing terms, arising out of low lying multiplets, was made as follows: The 1D and 3P and 3D terms of the $[\text{Kr}] 4d^5s^2$ multiplet were estimated at 25000, 30000, 34000 and 36000 cm^{-1} . The triplet $^3P, ^3D$ and G levels and the singlet $^1D, ^1F$ and G levels of the $[\text{Kr}] 4d^6$ configuration were estimated at 30000 cm^{-1} and 40000 cm^{-1} respectively.

Higher configurations such as $[\text{Kr}] 4d^4s^2(6p) 5d$ which have many septuplet and quintuplet terms were thought to lie close to the ionization limit. However, upon calculating a table which contains an extra 100 levels at 35000 cm^{-1} and 200 levels each at 40000 and 45000 cm^{-1} , the difference in free energy function at 6000°K is a negligible 0.008 gibbs/mol.

MOLYBDENUM UNIPOSITIVE ION (Mo⁺) (IDEAL GAS) GFW = 95.9395

Ground State Configuration $s_{2,1/2}$ $\Delta H_f^\circ = 320.957 \text{ kcal/mol}$
 $S_{298.15}^\circ = 43.154 \text{ gibbs/mol}$ $\Delta H_f^\circ = 322.823 \text{ kcal/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_1, \text{cm}^{-1}$	g_1
0	6	22864.4	4	42560	32
11783.4	2	22980.5	12	43976	28
12054.1	4	23248.2	14	47797	54
12417.3	6	23904	28	49426	18
12900.3	8	24879	34	50454	30
13460.7	10	28544	64	52216	28
15199.3	6	27646	40	55208	20
15330.6	8	28975	36	60090	182
15427.7	10	30144	36	62260	44
15447.0	12	32124	2	63143	116
15691.2	6	34419	4	64560	104
15699.2	4	33350	70	65989	110
15900.1	2	35241	26	67971	72
16796.1	2	38547	14	69202	98
17174.1	4	37777	18	71319	52
17344.1	6	39645	10	73794	68
16946.8	8	41537	12	78227	108
22444.4	6			83557	82

Heat of Formation

The heat of formation is obtained by adding the heat of ionization to the heat of formation of the gas at 0°K. The heat of ionization, 163.742 kcal/mol (7.10 eV), is obtained from G. E. Moore, Natl. Bur. Std. Circular 467, Vol. III, Washington, D. C. (1958).

Heat Capacity and Entropy

The electronic energy levels are taken from C. E. Moore, loc. cit. The configuration [Kr] 4d⁵s² is completely missing in Mo⁺, while in the isoelectronic Nb(g) this is a very low lying configuration. However, a comparison of Cr⁺ with Mo⁺ and V(g) with Nb(g) indicates that the similarities are much closer down a given group than across a row to an isoelectronic neighbor. Thus, by analogy with Cr⁺, the missing configuration is expected to lie >50,000 cm⁻¹ and thus be negligible.

The enthalpy at 0°K is calculated to be -1.481 kcal/mol.

T, °K	Cp ^o	$\frac{\text{gibbs/mol}}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$\frac{\text{kcal/mol}}{\Delta H^\circ}$	ΔG°	Log Kp
0						
100	4.968	43.154	4.000	322.823	310.508	-227.608
200	4.968	43.154	4.009	322.830	310.431	-226.149
300	4.968	43.154	4.013	322.833	310.408	-225.700
400	4.968	43.154	4.017	322.836	310.385	-225.261
500	4.968	43.154	4.021	322.839	310.363	-224.822
600	4.968	43.154	4.025	322.842	310.340	-224.383
700	4.968	43.154	4.029	322.845	310.317	-223.944
800	4.968	43.154	4.033	322.848	310.294	-223.505
900	4.968	43.154	4.037	322.851	310.271	-223.066
1000	4.968	43.154	4.041	322.854	310.248	-222.627
1100	4.968	43.154	4.045	322.857	310.225	-222.188
1200	4.968	43.154	4.049	322.860	310.202	-221.749
1300	4.968	43.154	4.053	322.863	310.179	-221.310
1400	4.968	43.154	4.057	322.866	310.156	-220.871
1500	4.968	43.154	4.061	322.869	310.133	-220.432
1600	4.968	43.154	4.065	322.872	310.110	-220.000
1700	4.968	43.154	4.069	322.875	310.087	-219.561
1800	4.968	43.154	4.073	322.878	310.064	-219.122
1900	4.968	43.154	4.077	322.881	310.041	-218.683
2000	4.968	43.154	4.081	322.884	310.018	-218.244
2100	4.968	43.154	4.085	322.887	310.000	-217.805
2200	4.968	43.154	4.089	322.890	310.000	-217.366
2300	4.968	43.154	4.093	322.893	310.000	-216.927
2400	4.968	43.154	4.097	322.896	310.000	-216.488
2500	4.968	43.154	4.101	322.899	310.000	-216.049
2600	4.968	43.154	4.105	322.902	310.000	-215.610
2700	4.968	43.154	4.109	322.905	310.000	-215.171
2800	4.968	43.154	4.113	322.908	310.000	-214.732
2900	4.968	43.154	4.117	322.911	310.000	-214.293
3000	4.968	43.154	4.121	322.914	310.000	-213.854
3100	4.968	43.154	4.125	322.917	310.000	-213.415
3200	4.968	43.154	4.129	322.920	310.000	-212.976
3300	4.968	43.154	4.133	322.923	310.000	-212.537
3400	4.968	43.154	4.137	322.926	310.000	-212.098
3500	4.968	43.154	4.141	322.929	310.000	-211.659
3600	4.968	43.154	4.145	322.932	310.000	-211.220
3700	4.968	43.154	4.149	322.935	310.000	-210.781
3800	4.968	43.154	4.153	322.938	310.000	-210.342
3900	4.968	43.154	4.157	322.941	310.000	-209.903
4000	4.968	43.154	4.161	322.944	310.000	-209.464
4100	4.968	43.154	4.165	322.947	310.000	-209.025
4200	4.968	43.154	4.169	322.950	310.000	-208.586
4300	4.968	43.154	4.173	322.953	310.000	-208.147
4400	4.968	43.154	4.177	322.956	310.000	-207.708
4500	4.968	43.154	4.181	322.959	310.000	-207.269
4600	4.968	43.154	4.185	322.962	310.000	-206.830
4700	4.968	43.154	4.189	322.965	310.000	-206.391
4800	4.968	43.154	4.193	322.968	310.000	-205.952
4900	4.968	43.154	4.197	322.971	310.000	-205.513
5000	4.968	43.154	4.201	322.974	310.000	-205.074
5100	4.968	43.154	4.205	322.977	310.000	-204.635
5200	4.968	43.154	4.209	322.980	310.000	-204.196
5300	4.968	43.154	4.213	322.983	310.000	-203.757
5400	4.968	43.154	4.217	322.986	310.000	-203.318
5500	4.968	43.154	4.221	322.989	310.000	-202.879
5600	4.968	43.154	4.225	322.992	310.000	-202.440
5700	4.968	43.154	4.229	322.995	310.000	-201.999
5800	4.968	43.154	4.233	322.998	310.000	-201.560
5900	4.968	43.154	4.237	322.999	310.000	-201.121
6000	4.968	43.154	4.241	322.999	310.000	-200.682

Molybdenum Monoxide (MoO)

MoO

(Ideal Gas) GFW = 111.9394

GFW = 111.9394

MOLYBDENUM MONOXIDE (MoO)

(IDEAL GAS)

Ground State Configuration [²]ΔH_f⁰ = 92.5 ± 15 kcal/molS_{298.15}⁰ = [56.9 ± 2] gibbs/molΔH_f⁰ = 92.5 ± 15 kcal/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i
[0]	[3]
[14000]	[1]
[17000]	[2]
[19000]	[5]

$\omega_e x_e = [3.61] \text{ cm}^{-1}$
 $\omega_e = [955] \text{ cm}^{-1}$
 $B_e = [0.37943] \text{ cm}^{-1}$
 $\alpha_e = [0.00188] \text{ cm}^{-1}$
 $r_e = [1.80] \text{ \AA}$
 $\sigma = 1$

Heat of Formation

The heat of formation, ΔH_f⁰298 (MoO, g) = 92.5 ± 15 kcal/mol, is derived from the heat of reaction, ΔH_r⁰298 = 32.9 kcal/mol for Mo(c) + O(g) + MoO(g) with all JANAF auxiliary data. The value of ΔH_f⁰298 is calculated by the third law method from the partial pressure data determined mass-spectrometrically in the temperature range from 2262 to 2466°K by G. DeMaria, et al. (1). The drift in the third law analysis is -14 ± 11 eu.

Heat Capacity and Entropy

The ground state configuration and the probable electronic levels are assumed to be similar to those for WO(g) (see JANAF WO(g) table of Sept. 30, 1966). T. M. Swaminathan and S. G. Krishnamurthy (2) observed ten band systems attributed to molybdenum oxide with lower state values of $\omega_e = 950 \pm 10 \text{ cm}^{-1}$. T. V. Iorns and F. E. Stafford (3) also observed a band with a peak at 969 cm⁻¹ in the vapor above MoO₃(c). It is surprising that the observed vibrational frequency of MoO(g) is lower than 1055 cm⁻¹ observed for WO(g). The latter comes not only from electronic spectra of the gas but also from infrared observation in matrix isolation; the former comes only from tentative assignments of electronic spectra presumably arising from MoO(g). It is possible that the observed states could be low lying excited states. We tentatively assume the fundamental vibrational frequency to be 955 cm⁻¹. The bond distance is then calculated by Guggenheimer's relation (4) for multiple bond molecules from the estimated vibrational frequency. The anharmonicity correction x_e is estimated from the relation $x_e^{1/2} = 0.014$ given by R. F. Barrow and A. D. Caunt (5). The constant (0.014) is assumed to be the same as that for WO(g). The value of α_e is calculated from the Morse potential function. The rotational constant B_e is calculated from the estimated bond distance.

References

1. G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960).
2. T. M. Swaminathan and S. G. Krishnamurthy, Current Sci. (India) **23**, 258 (1954).
3. T. V. Iorns and F. E. Stafford, J. Am. Chem. Soc. **88**, 4819 (1966).
4. K. M. Guggenheimer, Proc. Phys. Soc. (London) **53**, 456 (1946).
5. R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **213A**, 120 (1953).

T, °K	Cp ⁰	$\frac{\text{gibbs/mol}}{S^0 - (G^0 - H_{298}^0)/T}$	$H^0 - H_{298}^0$	$\frac{\text{kcal/mol}}{\Delta H^0}$	ΔG ⁰	Log Kp
100	6.000	INF	2.102	92.531	92.531	INF
200	6.059	49.226	1.002	92.761	92.761	INF
300	6.099	33.995	1.708	92.672	87.426	95.535
400	6.139	26.872	1.000	92.500	84.887	62.224
500	6.179	21.567	0.14	92.496	84.840	61.806
600	6.219	17.137	1.267	92.311	82.316	44.975
700	6.259	13.637	2.386	91.933	77.400	28.193
800	6.299	10.654	3.223	91.738	74.993	23.414
900	6.339	8.097	4.074	91.538	72.414	19.637
1000	6.379	6.035	5.001	91.333	70.262	17.062
1100	6.419	4.481	6.074	90.900	67.931	14.886
1200	6.459	3.311	7.551	90.667	65.424	13.038
1300	6.499	2.408	9.332	90.419	63.336	11.535
1400	6.539	1.762	11.377	90.153	61.068	10.266
1500	6.579	1.301	13.769	89.867	58.819	9.162
1600	6.619	1.002	16.665	89.560	56.593	8.246
1700	6.659	0.824	19.992	89.230	54.384	7.428
1800	6.699	0.713	23.764	88.875	52.195	6.710
1900	6.739	0.651	27.992	88.497	50.027	6.074
2000	6.779	0.587	32.764	88.091	47.880	5.507
2100	6.819	0.527	38.164	87.660	45.749	4.999
2200	6.859	0.471	44.264	87.204	43.644	4.542
2300	6.899	0.419	51.164	86.724	41.559	4.129
2400	6.939	0.371	58.964	86.224	39.494	3.753
2500	6.979	0.327	67.764	85.704	37.455	3.411
2600	7.019	0.287	77.564	85.164	35.435	3.098
2700	7.059	0.251	88.364	84.596	33.443	2.811
2800	7.099	0.219	100.164	84.004	31.473	2.548
2900	7.139	0.191	113.064	83.464	29.531	2.305
3000	7.179	0.167	127.064	82.874	27.641	2.083
3100	7.219	0.147	142.264	82.244	25.811	1.893
3200	7.259	0.131	158.664	81.574	24.041	1.716
3300	7.299	0.117	176.264	80.864	22.325	1.552
3400	7.339	0.105	195.064	80.114	20.655	1.399
3500	7.379	0.095	215.064	79.324	19.035	1.256
3600	7.419	0.087	236.264	78.494	17.465	1.122
3700	7.459	0.081	258.664	77.624	15.945	0.996
3800	7.499	0.076	282.264	76.714	14.475	0.879
3900	7.539	0.072	307.064	75.764	13.055	0.768
4000	7.579	0.069	333.064	74.774	11.685	0.664
4100	7.619	0.066	360.264	73.744	10.365	0.566
4200	7.659	0.064	388.664	72.674	9.095	0.473
4300	7.699	0.062	418.264	71.564	7.875	0.385
4400	7.739	0.061	449.064	70.414	6.705	0.302
4500	7.779	0.060	481.064	69.224	5.585	0.224
4600	7.819	0.059	514.264	67.994	4.505	0.149
4700	7.859	0.058	548.664	66.724	3.475	0.079
4800	7.899	0.057	584.264	65.414	2.495	0.012
4900	7.939	0.056	621.064	64.064	1.565	0.002
5000	7.979	0.055	659.064	62.674	0.685	0.000
5100	8.019	0.054	708.264	61.244	-0.245	-0.003
5200	8.059	0.053	758.664	59.774	-1.165	-0.006
5300	8.099	0.052	810.264	58.264	-2.085	-0.009
5400	8.139	0.051	863.064	56.714	-3.005	-0.012
5500	8.179	0.050	917.064	55.124	-3.925	-0.015
5600	8.219	0.049	972.264	53.494	-4.845	-0.018
5700	8.259	0.048	1028.664	51.824	-5.765	-0.021
5800	8.299	0.047	1086.264	50.114	-6.685	-0.024
5900	8.339	0.046	1145.064	48.364	-7.605	-0.027
6000	8.379	0.045	1205.064	46.574	-8.525	-0.030

June 30, 1967

MoO

Molybdenum Dioxide (MoO₂)
(Crystal) GFW = 127.9388

T, °K	Cp ^a	μbbs/mol S ^b - (C ^a - H [°] ° ₂₉₈)/T	H [°] - H [°] ₂₉₈	ΔH [°] kcal/mol	ΔG [°]	Log Kp
0	.000	INFINITE	- 1.988	- 139.317	- 139.317	INFINITE
100	9.866	21.276	- 1.964	- 140.004	- 135.960	297.141
200	9.866	13.059	- 1.157	- 140.434	- 131.718	143.935
298	13.390	11.254	.000	- 140.500	- 127.415	93.396
300	13.407	12.037	.025	- 140.499	- 127.334	92.763
400	15.189	16.165	1.464	- 140.361	- 122.963	67.184
500	16.237	19.674	3.039	- 140.134	- 118.439	51.857
600	17.011	22.705	4.702	- 139.856	- 114.364	41.487
700	17.671	25.378	6.437	- 139.542	- 110.140	34.387
800	18.281	27.777	8.235	- 139.194	- 105.964	28.968
900	18.873	29.965	10.092	- 138.809	- 101.832	24.728
1000	19.464	31.984	12.009	- 138.385	- 97.746	21.362
1100	20.048	33.867	13.984	- 137.921	- 93.706	18.617
1200	20.617	35.639	16.022	- 137.419	- 89.707	16.416
1300	21.107	37.319	18.121	- 136.878	- 85.752	14.416
1400	21.558	38.921	20.285	- 136.296	- 81.841	12.776
1500	22.029	40.459	22.514	- 135.675	- 77.972	11.360
1600	22.326	41.942	24.835	- 135.013	- 74.147	10.128
1700	22.041	43.377	27.179	- 134.306	- 70.344	9.066
1800	21.782	44.772	29.620	- 133.557	- 66.524	8.089
1900	21.546	46.132	32.136	- 132.761	- 62.624	7.238
2000	21.338	47.463	34.731	- 131.917	- 58.725	6.477
2100	21.153	48.767	37.405	- 131.028	- 55.664	5.793
2200	20.993	50.050	40.162	- 130.093	- 52.525	5.175
2300	20.858	51.313	43.004	- 129.092	- 49.376	4.616
2400	20.749	52.560	45.934	- 128.054	- 46.193	4.106
2500	20.665	53.793	48.955	- 126.980	- 42.963	3.642
2600	21.607	55.014	52.068	- 125.876	- 39.699	3.217
2700	32.574	56.225	55.277	- 124.749	- 36.409	2.829
2800	31.566	57.427	58.584	- 123.606	- 33.145	2.468
2900	31.585	58.623	61.991	- 122.077	- 29.831	2.135
3000	35.529	59.813	65.502	- 120.519	- 26.483	1.813

June 30, 1967

MOLYBDENUM DIOXIDE (MoO₂)

(CRYSTAL)

GFW = 127.9388

S[°]_{298.15} = 11.96 ± 2 gibbs/mol
Td = Unknown
ΔH[°]_F = -139.3 ± 0.5 kcal/mol
ΔH[°]_{298.15} = -140.5 ± 0.5 kcal/mol

Heat of Formation

The adopted heat of formation, -140.5 kcal/mol, is a weighted average of values derived from calorimetric determinations, emf measurements and equilibrium studies. The results are given below.

Ignition of the bomb products from the calorimetric studies of Staskiewicz et al. indicated that oxidation was only about 70 per cent complete. The authors also digested the products with NH₄OH to remove the trioxide. The residue was the dioxide, as indicated by both oxidation and reduction. This evidence does not necessarily eliminate the possibility of known intermediate oxides in the combustion products. Mah found 72 - 75 per cent conversion to trioxide by weighing the total combustion products; he performed no additional analysis.

Investigator	Method	Reaction	Temp. Range (°K)	No. of Points	ΔH [°] ₂₉₈ (kcal/mol)	Drift (eu)	ΔH [°] ₂₉₈ (kcal/mol)
1. Staskiewicz et al.	Calorimetric	A	-	-	-37.12	-	-140.86 ± 0.13**
2. Mah	Calorimetric	A	-	-	-37.52	-	-140.64 ± 0.13**
3. Rapp	EMF	B	1073-1223	35	-13.18	-13.42	0.140 ± 1
		C	1073-1273	22	-25.65	-25.63	0.40 ± 1
		F	873-1073	Equation	-138.66	-140.3	1.7
4. Barbi	EMF	D	1296-1341	9	-5.44	-0.3	-4.42 ± 2
5. Gleiser and Chipman	Equilibrium	E	949-1144	Equation	-24.58	-17.7	-6.0
6. Gokcen	Equilibrium	E	973-1173	Equation	-24.57	-22.2	-2.2
7. Collins	Equilibrium	E	981-1096	Equation	-24.0	-18.5	-5.4
8. Tonosaki	Equilibrium	E	-	-	-	-	-139.61*

*Third law value used in the calculation.

**Auxiliary data for Mo₂O₃(c) are taken from corresponding measurements of the same authors. See JANAF MoO₃(c) table for details.

Reaction: A. MoO₂(c) + 1/2 O₂(g) = MoO₃(c).

B. 2Fe₂O(c) + Mo(c) = MoO₂(c) + 2Fe(c).

C. 2NiO(c) + Mo(c) = MoO₂(c) + 2Ni(c).

D. Mo(c) + 2CO₂(g) = MoO₂(c) + 2CO(g).

E. Mo(c) + 2H₂O(g) = MoO₂(c) + 2H₂(g).

F. Mo(c) + O₂(g) = MoO₂(c) derived by the author from the cell reaction 2Fe₂O(c) + Mo(c) = MoO₂(c) + 2Fe(c) using ΔG[°] data for Fe₂O(c).

References

1. B. A. Staskiewicz, J. R. Tucker and P. E. Snyder, J. Am. Chem. Soc. **77**, 2987 (1955).
2. A. D. Mah, J. Am. Chem. Soc. **81**, 1572 (1957).
3. R. A. Rapp, Trans. AIME **227**, 371 (1963).
4. G. B. Barbi, J. Phys. Chem. **68**, 1025 (1964).
5. M. Gleiser and J. Chipman, J. Phys. Chem. **66**, 1539 (1962).
6. N. A. Gokcen, Trans. AIME **187**, 1019 (1953).
7. B. T. Collins, Sc. D. Thesis, Massachusetts Institute of Technology, 1949.
8. K. Tonosaki, Bull. Inst. Phys. Chem. Res. (Tokyo) **13**, 126 (1940).

Heat Capacity and Entropy

E. G. King, J. Am. Chem. Soc. **80**, 1799 (1958), measured the low temperature heat capacities from 53.3° to 296°K. E. G. King, W. M. Waller and A. U. Christensen, U. S. Bur. Mines RI 5684, 1960, measured the high temperature enthalpy changes from 399° to 1801°K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that there be a smooth joint at 298°K. Deviations of the enthalpy data from the adopted values are -1.3 to +0.7 percent, excluding the point at 1801°K. This point at the highest temperature deviates by +2.3 percent, which suggests that the apparent heat capacity is rising very rapidly. No explanation for this rapid rise is available.

The entropy S[°]₂₉₈ = 11.054 eu is obtained from the low temperature heat capacity data, based on S[°]₂₉₈ = 0.31 eu.

B. N. Figgis and J. Lewis, "Progress in Inorg. Chem.", Vol. **5**, page 123, Interscience Publishers, New York, 1964, indicated that MoO₂ is probably antiferromagnetic. Its small susceptibility is presumably due to Mo-Mo interactions. It is possible that at temperatures below 50°K entropy due to spin interactions of the d² electrons will appear, contributing up to 2.2 eu. The drifts in the equilibrium data do suggest that additional entropy may be appropriate; however, only the EMF data of Rapp appear to be sufficiently precise to influence the decision. These data suggest addition of 0.8 ± 0.1 eu and 0.9 ± 0.1 eu based on auxiliary data for Wüstite and NiO(c), respectively. We select the entropy of 11.954 eu from equilibrium data for NiO.

MoO₂

Molybdenum Dioxide (MoO₂)

(Ideal Gas)

GFW = 127.9388

MOLYBDENUM DIOXIDE (MoO₂)

(IDEAL GAS)

GFW = 127.9388

Point Group [C_{2v}] $\Delta H_f^\circ = -2.6 \pm 5 \text{ kcal/mol}$ $\Delta H_f^\circ_{298.15} = -3.1 \pm 5 \text{ kcal/mol}$ $S^\circ_{298.15} = [66.4 \pm 3] \text{ gibbs/mol}$

Ground State Quantum Weight = [3]

T, °K	Cp ^a	S ^b - (C ^a - H ^a)/T	gibbs/mol	H ^a - H ³⁰⁰	ΔH ^c	kcal/mol	ΔG ^d	Log Kp
0	6.500	INFINITE	INFINITE	-2.684	-2.613	-2.613	INFINITE	INFINITE
100	6.527	56.276	75.046	-1.877	-2.617	-2.617	8.405	8.405
200	9.487	62.475	87.359	-1.977	-2.654	-2.654	5.654	5.654
298	10.422	66.436	90.000	-2.000	-3.100	-3.100	6.259	6.259
300	10.430	66.501	90.198	-2.019	-3.105	-3.105	6.279	6.279
400	11.247	72.221	97.677	-2.272	-3.317	-3.317	7.304	7.304
500	12.410	78.442	104.624	-3.491	-3.667	-3.667	8.279	8.279
600	13.462	83.469	110.340	-4.701	-4.509	-4.509	9.218	9.218
700	14.257	87.359	115.000	-5.936	-5.950	-5.950	10.130	10.130
800	14.857	90.293	118.881	-7.186	-7.481	-7.481	11.000	11.000
900	15.282	92.442	121.984	-8.464	-8.830	-8.830	11.887	11.887
1000	15.572	94.000	124.368	-9.788	-10.130	-10.130	12.737	12.737
1100	15.747	95.056	125.984	-11.130	-11.486	-11.486	13.569	13.569
1200	15.842	95.722	126.722	-12.504	-12.850	-12.850	14.385	14.385
1300	15.875	96.000	127.200	-13.900	-14.240	-14.240	15.186	15.186
1400	15.857	96.000	127.200	-15.320	-15.656	-15.656	15.964	15.964
1500	15.792	95.722	126.722	-16.768	-17.088	-17.088	16.718	16.718
1600	15.687	95.056	125.984	-18.240	-18.540	-18.540	17.456	17.456
1700	15.547	93.984	124.368	-20.740	-21.040	-21.040	18.176	18.176
1800	15.377	92.442	121.984	-23.280	-23.580	-23.580	18.876	18.876
1900	15.182	90.293	118.881	-25.860	-26.160	-26.160	19.556	19.556
2000	14.962	87.359	115.000	-28.480	-28.780	-28.780	20.216	20.216
2100	14.722	83.469	110.340	-31.140	-31.440	-31.440	20.856	20.856
2200	14.462	78.442	104.624	-33.840	-34.140	-34.140	21.476	21.476
2300	14.182	72.221	97.677	-36.580	-36.880	-36.880	22.076	22.076
2400	13.882	66.436	90.000	-39.360	-39.660	-39.660	22.656	22.656
2500	13.562	60.293	82.442	-42.180	-42.480	-42.480	23.216	23.216
2600	13.232	53.722	74.200	-45.040	-45.340	-45.340	23.756	23.756
2700	12.892	46.722	65.624	-47.940	-48.240	-48.240	24.276	24.276
2800	12.542	39.293	56.722	-50.880	-51.180	-51.180	24.776	24.776
2900	12.182	31.442	47.442	-53.860	-54.160	-54.160	25.256	25.256
3000	11.812	23.200	37.722	-56.880	-57.180	-57.180	25.716	25.716
3100	11.432	14.624	27.500	-59.940	-60.240	-60.240	26.156	26.156
3200	11.042	6.500	16.722	-63.040	-63.340	-63.340	26.576	26.576
3300	10.642	-1.877	6.000	-66.180	-66.480	-66.480	26.976	26.976
3400	10.232	-8.405	-3.405	-69.360	-69.660	-69.660	27.356	27.356
3500	9.812	-15.186	-10.186	-72.580	-72.880	-72.880	27.716	27.716
3600	9.382	-22.076	-17.076	-75.840	-76.140	-76.140	28.056	28.056
3700	8.942	-29.056	-24.056	-79.140	-79.440	-79.440	28.376	28.376
3800	8.492	-36.140	-31.140	-82.480	-82.780	-82.780	28.676	28.676
3900	8.032	-43.320	-38.320	-85.860	-86.160	-86.160	28.956	28.956
4000	7.562	-50.540	-45.540	-89.280	-89.580	-89.580	29.216	29.216
4100	7.082	-57.780	-52.780	-92.740	-93.040	-93.040	29.456	29.456
4200	6.592	-65.040	-60.040	-96.240	-96.540	-96.540	29.676	29.676
4300	6.092	-72.320	-67.320	-99.780	-100.080	-100.080	29.876	29.876
4400	5.582	-79.620	-74.620	-103.360	-103.660	-103.660	30.056	30.056
4500	5.062	-86.940	-81.940	-106.980	-107.280	-107.280	30.216	30.216
4600	4.532	-94.280	-89.280	-110.640	-110.940	-110.940	30.356	30.356
4700	3.992	-101.640	-96.640	-114.340	-114.640	-114.640	30.476	30.476
4800	3.442	-109.020	-104.020	-118.080	-118.380	-118.380	30.576	30.576
4900	2.882	-116.420	-111.420	-121.860	-122.160	-122.160	30.656	30.656
5000	2.312	-123.840	-118.840	-125.680	-125.980	-125.980	30.716	30.716
5100	1.732	-131.280	-126.280	-129.540	-129.840	-129.840	30.756	30.756
5200	1.142	-138.740	-133.740	-133.440	-133.740	-133.740	30.776	30.776
5300	0.542	-146.220	-141.220	-137.380	-137.680	-137.680	30.776	30.776
5400	-0.058	-153.720	-148.720	-141.360	-141.660	-141.660	30.756	30.756
5500	-0.648	-161.240	-156.240	-145.380	-145.680	-145.680	30.716	30.716
5600	-1.228	-168.780	-163.780	-149.440	-149.740	-149.740	30.656	30.656
5700	-1.808	-176.340	-171.340	-153.540	-153.840	-153.840	30.576	30.576
5800	-2.388	-183.920	-178.920	-157.680	-157.980	-157.980	30.476	30.476
5900	-2.968	-191.520	-186.520	-161.860	-162.160	-162.160	30.356	30.356
6000	-3.548	-199.140	-194.140	-166.080	-166.380	-166.380	30.216	30.216

June 30, 1968

Heat of Formation

Burns et al. (1) have investigated mass-spectrometrically the vapor in equilibrium with powdered MoO₂(c) and also reported the partial pressures of MoO₂(g), MoO₃(g), (MoO₃)₂(g), and (MoO₃)₃(g). Second and third analyses of their partial pressure data are given in the table below. The adopted value, $\Delta H_f^\circ(\text{MoO}_2, g) = -3.1 \text{ kcal/mol}$, is calculated from their 3rd law value of $\Delta H_f^\circ = 137.4 \text{ kcal/mol}$ for MoO₂(c) + MoO₃(g), using all JANAF functions.

DeMaría et al. (2) have measured the partial pressures of gaseous oxides MoO, MoO₂, MoO₃ and O(g) in the Mo-Al₂O₃ system by mass spectrometry. Blackburn et al. (3) and Plante (4) have studied the vapor pressures above molybdenum dioxide(c) by the Knudsen effusion method. Second and third law analyses of these three sets of partial pressure data are reported in the following table.

Investigator	Reaction	Temp. °K	No. of Points	2nd law	3rd law	Drift	$\Delta H_f^\circ(\text{MoO}_2, g)$
1. Burns et al.	MoO ₂ (c) + MoO ₃ (g)	1598-1777	11*	137.9±3.1	137.38	-0.1±1.8	-3.1
2. DeMaría et al.	Mo(c) + 2O(g) + MoO ₂ (g)	2262-2466	11*	-61.8±32.1	-108.37	-19.9±13.6	10.7
3. Blackburn et al.	MoO ₂ (c) + MoO ₃ (g)	1818-2028	7	107.4±6.6	124.92	9.0±3.5	-15.6
4. Plante	MoO ₂ (c) + MoO ₃ (g)	1811-1802	6	149.5±13.0	140.92	-5.9±7.7	-0.4

*2 points rejected due to failure of statistical test

**based on the third law ΔH_f° value

Heat Capacity and Entropy

The MoO₂(g) is assumed to have a C_{2v} symmetry similar to that of TaO₂ reported by Weltner and McLeod (5). The bond angle O-Mo-O is estimated to be 110°. The bond distance Mo-O is estimated to be 1.80 Å, the same as that in MoO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectra of gaseous MoO₂Cl₂ and MoO₂Br₂, reported by Iorns and Stafford (6). The bending vibrational frequency (300 cm⁻¹) is estimated by comparison with other transition metal dioxides. The three principal moments of inertia are: I_A = 4.2470 × 10⁻³⁸, I_B = 11.5512 × 10⁻³⁸, and I_C = 15.7982 × 10⁻³⁸ g cm².

The electronic levels and quantum weights are estimated from the data reported by Weltner and McLeod (7) on W₂. The ground state is assumed to be ³A₁ and the first excited level is assumed to lie close to the observed transitions at 7800 Å and 7806 Å in W₂. Since both these states are presumed to be triplet, we have assigned a total degeneracy of 6. In addition, we expect from the electronic levels of Mo⁴⁺(g) (8) that other electronic states will also be found and these are arbitrarily estimated in the level at 25000 cm⁻¹.

References

1. R. P. Burns, G. DeMaría, J. Drowart and R. T. Grimley, *J. Chem. Phys.* **32**, 1363 (1960).
2. G. DeMaría, R. P. Burns, J. Drowart and M. G. Inghram, *J. Chem. Phys.* **32**, 1373 (1960).
3. P. E. Blackburn, M. Hoch and H. L. Johnston, *J. Phys. Chem.* **52**, 769 (1958).
4. E. R. Plante, Ph. D. Thesis, Univ. of Kansas, 1960.
5. W. Weltner, Jr., and D. McLeod, *Jr., J. Chem. Phys.* **42**, 882 (1965).
6. T. V. Iorns and F. E. Stafford, *J. Am. Chem. Soc.* **88**, 4819 (1966).
7. W. Weltner, Jr., and D. McLeod, *Jr., J. Mol. Spectry.* **12**, 276 (1965).
8. C. E. Moore, "Atomic Energy Levels," U. S. Natl. Bur. Std., Circ. 467, 1958.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	+0.00	+0.00	INFINITE	-	-176.900	-176.900	INFINITE
100	7.564	4.673	31.743	-2.707	-177.756	-171.947	375.570
200	14.168	12.164	20.109	-1.585	-178.120	-165.760	181.134
298	17.997	18.585	18.585	-0.000	-178.100	-159.687	117.054
300	17.951	18.696	18.585	-0.033	-178.097	-159.573	116.249
400	19.460	20.155	19.317	1.935	-177.852	-153.431	83.631
500	20.973	20.712	20.753	3.979	-177.520	-147.364	64.413
600	21.935	32.621	22.413	6.125	-177.134	-141.367	51.493
700	22.900	36.764	24.122	10.307	-176.708	-135.498	42.586
800	23.862	40.907	25.443	14.489	-176.245	-129.647	35.989
900	24.822	42.074	26.463	15.700	-175.651	-123.779	30.058
1000	26.061	44.760	29.060	15.700	-175.007	-118.048	25.799
1100	27.197	47.297	30.604	18.363	-174.277	-112.387	22.329
1200	28.465	49.744	32.096	21.037	-173.547	-106.728	19.050
1300	29.779	51.031	33.442	23.711	-172.817	-101.069	16.020
1400	30.779	54.266	34.942	27.054	-171.545	-95.433	14.960
1500	32.017	56.432	36.303	30.194	-170.448	-90.462	13.160

S_{298.15} = 18.585 ± 0.15 gibbs/mol
 ΔH_f⁰ = -176.9 ± 0.1 kcal/mol
 ΔH_{298.15} = -178.1 ± 0.1 kcal/mol
 ΔH_m⁰ = 11.60 kcal/mol
 T_m = 1074°K

Heat of Formation

The adopted heat of formation, -178.1 kcal/mol, is the weighted average of two recent calorimetric determinations. The results are given below.

Staskiewicz et al. (2) found that oxidation was only about 80 per cent complete and tentatively attributed this to formation of MoO₃(c). The table for MoO₃(c) details the analytical methods applied to the combustion products and the heat of combustion of the dioxide which is necessary for reduction of the data of the trioxide. Combination of these investigations gives ΔH_f⁰ = -177.98 kcal/mol. Subsequent discovery of oxides intermediate between MoO₂ and MoO₃ raises a possible uncertainty concerning the incomplete oxidation. Mah (1) also reported that completion of the combustion of Mo(c) sample ranged from 84 to 93 per cent, as determined only by weight gain of the total combustion products upon prolonged low temperature ignition. In contrast, the earlier workers reported almost complete combustion. Neumann et al. (3) found about 97 per cent completion using a wet analysis involving aqua regia. Moose and Parr (4) found that in several combustions, they obtained over 99 per cent completion, based on the weight of the oxide formed.

Investigator	Year	Method	Reaction	ΔH _f ⁰ (kcal/mol)
1. Mah	1957	Calorimetric	Mo(c) + 3/2O ₂ (g) + MoO ₃ (c)	-178.16
2. Staskiewicz et al.	1955	Calorimetric	Mo(c) + 3/2O ₂ (g) + MoO ₃ (c)	-177.98
3. Neumann et al.	1934	Calorimetric	Mo(c) + 3/2O ₂ (g) + MoO ₃ (c)	-180.4
4. Moose and Parr	1924	Calorimetric	Mo(c) + 3/2O ₂ (g) + MoO ₃ (c)	-175.6

Heat Capacity and Entropy

Smith et al. (5) measured low temperature heat capacities from 18.3 to 299.8°K. King et al. (6) measured high temperature enthalpy data from 399.3° to 1063.9°K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that there be a smooth joint at 298°K. Deviations of the enthalpy data from the adopted values are -0.65 percent to +0.17 percent. Seitz et al. (7) have also measured low temperature heat capacities from 70° to 298.7°K which are not in agreement with the values adopted. (The discrepancy has been discussed by Smith.) Cosgrove and Snyder (8) have also measured high temperature enthalpy data from 273° to 1068°K by drop calorimetry. Their smooth values are about 2 percent higher than the values adopted in the tabulation.

The entropy, S₂₉₈ = 18.585 eu, is obtained from the low temperature heat capacity data of Smith (5), based on S₀ = 0.197 eu. This starting entropy was obtained by the authors from a τ^2 extrapolation of the data. It is surprising that the entropy of MoO₃(c) is larger than that of WO₃(c) by about 0.4 eu. This may be due to the difference in the crystal structures, MoO₃ being orthorhombic and WO₃ monoclinic, and also to uncertainty in the entropy extrapolation below 50°K for WO₃(c).

Melting Data

The adopted melting point is obtained from King (6), and the heat of melting is calculated from the adopted enthalpies of the crystal and liquid based on the enthalpy data of King. Cosgrove and Snyder (8) found the melting point 1068°K by the cooling curve method, and derived ΔH_m⁰ = 12.54 kcal/mol from their smooth enthalpy values at the melting point.

References

1. A. D. Mah, J. Phys. Chem. **61**, 1572 (1957).
2. B. A. Staskiewicz, J. R. Tucker and P. E. Snyder, J. Am. Chem. Soc. **77**, 2987 (1955).
3. B. Neumann, C. Kroger and H. Kunz, Z. Anorg. Allgem. Chem. **218**, 387 (1934).
4. J. E. Moose and S. W. Parr, J. Am. Chem. Soc. **46**, 2656 (1924).
5. D. F. Smith, D. B. Brown, A. S. Dworin, D. J. Samor and E. R. Van Artadalen, J. Am. Chem. Soc. **78**, 1533 (1956).
6. E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664, 1960.
7. H. Seitz, F. J. Dunkerley and B. J. DeWitt, J. Am. Chem. Soc. **65**, 600 (1943).
8. L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. **75**, 1227 (1953).

Molybdenum Trioxide (MoO₃)
(Liquid) GFW = 143.9382

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	17.897	26.971	26.971	.000	-168.555	-152.642	111.890
300	17.951	27.082	26.971	.033	-168.552	-152.544	111.128
400	19.860	32.581	27.703	1.033	-167.975	-152.012	92.073
500	20.973	37.098	29.139	3.079	-167.975	-152.012	92.073
600	21.935	41.067	30.799	6.125	-167.593	-136.853	49.849
700	30.342	46.861	32.508	8.367	-167.161	-131.763	41.138
800	30.342	50.086	34.081	11.435	-165.789	-126.789	34.637
900	30.342	52.086	36.087	13.435	-163.493	-117.257	25.977
1000	30.342	55.283	37.813	17.469	-163.493	-117.257	25.977
1100	30.342	56.175	39.535	20.503	-162.592	-112.667	22.385
1200	30.342	56.815	41.200	23.538	-161.515	-108.177	19.702
1300	30.342	57.235	42.804	26.572	-160.469	-103.774	17.446
1400	30.342	58.492	44.325	29.606	-159.443	-99.453	15.525
1500	30.342	57.585	45.825	32.640	-158.457	-95.200	13.871
1600	30.342	59.544	47.287	35.674	-157.496	-91.014	12.432
1700	30.342	71.383	48.613	38.709	-156.564	-86.888	11.170
1800	30.342	73.758	49.867	41.743	-155.666	-82.816	10.055
1900	30.342	75.151	51.151	44.777	-154.793	-78.813	9.063
2000	30.342	76.314	52.469	47.811	-153.966	-74.818	8.176

MOLYBDENUM TRIOXIDE (MoO₃) (LIQUID)

S°_{298.15} = 26.971 gibbs/mol
Tm = 1074°
ΔH°_{298.15} = -168.555 ± 0.1 kcal/mol
ΔHm° = 11.80 kcal/mol

Heat of Formation
The heat of formation is calculated from that of the crystal by adding the heat of melting and the difference between H°₁₀₇₄ - H°₂₉₈ for the crystal and liquid.

Heat Capacity and Entropy
The heat capacity between the melting point and 1392.4°K is derived from the enthalpy data measured by E. G. King, W. W. Weiler and A. U. Christensen, U. S. Bur. Mines RI 5684 (1960). The heat capacity is assumed constant above and below the measured range. At 700°K, a glass transition is assumed, below which the heat capacity is taken to be the same as that of the crystal. The entropy at 298°K is obtained in a manner analogous to that of the heat of formation. L. A. Cosgrove and P. E. Snyder, J. Am. Chem. Soc. 75, 1227 (1953), also measured the enthalpy changes for MoO₃ (l) in the temperature range from 1068° to 1300°K. Their smooth values are ±2.5 percent to ±4.0 percent higher than our tabulated values. They have also found the melting point at 1068°K by the cooling curve method.

Melting Data
See JANAF MoO₃(c) table dated June 30, 1967.

Molybdenum Trioxide (MoO₃)

(Ideal Gas)

GFW = 143.9382

T, °K	Cp	gibbs/mol S° - (G° - H° ₃₀₀)/T	h ^o - H° ₃₀₀	kcal/mol ΔH°	ΔG°	Log Kp
0	9.000	INFINITE	3.225	85.217	85.217	INFINITE
100	9.299	54.186	78.191	85.550	84.591	184.274
200	12.276	61.618	88.173	85.946	83.473	91.215
298	14.347	66.924	91.000	86.200	82.199	60.254
300	14.380	67.013	92.7	86.204	82.175	59.846
400	15.297	71.371	105.08	86.331	80.808	44.151
500	16.472	75.046	115.658	86.406	79.416	34.713
600	17.688	78.208	123.927	86.434	78.014	26.417
700	18.862	80.974	130.368	86.449	76.610	23.519
800	19.932	83.226	135.725	86.461	75.202	21.055
900	20.917	85.014	140.127	86.468	73.792	18.920
1000	21.828	86.414	143.598	86.491	72.386	15.620
1100	19.123	89.430	147.501	86.519	70.975	14.101
1200	18.236	91.099	150.649	86.558	69.560	12.669
1300	17.326	92.482	153.126	86.618	68.146	11.456
1400	16.400	93.607	155.086	86.698	66.736	10.456
1500	15.567	94.517	156.786	86.795	65.287	9.512
1600	14.806	96.675	161.740	86.920	63.869	8.721
1700	14.156	97.558	165.854	87.070	62.402	8.022
1800	13.611	98.777	169.530	87.243	60.989	7.402
1900	13.156	100.281	172.804	87.438	59.479	6.862
2000	12.765	101.043	175.776	87.656	58.003	6.338
2100	19.656	102.001	185.958	87.965	56.512	5.881
2200	19.675	102.916	192.708	88.271	55.007	5.464
2300	19.582	103.793	197.432	88.593	53.489	5.083
2400	19.480	104.634	201.126	88.931	51.969	4.733
2500	19.371	105.434	203.807	89.284	50.402	4.406
2600	19.250	106.208	206.462	89.637	48.887	4.104
2700	19.118	106.952	209.091	90.014	47.237	3.824
2800	18.976	107.671	211.696	90.414	45.513	3.561
2900	18.825	108.371	214.281	90.835	43.761	3.316
3000	18.665	109.034	216.847	91.279	42.000	3.083
3100	18.500	109.662	219.394	91.743	40.252	2.861
3200	18.330	110.261	221.923	92.232	38.528	2.651
3300	18.155	110.834	224.436	92.745	36.837	2.452
3400	17.976	111.381	226.933	93.281	35.178	2.264
3500	17.793	111.903	229.416	93.839	33.552	2.087
3600	17.608	112.400	231.885	94.418	31.961	1.922
3700	17.421	112.873	234.340	94.999	30.404	1.767
3800	17.231	113.323	236.781	95.599	28.881	1.622
3900	17.038	113.751	239.208	96.218	27.392	1.487
4000	16.842	114.157	241.623	96.856	25.937	1.361
4100	16.644	114.542	244.027	97.513	24.516	1.244
4200	16.443	114.907	246.420	98.188	23.129	1.136
4300	16.240	115.251	248.803	98.889	21.776	1.036
4400	16.035	115.574	251.176	99.614	20.457	0.943
4500	15.828	115.877	253.539	100.363	19.172	0.856
4600	15.619	116.160	255.892	101.135	17.923	0.774
4700	15.408	116.424	258.236	101.930	16.707	0.696
4800	15.195	116.669	260.570	102.749	15.524	0.622
4900	14.980	116.895	262.894	103.592	14.374	0.552
5000	14.763	117.103	265.209	104.459	13.257	0.486
5100	14.544	117.293	267.514	105.348	12.172	0.424
5200	14.323	117.465	269.809	106.260	11.120	0.365
5300	14.100	117.619	272.094	107.195	10.099	0.310
5400	13.875	117.756	274.369	108.154	9.116	0.258
5500	13.648	117.877	276.634	109.136	8.171	0.209
5600	13.419	117.981	278.889	110.141	7.264	0.164
5700	13.188	118.069	281.134	111.169	6.394	0.122
5800	12.955	118.141	283.369	112.220	5.564	0.083
5900	12.720	118.197	285.594	113.293	4.774	0.047
6000	12.484	118.238	287.809	114.388	4.024	0.015
6100	12.247	118.264	290.014	115.504	3.314	0.007
6200	12.009	118.275	292.209	116.640	2.644	0.003
6300	11.770	118.271	294.394	117.796	2.014	0.001
6400	11.529	118.252	296.569	118.972	1.424	0.000
6500	11.286	118.219	298.734	120.168	0.874	0.000
6600	11.041	118.172	300.889	121.384	0.364	0.000
6700	10.794	118.111	303.034	122.619	-0.206	0.000
6800	10.545	118.036	305.169	123.874	-0.826	0.000
6900	10.294	117.947	307.294	125.148	-1.486	0.000
7000	10.041	117.844	309.409	126.441	-2.186	0.000
7100	9.786	117.727	311.514	127.754	-2.926	0.000
7200	9.529	117.596	313.609	129.087	-3.706	0.000
7300	9.270	117.451	315.694	130.440	-4.526	0.000
7400	9.009	117.293	317.769	131.813	-5.386	0.000
7500	8.746	117.122	319.834	133.206	-6.286	0.000
7600	8.481	116.938	321.889	134.619	-7.226	0.000
7700	8.214	116.741	323.934	136.052	-8.206	0.000
7800	7.945	116.531	325.969	137.505	-9.226	0.000
7900	7.674	116.308	327.994	138.978	-10.286	0.000
8000	7.401	116.072	329.999	140.471	-11.386	0.000
8100	7.126	115.824	331.994	141.984	-12.526	0.000
8200	6.849	115.563	333.979	143.517	-13.706	0.000
8300	6.570	115.289	335.954	145.069	-14.926	0.000
8400	6.289	115.002	337.919	146.640	-16.186	0.000
8500	6.006	114.703	339.874	148.229	-17.486	0.000
8600	5.721	114.391	341.819	149.836	-18.826	0.000
8700	5.434	114.066	343.754	151.461	-20.206	0.000
8800	5.145	113.729	345.679	153.104	-21.626	0.000
8900	4.854	113.380	347.594	154.765	-23.086	0.000
9000	4.561	113.019	349.499	156.444	-24.586	0.000
9100	4.266	112.646	351.394	158.141	-26.126	0.000
9200	3.969	112.261	353.279	159.856	-27.706	0.000
9300	3.670	111.864	355.154	161.589	-29.326	0.000
9400	3.369	111.455	357.019	163.340	-30.986	0.000
9500	3.066	111.034	358.874	165.109	-32.686	0.000
9600	2.761	110.601	360.719	166.894	-34.426	0.000
9700	2.454	110.156	362.554	168.694	-36.206	0.000
9800	2.145	109.700	364.379	170.509	-38.026	0.000
9900	1.834	109.232	366.194	172.339	-39.886	0.000
10000	1.521	108.753	368.009	174.184	-41.786	0.000
10100	1.206	108.263	369.814	176.044	-43.726	0.000
10200	0.889	107.762	371.609	177.919	-45.706	0.000
10300	0.570	107.250	373.394	179.809	-47.726	0.000
10400	0.249	106.727	375.169	181.714	-49.786	0.000
10500	0.000	106.193	376.934	183.634	-51.886	0.000
10600	-0.249	105.648	378.689	185.569	-54.026	0.000
10700	-0.498	105.092	380.434	187.519	-56.206	0.000
10800	-0.747	104.525	382.169	189.484	-58.426	0.000
10900	-0.996	103.947	383.894	191.464	-60.686	0.000
11000	-1.245	103.358	385.609	193.459	-62.986	0.000
11100	-1.494	102.759	387.314	195.469	-65.326	0.000
11200	-1.743	102.149	389.009	197.494	-67.706	0.000
11300	-1.992	101.528	390.694	199.534	-70.126	0.000
11400	-2.241	100.896	392.369	201.589	-72.586	0.000
11500	-2.490	100.253	394.034	203.659	-75.086	0.000
11600	-2.739	99.599	395.689	205.744	-77.626	0.000
11700	-2.988	98.934	397.334	207.844	-80.206	0.000
11800	-3.237	98.258	398.969	209.959	-82.826	0.000
11900	-3.486	97.571	400.594	212.089	-85.486	0.000
12000	-3.735	96.874	402.209	214.234	-88.186	0.000
12100	-3.984	96.166	403.814	216.394	-90.926	0.000
12200	-4.233	95.448	405.409	218.569	-93.706	0.000
12300	-4.482	94.719	406.994	220.759	-96.526	0.000
12400	-4.731	93.980	408.569	222.964	-99.386	0.000
12500	-4.980	93.231	410.134	225.184	-102.286	0.000
12600	-5.229	92.472	411.689	227.419	-105.226	0.000
12700	-5.478	91.703	413.234	229.669	-108.206	0.000
12800	-5.727	90.924	414.769	231.934	-111.226	0.000
12900	-5.976	90.135	416.294	234.214	-114.286	0.000
13000	-6.225	89.336	417.809	236.509	-117.386	0.000
13100	-6.474	88.527	419.314	238.819	-120.526	0.000
13200	-6.723	87.708	420.809	241.144	-123.706	0.000
13300	-6.972	86.879	422.294	243.484	-126.926	0.000
13400	-7.221	86.039	423.769	245.839	-130.186	0.000
13500	-7.470	85.189	425.234	248.209	-133.486	0.000
13600	-7.719	84.329	426.689	250.594	-136.826	0.000
13700	-7.968	83.459	428.134	253.004	-140.206	0.000
13800	-8.217	82.579	429.569	255.429	-143.626	0.000
13900	-8.466	81.689	431.004	257.869	-147.086	0.000
14000	-8.715	80.789	432.429	260.329	-150.586	0.000
14100	-8.964	79.879	433.844	262.804	-154.126	0.000
14200	-9.213	78.959	435.249	265.294	-157.706	0.000
14300	-9.462	78.029	436.644	267.804	-161.326	0.000
14400	-9.711	77.089	438.029	270.329	-164.986	0.000
14500	-9.960	76.139	439.404	272.869	-168.686	0.000
14600	-10.209	75.179	440.769	275.429	-172.426	0.000
14700	-10.458	74.209	442.124	277.994	-176.206	0.000
14800	-10.707	73.229	443.469	280.569	-180.026	0.000
14900	-10.956	72.239	444.804	283.154	-183.886	0.000
15000	-11.205	71.239	446.129	285		

Nitrogen, Monatomic (N)

(Ideal Gas) At. Wt. = 14.008

T, °K.	C _p ^o	S ^o - (F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _f
0	4.968	31.187	1.481	112,520	INFINITE	INFINITE
100	4.968	31.031	0.984	111,459	-243,585	-243,585
200	4.968	30.631	0.488	112,819	-120,191	-120,405
298	4.968	30.614	0.000	112,865	108,870	-79,600
300	4.968	30.614	0.009	112,968	109,885	-79,289
400	4.968	30.074	0.506	113,116	107,448	-76,704
500	4.968	30.183	1.003	113,261	106,014	-74,336
600	4.968	30.089	1.500	113,402	104,551	-71,881
700	4.968	30.012	2.000	113,540	103,062	-69,442
800	4.968	29.951	2.493	113,660	101,542	-67,017
900	4.968	29.903	2.990	113,778	100,002	-64,606
1000	4.968	29.867	3.487	113,887	98,510	-62,217
1100	4.968	29.840	3.984	113,990	96,967	-59,851
1200	4.968	29.819	4.479	114,087	95,375	-57,507
1300	4.968	29.801	4.972	114,178	93,737	-55,182
1400	4.968	29.786	5.464	114,264	92,052	-52,876
1500	4.968	29.773	5.951	114,346	90,319	-50,597
1600	4.968	29.762	6.438	114,425	88,539	-48,342
1700	4.968	29.753	6.925	114,500	86,705	-46,111
1800	4.968	29.745	7.412	114,571	84,818	-43,904
1900	4.968	29.738	7.898	114,638	82,878	-41,721
2000	4.968	29.732	8.385	114,702	80,885	-39,562
2100	4.970	29.727	8.872	114,778	78,848	-37,427
2200	4.972	29.723	9.359	114,850	76,763	-35,316
2300	4.975	29.720	9.846	114,918	74,633	-33,228
2400	4.978	29.718	10.333	114,982	72,458	-31,162
2500	4.982	29.716	10.820	115,042	70,238	-29,119
2600	4.987	29.715	11.307	115,098	67,973	-27,098
2700	4.993	29.714	11.794	115,150	65,663	-25,098
2800	4.999	29.713	12.281	115,200	63,308	-23,119
2900	5.006	29.712	12.768	115,246	60,913	-21,162
3000	5.011	29.712	13.255	115,289	58,478	-19,228
3100	5.022	29.712	13.742	115,333	56,000	-17,319
3200	5.035	29.712	14.229	115,373	53,478	-15,436
3300	5.047	29.712	14.716	115,410	50,913	-13,579
3400	5.060	29.712	15.203	115,444	48,308	-11,748
3500	5.074	29.712	15.690	115,475	45,653	-9,942
3600	5.107	29.711	16.177	115,503	42,948	-8,161
3700	5.130	29.711	16.664	115,528	40,193	-6,407
3800	5.153	29.711	17.151	115,550	37,388	-4,679
3900	5.183	29.711	17.638	115,569	34,533	-2,978
4000	5.213	29.711	18.125	115,584	31,628	-1,304
4100	5.245	29.711	18.612	115,596	28,673	3.281
4200	5.278	29.711	19.099	115,603	25,668	5.916
4300	5.314	29.711	19.586	115,608	22,613	8.501
4400	5.351	29.711	20.073	115,610	19,508	11,036
4500	5.390	29.711	20.560	115,610	16,353	13,521
4600	5.431	29.711	21.047	115,608	13,148	15,956
4700	5.473	29.711	21.534	115,603	9,893	18,341
4800	5.516	29.711	22.021	115,596	6,588	20,676
4900	5.562	29.711	22.508	115,584	3,233	22,961
5000	5.608	29.711	23.000	115,569	-1,172	25,196
5100	5.655	29.711	23.491	115,550	-4,517	27,381
5200	5.703	29.711	23.982	115,528	-7,762	29,516
5300	5.753	29.711	24.473	115,503	-10,907	31,601
5400	5.800	29.711	24.964	115,475	-13,952	33,636
5500	5.850	29.711	25.455	115,444	-16,897	35,621
5600	5.900	29.711	25.946	115,410	-19,742	37,556
5700	5.950	29.711	26.437	115,373	-22,487	39,441
5800	6.000	29.711	26.928	115,333	-25,132	41,276
5900	6.050	29.711	27.419	115,289	-27,677	43,061
6000	6.100	29.711	27.910	115,246	-30,122	44,796

March 31, 1961

N

NITROGEN, MONATOMIC (N) (IDEAL GAS) AT. WT. = 14.008

$\Delta H_{f0}^{\circ} = 112.5 \pm 1 \text{ kcal. mole}^{-1}$
 $\Delta H_{f298.15}^{\circ} = 113.0 \pm 1 \text{ kcal. mole}^{-1}$
 $S_{298.15}^{\circ} = 36.61 \pm 0.01 \text{ cal. deg. mole}^{-1}$

Electronic Levels and Multiplicities

E ₁	E ₂	E ₃	E ₄	E ₅	E ₆
0	4	4	4	4	4
19,225.9	19,225.9	19,225.9	19,225.9	19,225.9	19,225.9
19,225.1	19,225.1	19,225.1	19,225.1	19,225.1	19,225.1
28,840	28,840	28,840	28,840	28,840	28,840
83,285.5	83,285.5	83,285.5	83,285.5	83,285.5	83,285.5
83,319.3	83,319.3	83,319.3	83,319.3	83,319.3	83,319.3
83,366	83,366	83,366	83,366	83,366	83,366
86,131.4	86,131.4	86,131.4	86,131.4	86,131.4	86,131.4
96,223.2	96,223.2	96,223.2	96,223.2	96,223.2	96,223.2
96,109.5	96,109.5	96,109.5	96,109.5	96,109.5	96,109.5
98,153.4	98,153.4	98,153.4	98,153.4	98,153.4	98,153.4
93,582.3	93,582.3	93,582.3	93,582.3	93,582.3	93,582.3
94,772.2	94,772.2	94,772.2	94,772.2	94,772.2	94,772.2
94,794.6	94,794.6	94,794.6	94,794.6	94,794.6	94,794.6
94,832.1	94,832.1	94,832.1	94,832.1	94,832.1	94,832.1
88,173	88,173	88,173	88,173	88,173	88,173
104,615.4	104,615.4	104,615.4	104,615.4	104,615.4	104,615.4
104,810.9	104,810.9	104,810.9	104,810.9	104,810.9	104,810.9
104,864.2	104,864.2	104,864.2	104,864.2	104,864.2	104,864.2
104,882.7	104,882.7	104,882.7	104,882.7	104,882.7	104,882.7
105,845	105,845	105,845	105,845	105,845	105,845
110,091.1	110,091.1	110,091.1	110,091.1	110,091.1	110,091.1
111,849.3	111,849.3	111,849.3	111,849.3	111,849.3	111,849.3
113,144.5	113,144.5	113,144.5	113,144.5	113,144.5	113,144.5
114,288	114,288	114,288	114,288	114,288	114,288
115,214.5	115,214.5	115,214.5	115,214.5	115,214.5	115,214.5
115,808	115,808	115,808	115,808	115,808	115,808
116,200	116,200	116,200	116,200	116,200	116,200
116,450	116,450	116,450	116,450	116,450	116,450

Heat of Formation

The dissociation energy of N₂ has been the subject of considerable controversy and is presented by A. G. Gaydon, "Dissociation Energies", Chapman and Hall, London, 1953. L. Brewer and A. W. Searcy, Ann. Rev. Phys. Chem., 7, 259 (1956), discuss extensive and varied experiments which have now fixed the value of 9.76 e.v. as being highly probable. Additional support for this value is afforded by the recently observed predissociation in the x \sum_g^+ state by A. Jortus, Nature 186, 302 (1960).

Heat Capacities and Entropies

The electronic levels noted above are listed by C. E. Moore, Nat. Bur. Standards (U.S.) Circ. 467, Vol. I (1949), Vol. III (1958).

N

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞.000	INFINITE	- 2.197	21.456	21.456	INFINITE
100	7.721	42.286	1.451	21.503	21.256	- 46.453
200	7.271	47.477	1.003	21.558	20.984	- 22.029
298	7.133	50.347	∞.000	21.580	20.937	- 15.171
300	7.132	50.392	∞.013	21.580	20.932	- 15.073
400	7.157	52.444	20.627	21.590	20.904	- 11.142
500	7.287	54.053	21.157	21.594	20.895	- 8.783
600	7.466	55.397	21.755	21.598	20.795	- 7.210
700	7.682	56.528	22.412	21.601	20.695	- 6.066
800	7.932	57.506	23.091	21.604	20.592	- 5.192
900	8.208	58.358	23.712	21.607	20.487	- 4.457
1000	8.513	59.377	24.064	21.615	20.388	- 3.822
1100	8.838	60.157	24.563	21.620	20.285	- 3.253
1200	9.181	61.115	25.000	21.626	20.178	- 2.742
1300	9.499	62.158	25.500	21.631	20.068	- 2.282
1400	9.841	62.175	26.001	21.633	19.953	- 1.873
1500	10.152	62.763	26.432	21.635	19.835	- 1.509
1600	10.465	63.317	26.845	21.635	19.765	- 1.200
1700	10.772	64.339	27.632	21.635	19.651	- 0.935
1800	11.072	65.339	28.406	21.630	19.583	- 0.700
1900	11.365	66.315	29.169	21.626	19.548	- 0.485
2000	11.652	67.273	29.927	21.619	19.544	- 0.296
2100	11.934	68.215	30.680	21.611	19.541	- 0.130
2200	12.211	69.143	31.428	21.601	19.536	- 0.000
2300	12.483	70.057	32.172	21.589	19.533	- 0.127
2400	12.750	70.957	32.912	21.574	19.533	- 0.277
2500	13.012	71.843	33.648	21.558	19.532	- 0.440
2600	13.269	72.715	34.380	21.540	19.530	- 0.615
2700	13.521	73.573	35.108	21.520	19.526	- 0.800
2800	13.768	74.417	35.832	21.500	19.520	- 0.995
2900	14.011	75.248	36.552	21.478	19.513	- 1.200
3000	14.250	76.063	37.268	21.454	19.504	- 1.415
3100	14.485	76.863	37.970	21.429	19.493	- 1.640
3200	14.716	77.648	38.668	21.403	19.480	- 1.875
3300	14.943	78.419	39.362	21.376	19.465	- 2.120
3400	15.166	79.176	40.052	21.348	19.449	- 2.375
3500	15.385	79.919	40.738	21.320	19.432	- 2.640
3600	15.600	80.648	41.420	21.294	19.415	- 2.915
3700	15.812	81.363	42.100	21.269	19.398	- 3.200
3800	16.021	82.063	42.778	21.244	19.380	- 3.495
3900	16.227	82.748	43.452	21.219	19.362	- 3.800
4000	16.430	83.419	44.122	21.194	19.344	- 4.115
4100	16.630	84.076	44.788	21.169	19.326	- 4.440
4200	16.827	84.719	45.450	21.144	19.308	- 4.775
4300	17.021	85.348	46.108	21.119	19.289	- 5.120
4400	17.212	85.963	46.762	21.094	19.271	- 5.475
4500	17.400	86.563	47.412	21.069	19.253	- 5.840
4600	17.585	87.148	48.058	21.044	19.235	- 6.215
4700	17.768	87.719	48.700	21.019	19.217	- 6.600
4800	17.948	88.276	49.338	20.994	19.199	- 6.995
4900	18.125	88.819	49.972	20.969	19.181	- 7.400
5000	18.300	89.348	50.602	20.944	19.163	- 7.815
5100	18.472	89.863	51.228	20.919	19.145	- 8.240
5200	18.642	90.365	51.850	20.894	19.127	- 8.675
5300	18.810	90.853	52.468	20.869	19.109	- 9.120
5400	18.976	91.328	53.082	20.844	19.091	- 9.575
5500	19.140	91.789	53.692	20.819	19.073	- 10.040
5600	19.302	92.237	54.298	20.794	19.055	- 10.515
5700	19.462	92.672	54.900	20.769	19.037	- 11.000
5800	19.620	93.093	55.498	20.744	19.019	- 11.495
5900	19.776	93.500	56.092	20.719	18.999	- 12.000
6000	19.930	93.893	56.682	20.694	18.981	- 12.515

Dec. 31, 1960; June 30, 1963

NITRIC OXIDE (NO)

(IDEAL GAS)

MOL. WT. = 30.008

Ground State Configuration 2Π

$$\Delta H_f^0 = 21.46 \pm 0.04 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 50.347 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^0 = 21.58 \pm 0.04 \text{ kcal. mole}^{-1}$$

Electronic Levels and Multiplicities

E_i , cm. ⁻¹	g_i
0	2
121.1	2

$$\omega_e x_e = 13.37 \text{ cm.}^{-1}$$

$$\omega_e = 0.0178 \text{ cm.}^{-1}$$

$$r_e = 1.1508 \text{ Å}$$

$$\sigma^- = 1$$

Heat of Formation.

G. Herzberg, Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, D. van Nostrand Co., Inc., New York, 1950, lists two $D_0(\text{NO})$ values, 5.296 and 6.487 e.v. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall, Ltd., London, 1953, lists $D_0(\text{NO}) = 6.49 \pm 0.05$ e.v. A Birge-Sponer extrapolation of the vibrational levels, up to $v = 19$, of the ground state leads to a D_0 of about 6.5 e.v. Gaydon's, loc. cit., analysis on the predissociation of NO also leads to the higher value for $D_0(\text{NO})$.

Y. Tanaka, J. Chem. Phys. 22, 2045 (1954), has observed and analyzed the emission bands of NO in the vacuum ultraviolet region. Tanaka's, loc. cit., observation and interpretation of the abrupt cutoff (predissociation) of certain v' values in the β , δ , and ϵ bands and of the complete non appearance of ϵ and β bands strongly favors a $D_0(\text{NO}) = 6.48$ e.v. ΔH_f^0 298.15 (NO)G was calculated on this basis to be 22.033 ± 1 kcal. mole⁻¹.

More recently M. A. Frisch, Diss. Abstr. 23, 1940 (1961), Thesis, University of Wisconsin, Madison, Wisconsin, 1962, has calorimetrically determined the heat of reaction for



at 298.15°K , from which the author derives a ΔH_f^0 298.15 NO(g) = 21.58 ± 0.04 kcal. mole⁻¹. The auxiliary values used by Frisch to calculate the heat of formation of nitric oxide were based upon the 1961 atomic weight scale. Recalculating ΔH_f^0 298.15 NO(g) using auxiliary functions based on the 1956 atomic weight scale had a negligible effect on the final result.

The calorimetrically determined heat of formation for nitric oxide, 21.58 ± 0.04 kcal. mole⁻¹, was selected as the best value.

Heat Capacity and Entropy.

The spectroscopic constants were taken from R. H. Gillette and E. H. Eyster, Phys. Revs. 59, 1113 (1959), who measured and analyzed the fundamental rotation-vibration band of nitric oxide using a grating spectrometer. The constants used in this calculation were adjusted to correspond to the naturally occurring isotopic mixture.

(Ideal Gas) $GFW = 30.00555$ June 30, 1966

GFW = 30.00555

(IDEAL GAS)

NITRIC OXIDE UNIPOSITIVE ION (NO^+)Ground State $1\Sigma^+$
$$\Delta H_f^\circ = 235.18 + 0.2 \text{ kcal/mol}$$
$$\Delta H_{298}^{\circ} = 47.35 \text{ gibbs/mol}$$

Electronic Levels and Quantum Weights

 $\epsilon_1, \text{ cm}^{-1} \quad g_1$
$$(4) \quad \gamma = 16.35 \text{ cm}^{-1}$$

75

 $\alpha_c = 0.0202 \text{ cm}^{-1}$ $r_c = 1.0619 \text{ \AA}$

Heat of Formation.

K. Mettenberg, *J. Chem. Phys.* **22**, 1564 (1954), and W. C. Walker and O. L. Weisauer, *J. Chem. Phys.* **23**, 1982 (1955), have measured the ionization potential of NO(g) by photoelectron spectroscopy, yielding $I.P. = 9.25 \pm 0.02$ and 9.20 ± 0.03 eV, respectively. H. D. Hagstrum, *J. Chem. Phys.* **23**, 1178 (1955), reported $I.P. = 9.4 \pm 0.2$ eV by electron impact. K. F. Huber, *Helv. Phys. Acta* **34**, 929 (1961), determined spectroscopically the ionization potential for NO(g). $I.P. = 9.267 \pm 0.005$ eV (213.72 \pm 0.1 kcal/mol). The last value has been selected, and yields the heat of formation of $\text{NO}^+(\text{g})$, $\Delta H_f^\circ = 235.18$ kcal/mol, using $\Delta H_f^\circ(\text{NO}, \text{g}) = 21.46 \pm 0.04$ kcal/mol.

Heat Capacity and Entropy.

The selected molecular constants were obtained from the ultraviolet spectra by E. Miescher, Can. J. Phys. 33, 355 (1955). *Helv. Phys. Acta* 29, 135 (1956).

The tabulated thermodynamic functions are in reasonable agreement with those calculated by J. Hilsenrath and Carla G. Messina, NBS Report 8504, July 1, 1964, who have used slightly different molecular constants.

Nitrogen Dioxide (NO₂)

(Ideal Gas) Mol. Wt. = 46.008

T. °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	7.953	48.387	64.785	8.586	9.545	INFINITE
200	8.218	53.954	56.130	8.526	9.545	20.859
298	8.637	57.343	50.000	8.069	10.853	11.859
300	8.650	57.398	50.015	8.077	12.274	8.977
400	9.401	60.406	47.700	7.770	15.258	8.041
500	10.327	62.268	46.107	7.684	18.302	7.513
600	10.955	64.208	45.207	7.638	21.826	6.669
700	11.469	65.937	44.423	7.618	25.879	6.111
800	11.905	67.402	43.781	7.610	30.400	5.714
900	12.268	68.615	43.245	7.609	35.484	5.467
1000	12.468	70.215	42.685	7.609	41.192	5.285
1100	12.677	71.414	42.243	7.674	47.025	5.100
1200	12.847	72.524	41.891	7.702	53.051	4.948
1300	12.985	73.556	41.626	7.731	59.282	4.721
1400	13.098	74.521	41.421	7.760	65.714	4.512
1500	13.193	75.432	41.265	7.790	72.346	4.318
1600	13.273	76.286	41.149	7.818	79.174	4.141
1700	13.340	77.093	41.063	7.846	86.192	3.979
1800	13.395	77.857	41.000	7.869	93.400	3.828
1900	13.440	78.583	40.954	7.890	100.792	3.684
2000	13.476	79.274	40.924	7.908	108.360	3.546
2100	13.527	79.933	40.906	7.923	116.100	3.412
2200	13.560	80.563	40.898	7.933	124.010	3.282
2300	13.586	81.166	40.900	7.939	132.090	3.156
2400	13.614	81.744	40.911	7.942	140.340	3.034
2500	13.636	82.301	40.929	7.939	148.760	2.916
2600	13.656	82.836	40.952	7.933	157.350	2.802
2700	13.674	83.352	40.979	7.922	166.110	2.692
2800	13.690	83.848	41.010	7.907	175.040	2.586
2900	13.705	84.330	41.044	7.884	184.140	2.484
3000	13.718	84.799	41.080	7.863	193.410	2.386
3100	13.730	85.245	41.117	7.836	202.850	2.292
3200	13.741	85.681	41.154	7.803	212.460	2.202
3300	13.750	86.104	41.191	7.767	222.240	2.116
3400	13.758	86.514	41.228	7.726	232.190	2.034
3500	13.768	86.914	41.265	7.683	242.310	1.956
3600	13.776	87.302	41.302	7.635	252.600	1.882
3700	13.783	87.679	41.339	7.584	263.060	1.812
3800	13.789	88.047	41.376	7.529	273.690	1.746
3900	13.794	88.405	41.413	7.474	284.490	1.684
4000	13.801	88.755	41.450	7.412	295.460	1.624
4100	13.806	89.096	41.487	7.347	306.600	1.566
4200	13.811	89.428	41.524	7.281	317.910	1.512
4300	13.816	89.751	41.561	7.215	329.390	1.462
4400	13.820	90.071	41.598	7.149	341.040	1.416
4500	13.824	90.382	41.635	7.086	352.860	1.374
4600	13.828	90.686	41.672	7.023	364.860	1.334
4700	13.831	90.983	41.709	6.960	377.030	1.296
4800	13.834	91.274	41.746	6.911	389.370	1.262
4900	13.837	91.559	41.783	6.860	401.880	1.230
5000	13.840	91.839	41.820	6.808	414.560	1.198
5100	13.843	92.113	41.857	6.757	427.410	1.168
5200	13.846	92.382	41.894	6.705	440.430	1.138
5300	13.848	92.646	41.931	6.653	453.630	1.110
5400	13.850	92.905	41.968	6.601	467.000	1.084
5500	13.852	93.159	42.005	6.549	480.540	1.058
5600	13.854	93.408	42.042	6.497	494.260	1.034
5700	13.856	93.654	42.079	6.445	508.160	1.010
5800	13.858	93.896	42.116	6.393	522.240	0.988
5900	13.860	94.133	42.153	6.341	536.500	0.966
6000	13.862	94.365	42.190	6.289	550.940	0.946

Dec. 31, 1960 June 30, 1963 Sept. 30, 1964

NITROGEN DIOXIDE (NO₂)

(IDEAL GAS)

MOL. WT. = 46.008

Point Group C_{2v}

$$\Delta H_f^0 = 8.59 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$S_{298.15} = 57.34 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_f^{298.15} = 7.91 \pm 0.2 \text{ kcal. mole}^{-1}$$

Ground State Quantum Weight = 2

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹
1357.8 (1)
756.8 (1)
1665.5 (1)

Bond Distances: N-O = 1.197 Å

Bond Angle: O-N-O = 134° 15'

Product of the Moments of Inertia: $I_A I_B I_C = 15.3993 \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

$$\sigma = 2$$

Heat of Formation.

The equilibrium constants for $\text{NO(g)} + 1/2 \text{O}_2 \rightarrow \text{NO}_2\text{(g)}$ of Bodenstein and Lindner, Zeits. fur physik. Chem. 100, 82 (1922) as given by W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) were subjected to 2nd and 3rd law analysis. Third law analysis gave $\Delta H_{298} = -13.67 \text{ kcal.}$ and 2nd law $\Delta H_{298} = -13.52 \pm 0.01 \text{ kcal.}$ The third law value had a very slight trend with temperature which was consistent with an entropy error of 0.25 cal. deg.⁻¹ mole⁻¹, the second law

entropy was also consistent with an entropy error of 0.25 cal. deg.⁻¹ mole⁻¹. However the functions for all three gases are well established to about 0.03 cal. deg.⁻¹ mole⁻¹ or better and so this must be interpreted as due to errors in the data. On this basis the 3rd law value of the heat was chosen and combined with JANAF auxiliary data to give $\Delta H_f^{298} = 7.91 \pm 0.2 \text{ kcal. mole}^{-1}$, where the uncertainty includes that due to the possible error in the equilibrium constants.

Heat Capacity and Entropy.

O. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl Jr., A. C. Kunkle, J. W. Evansford, J. Rastrop-Andersen and J. Rosenthal, J. Chem. Phys. 40, 3378 (1964) have given a complete review of the microwave spectrum of NO₂. They also give a corrected infrared vibrational assignment, adopted here, which is in excellent agreement with calculations from the microwave data. They report $I_A = 0.34981 \times 10^{-39} \text{ g. cm.}^2$ and $I_B = 6.45446 \times 10^{-39} \text{ g. cm.}^2$ and $I_C = 6.81994 \times 10^{-39} \text{ g. cm.}^2$. The bond length and angle were chosen to give the best fit of the moments of inertia.

Nitrogen Dioxide Uninegative Ion (NO_2^-)
(Ideal Gas) Mol. Wt. = 46.00605

T. °K.	C_p^0	S^0	$-(F^0 - H_{298}^0)/T$	$H^0 - H_{298}^0$	ΔH_f^0	ΔF_f^0	Log K _p
0							
100							
200							
298	9.016	56.517	56.517	0.000	- 85.850	- 79.780	58.477
300	9.033	56.573	56.573	0.017	- 85.862	- 79.742	58.089
400	9.951	56.882	56.882	0.966	- 86.469	- 77.609	42.401
500	10.766	61.009	61.009	2.003	- 87.011	- 75.330	32.925
600	11.412	63.631	63.631	3.114	- 87.509	- 72.945	26.569
700	11.905	65.429	65.429	4.281	- 87.980	- 70.480	22.004
800	12.279	67.044	67.044	5.491	- 88.436	- 67.950	18.562
900	12.584	68.508	68.508	6.733	- 88.884	- 65.363	15.871
1000	12.875	69.844	69.844	8.001	- 89.327	- 62.725	13.708
1100	12.958	71.071	71.071	9.289	- 89.770	- 60.044	11.929
1200	13.095	72.204	72.204	10.592	- 90.212	- 57.322	10.439
1300	13.206	73.257	73.257	11.907	- 90.656	- 54.562	9.172
1400	13.296	74.236	74.236	13.232	- 91.102	- 51.770	8.091
1500	13.370	75.159	75.159	14.566	- 91.551	- 48.945	7.131
1600	13.432	76.024	76.024	15.906	- 92.003	- 46.089	6.295
1700	13.483	76.840	76.840	17.251	- 92.458	- 43.206	5.554
1800	13.528	77.612	77.612	18.602	- 92.916	- 40.295	4.892
1900	13.565	78.334	78.334	19.957	- 93.380	- 37.359	4.297
2000	13.598	79.001	79.001	21.315	- 93.848	- 34.400	3.759
2100	13.626	79.705	79.705	22.676	- 94.320	- 31.414	3.269
2200	13.650	80.339	80.339	24.042	- 94.798	- 28.408	2.822
2300	13.672	80.946	80.946	25.406	- 95.278	- 25.378	2.411
2400	13.691	81.559	81.559	26.774	- 95.765	- 22.330	2.033
2500	13.708	82.088	82.088	28.144	- 96.257	- 19.261	1.684
2600	13.723	82.626	82.626	29.516	- 96.753	- 16.170	1.359
2700	13.736	83.144	83.144	30.889	- 97.255	- 13.062	1.057
2800	13.748	83.644	83.644	32.263	- 97.761	- 9.935	0.775
2900	13.759	84.126	84.126	33.638	- 98.271	- 6.786	0.511
3000	13.769	84.593	84.593	35.015	- 98.787	- 3.642	0.264
3100	13.778	85.045	85.045	36.392	- 99.306	- 0.493	0.031
3200	13.786	85.482	85.482	37.770	- 99.831	2.753	0.188
3300	13.793	85.907	85.907	39.149	- 100.360	5.964	0.395
3400	13.800	86.318	86.318	40.529	- 100.893	9.198	0.591
3500	13.806	86.719	86.719	41.909	- 101.429	12.438	0.777
3600	13.812	87.108	87.108	43.290	- 101.971	15.701	0.953
3700	13.817	87.486	87.486	44.671	- 102.515	18.982	1.121
3800	13.822	87.855	87.855	46.053	- 103.063	22.270	1.281
3900	13.826	88.214	88.214	47.436	- 103.614	25.574	1.433
4000	13.830	88.564	88.564	48.819	- 104.168	28.894	1.579
4100	13.834	88.905	88.905	50.202	- 104.726	32.232	1.718
4200	13.838	89.239	89.239	51.585	- 105.287	35.573	1.851
4300	13.841	89.564	89.564	52.969	- 105.850	38.940	1.979
4400	13.844	89.883	89.883	54.354	- 106.416	42.306	2.101
4500	13.847	90.194	90.194	55.738	- 106.984	45.696	2.219
4600	13.850	90.498	90.498	57.123	- 107.555	49.100	2.333
4700	13.852	90.796	90.796	58.508	- 108.129	52.510	2.442
4800	13.855	91.088	91.088	59.893	- 108.705	55.935	2.547
4900	13.857	91.373	91.373	61.279	- 109.282	59.366	2.648
5000	13.859	91.653	91.653	62.665	- 109.861	62.814	2.745
5100	13.861	91.928	91.928	64.051	- 110.443	66.275	2.840
5200	13.863	92.197	92.197	65.437	- 111.025	69.742	2.931
5300	13.865	92.461	92.461	66.823	- 111.610	73.230	3.020
5400	13.866	92.720	92.720	68.210	- 112.197	76.720	3.105
5500	13.868	92.975	92.975	69.597	- 112.784	80.225	3.188
5600	13.870	93.225	93.225	70.984	- 113.373	83.739	3.268
5700	13.871	93.470	93.470	72.371	- 113.963	87.261	3.346
5800	13.872	93.711	93.711	73.758	- 114.555	90.805	3.421
5900	13.874	93.948	93.948	75.145	- 115.148	94.349	3.495
6000	13.875	94.182	94.182	76.533	- 115.743	97.899	3.566

Dec. 31, 1965

NITROGEN DIOXIDE UNINEGATIVE ION (NO_2^-) (IDEAL GAS)

Point Group C_{2v}
 $S_{298.15}^0 = [56.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $S_{298.15}^0 = -85.9 \pm 12 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = 1

$\Delta H_f^0 = -85.7 \pm 12 \text{ kcal. mole}^{-1}$
 $\Delta F_f^0 = -85.9 \pm 12 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹
[1320] (1)
[750] (1)
[1220] (1)

$\sigma = 2$

Bond Distances: N-O = $[1.23] \text{ \AA}$
 Bond Angle: O-N-O = $[116]^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = [25.6905] \times 10^{-117} \text{ g.}^3 \text{ cm.}^6$

Heat of Formation.

The heat of formation of $\text{NO}_2^-(g)$ was calculated from the electron affinity of $\text{NO}_2(g)$ and the JANAF value of ΔH_f^0 for $\text{NO}_2(g)$, $4.0 \pm 0.5 \text{ ev}$ and $8.6 \pm 0.2 \text{ kcal. mole}^{-1}$, respectively. The former was obtained from the National Bureau of Standards Report 6820, "Preliminary Report on the Thermodynamic Properties of Selected Light Element and Some Related Compounds", January 1965.

Heat Capacity and Entropy.

The bond distance N-O and the angle O-N-O of $\text{NO}_2^-(g)$ were estimated to be the same as those in $\text{NaNO}_2(c)$ which have been determined by G. B. Carpenter, Acta Cryst. 5, 132(1952). The three individual moments of inertia are $I_A = [0.6872] \times 10^{-39} \text{ g. cm.}^2$, $I_B = [5.7804] \times 10^{-39} \text{ g. cm.}^2$ and $I_C = [6.4676] \times 10^{-39} \text{ g. cm.}^2$

The vibrational frequencies of $\text{NO}_2^-(g)$ were assumed to be the same as those for nitrite ion in solution which have been measured by D. Williams, J. Am. Chem. Soc. 61, 2987(1939). These measured frequencies in nitrite solution are comparable to those in $\text{NO}_2(g)$ (1357.8, 756.8 and 1665.5 cm.⁻¹), reported by G. R. Bird et al., J. Chem. Phys. 40, 3378 (1964).

Nitrogen Trioxide (NO₃)
(Ideal Gas) Mol. Wt. = 62.008

NO₃

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	INFINITE	-2.619	18.529	18.529	INFINITE
100	7.970	50.613	68.855	-1.824	20.985	-45.860
200	9.050	56.354	9.960	-17.912	24.272	-28.522
298	11.218	60.352	-0.000	17.000	27.745	-20.437
300	11.260	60.422	60.353	-0.21	27.811	-20.260
400	13.368	63.961	60.821	1.256	31.449	-17.182
500	14.962	67.125	2.677	16.788	35.113	-15.347
600	16.105	69.900	62.004	4.233	38.774	-14.123
700	16.920	72.407	64.007	15.956	42.417	-12.543
800	17.511	74.807	65.294	17.133	46.040	-12.077
900	17.949	76.896	66.669	9.384	49.644	-12.555
1000	18.279	78.805	67.809	11.106	53.228	-11.632
1100	18.533	80.559	69.707	13.037	56.792	-11.283
1200	18.732	82.181	71.601	14.901	60.336	-10.689
1300	18.891	83.687	73.477	16.782	63.870	-10.737
1400	19.019	85.092	75.350	18.678	67.386	-10.519
1500	19.124	86.407	77.224	20.585	70.890	-10.328
1600	19.211	87.644	79.091	22.502	74.382	-10.160
1700	19.284	88.811	80.943	24.427	77.862	-10.009
1800	19.346	89.915	82.772	26.359	81.331	-9.874
1900	19.398	90.963	84.600	28.296	84.790	-9.753
2000	19.443	91.959	86.440	30.236	88.240	-9.642
2100	19.482	92.900	88.284	32.184	91.682	-9.541
2200	19.516	93.816	90.134	34.134	95.117	-9.449
2300	19.546	94.684	91.987	36.087	98.546	-9.364
2400	19.572	95.516	93.843	38.043	101.972	-9.285
2500	19.595	96.316	95.695	40.002	105.385	-9.212
2600	19.616	97.085	97.545	41.962	108.798	-9.145
2700	19.634	97.825	99.395	43.925	112.208	-9.082
2800	19.651	98.540	101.241	45.889	115.609	-9.023
2900	19.666	99.230	103.085	47.855	119.010	-8.968
3000	19.679	99.897	104.928	49.822	122.406	-8.917
3100	19.691	100.542	106.763	51.791	125.800	-8.868
3200	19.702	101.167	108.597	53.760	129.190	-8.823
3300	19.712	101.774	110.428	55.731	132.575	-8.780
3400	19.721	102.362	112.253	57.703	135.963	-8.739
3500	19.730	102.934	114.074	59.675	139.343	-8.701
3600	19.738	103.490	115.889	61.649	142.728	-8.664
3700	19.745	104.031	117.698	63.623	146.107	-8.630
3800	19.751	104.558	119.503	65.598	149.487	-8.597
3900	19.757	105.071	121.304	67.573	152.861	-8.566
4000	19.763	105.571	123.104	69.549	156.237	-8.536
4100	19.768	106.059	124.899	71.526	159.610	-8.507
4200	19.773	106.536	126.690	73.503	162.985	-8.480
4300	19.778	107.001	128.476	75.480	166.366	-8.455
4400	19.782	107.454	130.257	77.458	169.734	-8.430
4500	19.786	107.900	132.034	79.437	173.110	-8.407
4600	19.790	108.335	133.807	81.416	176.488	-8.385
4700	19.793	108.761	135.576	83.395	179.866	-8.362
4800	19.796	109.177	137.341	85.374	183.234	-8.342
4900	19.799	109.586	139.102	87.354	186.593	-8.322
5000	19.802	109.986	140.858	89.334	189.957	-8.303
5100	19.805	110.378	142.607	91.314	193.324	-8.285
5200	19.808	110.763	144.352	93.294	196.690	-8.268
5300	19.810	111.140	146.093	95.276	200.057	-8.250
5400	19.812	111.510	147.829	97.257	203.423	-8.234
5500	19.815	111.874	149.562	99.238	206.790	-8.218
5600	19.817	112.231	151.292	101.220	210.157	-8.203
5700	19.820	112.582	153.016	103.202	213.524	-8.188
5800	19.822	112.926	154.741	105.184	216.890	-8.174
5900	19.824	113.265	156.466	107.166	220.257	-8.161
6000	19.824	113.598	158.191	109.148	223.624	-8.148

Dec. 31, 1964

NITROGEN TRIOXIDE (NO₃) (IDEAL GAS)

Point Group [D_{3h}]
 $S_{298.15}^o = [60.4] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 Ground State Quantum Weight = 2
 $\Delta H_f^o = 18.5 \pm 5 \text{ kcal. mole}^{-1}$
 $\Delta F_f^o = 17.0 \pm 5 \text{ kcal. mole}^{-1}$

Vibrational Frequencies and Degeneracies

ν , cm. ⁻¹
[1158] (2)
[940] (1)
[704] (2)
[765] (1)

Bond Distance: O-N = [1.27] Å
 Bond Angle: O-N-O = [120°]
 Product of the Moments of Inertia: $I_A I_B I_C = [5.309 \times 10^{-115}] \text{ g. cm.}^6$
 $\sigma = [6]$

Heat of Formation.

The heat of formation is based on equilibrium constants for the reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$ obtained from shock wave studies by Schott and Davidson, J. Am. Chem. Soc. 80, 1941 (1958). These equilibria give a second law value of $\Delta H_f^o 495 = 21.5 \pm 1.4 \text{ kcal.}$, corresponding to $\Delta H_f^o 298.15 = 22.2 \text{ kcal.}$, and a third law value of $\Delta H_f^o 298.15 = 22.2 \text{ kcal.}$. The resulting heat of formation is $17.0 \text{ kcal. mole}^{-1}$.

Quillory and Johnston, J. Am. Chem. Soc. 85, 1695 (1963) report an equilibrium constant based on estimated Beer's law constants for NO₃ and attributed to the reaction $\text{O}_2 + \text{NO} \rightarrow \text{NO}_3$. This gives a third law heat of formation of $12 \pm 2 \text{ kcal. mole}^{-1}$, which was not considered. A tentative value of $23 \text{ kcal. mole}^{-1}$ (or greater) may be derived from the D₀ given by D. A. Ramsay, Proc. 10th Colloq. Spect. Internl. (1962), Univ. Maryland, pp. 583-596, 1963.

Heat Capacity and Entropy.

The structure and frequencies are those estimated by I. C. Haataune, J. Phys. Chem. 65, 2249 (1961). A symmetry of D_{3h} was chosen on the basis of Valan's correlation, J. Chem. Soc. 1953, 2301 (1953) and the bond distance was taken as 2% longer than in the nitrate ion. The planar mode frequencies were calculated from estimated Urey-Bradley force constants, while the out-of-plane wagging frequency (765 cm.⁻¹) was assumed the same as in HNO₃(g).

There are several conflicting bits of information concerning NO₃ radicals. Chantry, Horsfield, Morton and Whiffen, Mol. Phys. 5, 589 (1962) studied the electron resonance and optical absorption spectra of what appear to be NO₃ radicals trapped in crystals of urea nitrate. The authors suggest a planar structure without a threefold axis (thus C_{2v} symmetry), at least for the trapped radicals. Quillory and Johnston, loc. cit., report for gaseous NO₃ radicals an infrared frequency at 1840 cm.⁻¹ which they assign as the N-O stretch. The similarity of this frequency to those in N-O and X-N-O molecules led the authors to suggest an OONO structure (thus C_{2v} symmetry) rather than the nitrate structure. The remaining frequencies for such a structure may be crudely estimated by analogy with those measured for (NO₂)₂ by Smith, Keller and Johnston, J. Chem. Phys. 19, 189 (1951). Based on such frequencies and reasonable bond distances, the room temperature entropy for the OONO structure would be 68-72 cal. deg.⁻¹ mole⁻¹. Such an entropy is quite inconsistent with the second law $\Delta S_f^o 495 = 33.2 \pm 3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ for $\text{H}_2\text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{NO}_3(\text{g})$ obtained from the shock wave studies of Schott and Davidson. The Haataune functions based on the nitrate structure were selected because they are consistent with the experimental entropy. The principal moments of inertia for this structure are $I_A = 6.427 \times 10^{-39}$, $I_B = 6.427 \times 10^{-39}$ and $I_C = 12.853 \times 10^{-39} \text{ g. cm.}^2$. A structure of C_{2v} symmetry would result if the nitrate structure were distorted to give one non-equivalent oxygen. Ramsay, loc. cit., suggests that such distortion can only be small, based on the high dispersion optical spectra of the gas phase.

NO₃

Monophosphorus Mononitride (PN)

(Ideal Gas) Mol. Wt. = 44.983

NP

MONOPHOSPHORUS MONONITRIDE (PN) (IDEAL GAS) MOL. WT. = 44.983

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _f
0	0.000	INFINITE	- 2.080	24.861	INFINITE	
100	6.956	47.812	50.565	22.896	- 50.038	
200	6.971	47.255	51.231	20.644	- 22.958	
298	7.026	50.437	50.437	25.043	- 13.526	
300	7.100	50.437	50.437	25.041	- 13.413	
400	7.253	52.526	50.718	24.951	- 8.865	
500	7.253	54.223	51.855	24.778	- 6.155	
600	7.385	56.643	51.874	24.528	- 4.361	
700	8.088	56.874	52.504	24.330	- 3.090	
800	8.245	57.965	53.118	24.053	- 2.539	
900	8.272	58.834	53.712	23.758	- 2.094	
1000	8.476	58.832	54.281	23.552	- 1.681	
1100	8.557	60.644	54.923	23.422	- 1.317	
1200	8.623	61.392	55.339	23.283	- 1.047	
1300	8.678	62.084	55.632	23.128	- 0.824	
1400	8.723	62.739	55.902	22.966	- 0.635	
1500	8.762	63.352	56.151	22.792	- 0.471	
1600	8.794	63.929	57.130	22.606	- 0.328	
1700	8.823	64.433	57.951	22.411	- 0.202	
1800	8.848	64.938	58.585	22.208	- 0.091	
1900	8.869	65.437	59.164	22.000	- 0.000	
2000	8.886	65.872	59.728	21.786	- 0.078	
2100	8.907	66.306	60.278	21.565	- 0.168	
2200	8.923	66.724	60.810	21.336	- 0.269	
2300	8.938	67.110	61.323	21.093	- 0.382	
2400	8.951	67.479	61.810	20.835	- 0.507	
2500	8.964	67.834	62.265	20.565	- 0.644	
2600	8.975	68.176	62.698	20.283	- 0.794	
2700	8.986	68.505	63.105	20.000	- 0.957	
2800	8.996	68.822	63.482	19.711	- 1.132	
2900	9.006	69.127	63.832	19.411	- 1.317	
3000	9.015	69.421	64.154	19.100	- 1.512	
3100	9.024	69.709	64.450	18.786	- 1.717	
3200	9.032	70.083	64.723	18.465	- 1.932	
3300	9.041	70.454	64.978	18.136	- 2.157	
3400	9.048	70.824	65.215	17.800	- 2.392	
3500	9.056	70.853	65.435	17.455	- 2.637	
3600	9.063	71.151	65.637	17.100	- 2.892	
3700	9.070	71.430	65.820	16.735	- 3.157	
3800	9.077	71.692	65.986	16.360	- 3.432	
3900	9.084	71.938	66.128	15.975	- 3.717	
4000	9.090	72.168	66.250	15.580	- 4.012	
4100	9.097	72.332	66.352	15.175	- 4.317	
4200	9.103	72.552	66.427	14.760	- 4.632	
4300	9.109	72.766	66.479	14.335	- 4.957	
4400	9.116	72.975	66.508	13.900	- 5.292	
4500	9.122	73.165	66.515	13.455	- 5.637	
4600	9.127	73.331	66.502	13.000	- 5.992	
4700	9.133	73.477	66.467	12.535	- 6.357	
4800	9.139	73.609	66.410	12.060	- 6.732	
4900	9.145	73.758	66.335	11.575	- 7.117	
5000	9.150	73.814	66.250	11.080	- 7.512	
5100	9.156	73.824	66.150	10.575	- 7.917	
5200	9.161	73.802	66.035	10.060	- 8.332	
5300	9.167	73.766	65.908	9.535	- 8.757	
5400	9.172	73.715	65.770	9.000	- 9.192	
5500	9.178	73.651	65.615	8.455	- 9.637	
5600	9.183	73.582	65.445	7.900	- 10.092	
5700	9.188	73.504	65.260	7.335	- 10.557	
5800	9.194	73.415	65.060	6.760	- 11.032	
5900	9.199	73.315	64.845	6.175	- 11.517	
6000	9.204	73.205	64.615	5.580	- 12.012	

Dec. 31, 1960; Sept. 30, 1962

$\Delta H_f^o = 24.9 \pm 1.2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^o = 298.15 = 25.0 \pm 1.2 \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = 50.437 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Level and Multiplicity

ϵ , cm. ⁻¹	E_1
0	1

$\omega_e = 1337.24 \text{ cm.}^{-1}$
 $\omega_e x_e = 6.993 \text{ cm.}^{-1}$
 $B_e = 0.7862 \text{ cm.}^{-1}$
 $\alpha_e = 0.00557 \text{ cm.}^{-1}$
 $D_e = 1.09 \times 10^{-6} \text{ cm.}^{-1}$
 $r_e = 1.4910 \text{ \AA}$
 $\sigma = 1$

Heat of Formation.

The selected ΔH_f^o 298.15 was calculated from the $D_0^o = 165.8 \pm 1.2 \text{ kcal. mole}^{-1}$ reported by R. L. Potter and V. N. Distefano, J. Phys. Chem., **65**, 849 (1961). $A D_0^o = 163.7 \pm 1.2 \text{ kcal. mole}^{-1}$ was experimentally determined by E. O. Huffman, G. Tarbuton, K. L. Elmore, W. E. Cate, H. K. Walters, Jr., and G. V. Elmore, J. Am. Chem. Soc., **76**, 6239 (1954). The D_0^o reported by Huffman et al. was derived using a pressure-composition method i.e. measurement of equilibrium vapor pressure at 1173°K for the reaction $[\text{PN}(g) \rightarrow \text{P}_2(g) + \text{N}_2(g)]$. Potter and Distefano (loc. cit.) recalculated Huffman's results to obtain their D_0^o value. A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", Chapman and Hall (1953), lists a $D_0^o = 138.4 \pm 19 \text{ kcal. mole}^{-1}$. The corresponding heats of formation are:

ΔH_f^o 298.15	Source
$25.0 \pm 1.2 \text{ kcal. mole}^{-1}$	Potter and Distefano (loc. cit.)
$27.1 \pm 1.2 \text{ kcal. mole}^{-1}$	Huffman et al. (loc. cit.)
$53 \pm 19 \text{ kcal. mole}^{-1}$	Gaydon (loc. cit.)

Heat Capacity and Entropy.

The molecular constants are taken from G. Herzburg, "Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., (1960) 2nd Ed.

NP

MOL. WT. = 46.074

(IDEAL GAS)

MONOSULFUR MONONITRIDE (SN)

$D_0 = 115 \pm 25 \text{ kcal. mole}^{-1}$
Ground State Configuration $2\pi_r$
 $\Delta H_f^\circ 298.15 = 63 \pm 25 \text{ kcal. mole}^{-1}$
 $S^\circ_{298.15} = 53.055 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Multiplicities

$E_e, \text{ cm.}^{-1}$	g_e
0	2
223	2

$\omega_e x_e = 7.75 \text{ cm.}^{-1}$
 $\omega_e = [0.7762] \text{ cm.}^{-1}$
 $\alpha_e = [0.0064]$
 $r_e = 1.495(\text{?}) \text{ \AA}$

Heat of Formation

The dissociation energy is listed by A. O. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd Edn., Chapman and Hall, London (1955).

Heat Capacity and Entropy

The spectroscopic constants other than B_e and α_e are from O. Herzberg "Spectra of Diatomic Molecules", 2nd Edn., D. Van Nostrand Company, New York (1950). r_e is from "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London (1958), and has been used, together with the equation to calculate B_e and α_e .

$$\alpha_e = \frac{6}{\omega_e} \left(\frac{D_0 x_e B_e^3}{\omega_e} - 6B_e^2 / \omega_e \right) \quad (\text{Herzberg, op. cit., p. 108})$$

T, °K.	C_p°	$S^\circ - (F^\circ - H^\circ_{300})/T$	$H^\circ - H^\circ_{300}$	ΔH_f°	ΔF_f°	Log K_p
0	0.000	19.1011E	2.244	42.843	42.843	19.1011E
100	7.720	46.614	1.426	61.522	60.795	19.274E
200	7.687	50.011	3.751	61.089	58.510	19.393E
298	7.599	53.055	5.000	61.000	56.276	19.425E
300	7.599	53.102	5.056	60.988	56.237	19.425E
400	7.422	53.105	5.117	60.984	56.234	19.425E
500	7.241	53.025	5.126	61.411	57.012	19.425E
600	7.064	52.822	5.153	61.403	57.002	19.425E
700	6.896	52.599	5.193	61.062	56.259	19.425E
800	6.741	52.361	5.244	60.383	55.182	19.425E
900	6.596	52.111	5.304	60.383	55.182	19.425E
1000	6.464	51.854	5.374	60.383	55.182	19.425E
1100	6.343	51.600	5.450	60.383	55.182	19.425E
1200	6.231	51.354	5.530	60.383	55.182	19.425E
1300	6.126	51.114	5.614	60.383	55.182	19.425E
1400	6.028	50.884	5.700	60.383	55.182	19.425E
1500	5.936	50.664	5.788	60.383	55.182	19.425E
1600	5.850	50.454	5.878	60.383	55.182	19.425E
1700	5.768	50.254	5.970	60.383	55.182	19.425E
1800	5.690	50.064	6.064	60.383	55.182	19.425E
1900	5.616	49.884	6.160	60.383	55.182	19.425E
2000	5.546	49.714	6.258	60.383	55.182	19.425E
2100	5.480	49.554	6.358	60.383	55.182	19.425E
2200	5.418	49.404	6.460	60.383	55.182	19.425E
2300	5.360	49.264	6.564	60.383	55.182	19.425E
2400	5.306	49.134	6.670	60.383	55.182	19.425E
2500	5.256	49.014	6.778	60.383	55.182	19.425E
2600	5.210	48.904	6.888	60.383	55.182	19.425E
2700	5.168	48.804	6.998	60.383	55.182	19.425E
2800	5.128	48.714	7.110	60.383	55.182	19.425E
2900	5.090	48.634	7.224	60.383	55.182	19.425E
3000	5.054	48.564	7.340	60.383	55.182	19.425E
3100	5.020	48.504	7.458	60.383	55.182	19.425E
3200	5.000	48.454	7.578	60.383	55.182	19.425E
3300	4.980	48.414	7.698	60.383	55.182	19.425E
3400	4.960	48.384	7.818	60.383	55.182	19.425E
3500	4.940	48.354	7.938	60.383	55.182	19.425E
3600	4.920	48.324	8.058	60.383	55.182	19.425E
3700	4.900	48.294	8.178	60.383	55.182	19.425E
3800	4.880	48.264	8.298	60.383	55.182	19.425E
3900	4.860	48.234	8.418	60.383	55.182	19.425E
4000	4.840	48.204	8.538	60.383	55.182	19.425E
4100	4.820	48.174	8.658	60.383	55.182	19.425E
4200	4.800	48.144	8.778	60.383	55.182	19.425E
4300	4.780	48.114	8.898	60.383	55.182	19.425E
4400	4.760	48.084	9.018	60.383	55.182	19.425E
4500	4.740	48.054	9.138	60.383	55.182	19.425E
4600	4.720	48.024	9.258	60.383	55.182	19.425E
4700	4.700	47.994	9.378	60.383	55.182	19.425E
4800	4.680	47.964	9.498	60.383	55.182	19.425E
4900	4.660	47.934	9.618	60.383	55.182	19.425E
5000	4.640	47.904	9.738	60.383	55.182	19.425E
5100	4.620	47.874	9.858	60.383	55.182	19.425E
5200	4.600	47.844	9.978	60.383	55.182	19.425E
5300	4.580	47.814	10.098	60.383	55.182	19.425E
5400	4.560	47.784	10.218	60.383	55.182	19.425E
5500	4.540	47.754	10.338	60.383	55.182	19.425E
5600	4.520	47.724	10.458	60.383	55.182	19.425E
5700	4.500	47.694	10.578	60.383	55.182	19.425E
5800	4.480	47.664	10.698	60.383	55.182	19.425E
5900	4.460	47.634	10.818	60.383	55.182	19.425E
6000	4.440	47.604	10.938	60.383	55.182	19.425E

Silicon Nitride (SiN)

(Ideal Gas) GFW = 42.0927

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ²⁹⁸)/T	H - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	6.956	44.118	INFINITE	88.718	88.718	INFINITE
100	6.956	44.118	51.060	88.718	88.718	INFINITE
200	6.956	44.118	51.060	88.718	88.718	INFINITE
298	6.956	44.118	51.060	88.718	88.718	INFINITE
300	7.216	51.837	51.793	88.718	81.722	59.502
400	7.541	53.957	52.079	88.718	79.254	43.302
500	7.843	55.673	52.632	88.718	76.863	33.597
600	8.086	57.125	53.263	88.718	74.496	27.135
700	8.273	58.387	53.907	88.718	72.151	22.526
800	8.421	59.501	54.538	88.718	69.825	19.075
900	8.545	60.501	55.146	88.718	67.517	16.395
1000	8.657	61.407	55.727	88.718	65.225	14.255
1100	8.767	62.237	56.282	88.718	62.948	12.507
1200	8.860	63.005	56.810	88.718	60.684	11.052
1300	8.949	63.720	57.315	88.718	58.438	9.824
1400	9.033	64.392	57.796	88.718	56.202	8.773
1500	9.113	65.025	58.257	88.718	53.980	7.865
1600	9.188	65.627	58.699	88.718	51.768	7.071
1700	9.258	66.200	59.124	88.718	49.572	6.386
1800	9.324	66.747	59.532	88.718	47.393	5.811
1900	9.387	67.272	59.926	88.718	45.231	5.374
2000	9.446	67.776	60.306	88.718	43.085	4.945
2100	9.498	68.261	60.673	88.718	40.955	4.527
2200	9.545	68.729	61.029	88.718	38.833	4.120
2300	9.588	69.180	61.373	88.718	36.717	3.724
2400	9.627	69.615	61.708	88.718	34.613	3.338
2500	9.662	70.036	62.033	88.718	32.519	2.962
2600	9.693	70.446	62.348	88.718	30.435	2.596
2700	9.720	70.847	62.655	88.718	28.360	2.240
2800	9.744	71.241	62.955	88.718	26.294	1.894
2900	9.765	71.629	63.246	88.718	24.238	1.558
3000	9.783	71.999	63.530	88.718	22.192	1.232
3100	9.798	72.352	63.807	88.718	20.156	0.916
3200	9.810	72.689	64.077	88.718	18.129	0.600
3300	9.820	72.999	64.342	88.718	16.111	0.284
3400	9.828	73.272	64.600	88.718	14.100	0.000
3500	9.834	73.560	64.852	88.718	12.096	-0.284
3600	9.838	73.819	65.098	88.718	10.100	-0.568
3700	9.840	74.070	65.340	88.718	8.111	-0.852
3800	9.841	74.295	65.576	88.718	6.129	-1.136
3900	9.842	74.495	65.807	88.718	4.154	-1.420
4000	9.843	74.666	66.033	88.718	2.186	-1.704
4100	9.844	74.812	66.255	88.718	0.224	-1.988
4200	9.845	74.938	66.472	88.718	-1.733	-2.272
4300	9.846	75.046	66.686	88.718	-3.744	-2.556
4400	9.847	75.138	66.895	88.718	-5.755	-2.840
4500	9.848	75.216	67.100	88.718	-7.766	-3.124
4600	9.849	75.270	67.301	88.718	-9.777	-3.408
4700	9.850	75.304	67.498	88.718	-11.788	-3.692
4800	9.851	75.329	67.692	88.718	-13.799	-3.976
4900	9.852	75.346	67.883	88.718	-15.810	-4.260
5000	9.853	75.354	68.070	88.718	-17.821	-4.544
5100	9.854	75.355	68.254	88.718	-19.832	-4.828
5200	9.855	75.358	68.435	88.718	-21.843	-5.112
5300	9.856	75.361	68.612	88.718	-23.854	-5.396
5400	9.857	75.364	68.789	88.718	-25.865	-5.680
5500	9.858	75.367	68.966	88.718	-27.876	-5.964
5600	9.859	75.369	69.140	88.718	-29.887	-6.248
5700	9.860	75.371	69.312	88.718	-31.898	-6.532
5800	9.861	75.373	69.484	88.718	-33.909	-6.816
5900	9.862	75.375	69.656	88.718	-35.920	-7.100
6000	9.863	75.377	69.827	88.718	-37.931	-7.384

Dec. 31, 1960; Mar. 31, 1967

SILICON NITRIDE (SiN)

(IDEAL GAS)

OPW = 42.0927

Ground State Configuration 2 Σ⁺

ΔH_f^o = 89.7 ± 15 kcal/mol

ΔH_f^o = 89 ± 15 kcal/mol

S_{298.15} = 51.792 gibbs/mol

Electronic Levels and Quantum Weights

ci, cm ⁻¹	ΔE
0	2
[6000]	4
24299.4	2
[31000]	4

ω_e = 1150.8 cm⁻¹
 ω_ex_e = 6.55 cm⁻¹
 B_e = 0.7299 cm⁻¹
 α_e = 0.00567
 σ = 1
 r_e = 1.578 Å

Heat of Formation

A linear Birge-Sponer extrapolation of the ground state gives a dissociation energy of 142.9 kcal. The ground state can correlate with normal atoms Si(³P) + N(²D); in this latter case D₀ would be 68 kcal. The uncertainty in the extrapolation is quite large, ± 30 kcal, since only 6 levels, of the estimated total of 87 levels, are observed.

A dissociation energy can also be calculated from the B²Σ⁺ state by a much shorter extrapolation. This extrapolation is done graphically since some curvature is evident in the first six levels. A value of D₀(B²Σ) = 50.4 kcal is obtained. This corresponds to D₀(X²Σ) = 119.9 kcal for normal products or D₀(X²Σ) = 65 kcal for excited nitrogen as a product. The uncertainty in this extrapolation is less than the ground state and is probably ± 20 kcal.

An estimate of D₀(SiN) may be obtained by equating D₀(SiN)/D₀(SiO) = D₀(CN)/D₀(CO); this yields D₀(SiN) = 135 kcal. A comparison of the isoelectronic molecules CP, BS and BeCl and the related molecules CN, BO, BeF indicates D₀(SiN) > 115 kcal.

A value of D₀(SiN) = 130 ± 15 kcal/mol is in agreement within the uncertainties of both ground state and B state extrapolations assuming normal atoms as products, and is in agreement with the other estimates. This value is adopted and yields ΔH_f^o = 89 kcal/mol.

Heat Capacity and Entropy

The B-X transition has been reported by R. A. Jenkins and H. de Lae, Proc. Roy. Soc. (London) 122, 103 (1929). The rotational and vibrational constants are derived from their work and adjusted to normal isotopic abundance. The A²Π-²Σ⁺ transition has been observed by M. D. Shetler, Ph.D. Thesis, Univ. of California, Berkeley (1965). The height of the A state is estimated by correlation with CF(g). The level of the B state is taken from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., 2nd Edition, New York, 1950.

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈)/T	H ^o - H ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	.000	INFINITE	- 2.625	94.749	94.749	INFINITE
100	8.581	50.108	- 2.095	95.015	92.094	- 201.275
200	10.659	54.797	- 1.112	95.007	89.134	- 47.406
298	11.922	61.275	.000	95.000	86.235	-
300	11.942	61.349	.022	94.998	86.182	- 62.783
400	12.803	66.910	1.262	94.875	83.261	- 45.492
500	13.374	67.833	2.571	94.747	80.374	- 35.131
600	13.755	70.307	3.931	94.612	77.511	- 28.233
700	14.017	72.449	5.320	94.468	74.672	- 23.314
800	14.202	74.333	6.732	94.308	71.853	- 19.629
900	14.336	76.014	8.159	94.131	69.059	- 16.770
1000	14.435	77.530	9.594	93.935	66.283	- 14.866
1200	14.512	78.909	11.045	93.719	63.528	- 12.622
1400	14.571	80.175	12.499	93.482	60.793	- 11.072
1600	14.618	81.343	13.959	93.226	58.078	- 9.764
1800	14.656	82.428	15.421	92.950	55.385	- 8.646
2000	14.687	83.440	16.890	92.652	52.713	- 7.680
2200	14.712	84.389	18.360	92.334	50.061	- 6.830
2400	14.733	85.281	19.832	92.000	47.431	- 6.125
2600	14.751	86.124	21.306	91.659	44.821	- 5.640
2800	14.767	86.922	22.782	91.308	42.237	- 5.208
3000	14.780	87.680	24.260	90.957	40.671	- 4.820
3200	14.791	88.401	25.738	90.604	39.131	- 4.471
3400	14.801	89.089	27.214	90.251	37.621	- 4.154
3600	14.810	89.747	28.689	89.897	36.145	- 3.867
3800	14.817	90.378	30.160	89.544	34.705	- 3.604
4000	14.824	90.983	31.632	89.191	33.298	- 3.363
4200	14.830	91.564	33.105	88.838	31.925	- 3.142
4400	14.836	92.124	34.579	88.485	30.587	- 2.937
4600	14.841	92.664	36.052	88.132	29.281	- 2.748
4800	14.846	93.185	37.526	87.779	28.006	- 2.573
5000	14.851	93.688	39.001	87.426	26.761	- 2.410
5200	14.856	94.175	40.476	87.073	25.546	- 2.258
5400	14.860	94.647	41.951	86.720	24.361	- 2.117
5600	14.865	95.104	43.426	86.367	23.206	- 1.984
5800	14.869	95.548	44.901	86.014	22.081	- 1.860
6000	14.874	95.979	46.376	85.661	20.986	- 1.743
6200	14.879	96.398	47.851	85.308	19.921	- 1.636
6400	14.885	96.806	49.326	84.955	18.886	- 1.538
6600	14.890	97.203	50.797	84.602	17.881	- 1.446
6800	14.896	97.590	52.268	84.249	16.906	- 1.360
7000	14.903	97.967	53.739	83.896	15.961	- 1.279
7200	14.910	98.335	55.210	83.543	15.046	- 1.203
7400	14.918	98.695	56.681	83.190	14.161	- 1.132
7600	14.926	99.046	58.152	82.837	13.306	- 1.066
7800	14.934	99.389	59.623	82.484	12.481	- 1.004
8000	14.944	99.725	61.094	82.131	11.686	- 0.946
8200	14.953	100.053	62.565	81.778	10.921	- 0.892
8400	14.964	100.375	64.036	81.425	10.186	- 0.842
8600	14.975	100.690	65.507	81.072	9.481	- 0.797
8800	14.986	101.000	66.978	80.719	8.806	- 0.756
9000	14.999	101.302	68.449	80.366	8.161	- 0.719
9200	15.011	101.599	69.920	80.013	7.546	- 0.686
9400	15.025	101.891	71.391	79.660	6.961	- 0.656
9600	15.039	102.177	72.862	79.307	6.406	- 0.629
9800	15.053	102.458	74.333	78.954	5.881	- 0.604
10000	15.068	102.735	75.804	78.601	5.386	- 0.580
10200	15.084	103.006	77.275	78.248	4.921	- 0.558
10400	15.100	103.273	78.746	77.895	4.486	- 0.537
10600	15.116	103.536	79.217	77.542	4.081	- 0.518
10800	15.133	103.795	80.688	77.189	3.706	- 0.502
11000	15.151	104.049	82.159	76.836	3.361	- 0.487
11200	15.169	104.300	83.630	76.483	3.046	- 0.473
11400	15.188	104.549	85.101	76.130	2.761	- 0.460
11600	15.208	104.796	86.572	75.777	2.506	- 0.448
11800	15.228	105.040	88.043	75.424	2.281	- 0.437
12000	15.249	105.282	89.514	75.071	2.086	- 0.427
12200	15.270	105.522	90.985	74.718	1.921	- 0.418
12400	15.292	105.761	92.456	74.365	1.776	- 0.410
12600	15.314	106.000	93.927	74.012	1.651	- 0.403
12800	15.337	106.237	95.398	73.659	1.546	- 0.397
13000	15.361	106.473	96.869	73.306	1.461	- 0.392
13200	15.386	106.708	98.340	72.953	1.396	- 0.387
13400	15.411	106.942	99.811	72.600	1.351	- 0.383
13600	15.437	107.176	101.282	72.247	1.326	- 0.380
13800	15.463	107.409	102.753	71.894	1.311	- 0.377
14000	15.490	107.642	104.224	71.541	1.306	- 0.374
14200	15.517	107.875	105.695	71.188	1.311	- 0.371
14400	15.545	108.107	107.166	70.835	1.326	- 0.368
14600	15.573	108.339	108.637	70.482	1.351	- 0.365
14800	15.602	108.571	110.108	70.129	1.386	- 0.362
15000	15.631	108.803	111.579	69.776	1.431	- 0.359
15200	15.661	109.035	113.050	69.423	1.486	- 0.356
15400	15.691	109.267	114.521	69.070	1.551	- 0.353
15600	15.722	109.499	115.992	68.717	1.626	- 0.350
15800	15.753	109.731	117.463	68.364	1.711	- 0.347
16000	15.785	109.963	118.934	68.011	1.806	- 0.344
16200	15.817	110.195	120.405	67.658	1.911	- 0.341
16400	15.850	110.427	121.876	67.305	2.026	- 0.338
16600	15.883	110.659	123.347	66.952	2.151	- 0.335
16800	15.916	110.891	124.818	66.600	2.286	- 0.332
17000	15.950	111.123	126.289	66.247	2.431	- 0.329
17200	15.984	111.355	127.760	65.894	2.586	- 0.326
17400	16.018	111.587	129.231	65.541	2.751	- 0.323
17600	16.053	111.819	130.702	65.188	2.926	- 0.320
17800	16.088	112.051	132.173	64.835	3.111	- 0.317
18000	16.123	112.283	133.644	64.482	3.306	- 0.314
18200	16.158	112.515	135.115	64.129	3.511	- 0.311
18400	16.193	112.747	136.586	63.776	3.726	- 0.308
18600	16.228	112.979	138.057	63.423	3.951	- 0.305
18800	16.263	113.211	139.528	63.070	4.186	- 0.302
19000	16.298	113.443	140.999	62.717	4.431	- 0.300
19200	16.333	113.675	142.470	62.364	4.686	- 0.297
19400	16.368	113.907	143.941	62.011	4.951	- 0.294
19600	16.403	114.139	145.412	61.658	5.226	- 0.291
19800	16.438	114.371	146.883	61.305	5.511	- 0.288
20000	16.473	114.603	148.354	60.952	5.806	- 0.285
20200	16.508	114.835	149.825	60.600	6.111	- 0.282
20400	16.543	115.067	151.296	60.247	6.426	- 0.279
20600	16.578	115.299	152.767	59.894	6.751	- 0.276
20800	16.613	115.531	154.238	59.541	7.086	- 0.273
21000	16.648	115.763	155.709	59.188	7.431	- 0.270
21200	16.683	116.000	157.180	58.835	7.786	- 0.267
21400	16.718	116.232	158.651	58.482	8.151	- 0.264
21600	16.753	116.464	160.122	58.129	8.526	- 0.261
21800	16.788	116.696	161.593	57.776	8.911	- 0.258
22000	16.823	116.928	163.064	57.423	9.306	- 0.255
22200	16.858	117.160	164.535	57.070	9.711	- 0.252
22400	16.893	117.392	166.006	56.717	10.126	- 0.249
22600	16.928	117.624	167.477	56.364	10.551	- 0.246
22800	16.963	117.856	168.948	56.011	10.986	- 0.243
23000	16.998	118.088	170.419	55.658	11.431	- 0.240
23200	17.033	118.320	171.890	55.305	11.886	- 0.237
23400	17.068	118.552	173.361	54.952	12.351	- 0.234
23600	17.103	118.784	174.832	54.600	12.826	- 0.231
23800	17.138	119.016	176.303	54.247	13.311	- 0.228
24000	17.173	119.248	177.774	53.894	13.806	- 0.225
24200	17.208	119.480	179.245	53.541	14.311	- 0.222
24400	17.243	119.712	180.716	53.188	14.826	- 0.219
24600	17.278	119.944	182.187	52.835	15.351	- 0.216
24800	17.313	120.176	183.658	52.482	15.886	- 0.213
25000	17.348	120.408	185.129	52.129	16.431	- 0.210
25200	17.383	120.640	186.600	51.776	16.986	- 0.207
25400	17.418	120.872	188.071	51.423	17.551	- 0.204
25600	17.453	121.104	189.542	51.070	18.126	- 0.201
25800	17.488	121.336	191.013	50.717	18.711	- 0.198
26000	17.523	121.568	192.484	50.364	19.306	- 0.195
26200	17.558	121.800	193.955	50.011	19.911	- 0.192
26400	17.593	122.032	195.426	49.658	20.526	- 0.189
26600	17.628	122.264	196.897	49.305	21.151	- 0.186
26800	17.663	122.496	198.368	48.952	21.786	- 0.183
27000	17.698	122.728	199.839	48.600	22.431	- 0.180
27200	17.733	122.960	201.310	48.247	23.086	- 0.177
27400	17.768	123.192	202.781	47.894	23.751	- 0.174
27600	17.803	123.424	204.252	47.541	24.426	- 0.171
27800	17.838	123.656	205.723	47.188	25.111	- 0.168
28000	17.873	123.888	207.194	46.835	25.806	- 0.165
28200	17.908	124.120	20			

Titanium Nitride (TiN)

(Crystal)

GFW = 61.9067

TITANIUM NITRIDE (TiN)

(CRYSTAL)

NTi

GFW = 61.9067

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	2.572	1.057	1.3395	1.311	79.823	79.823	INFINITE
200	6.532	4.104	7.971	1.234	80.226	78.227	170.944
298	8.662	7.226	11.006	.765	80.564	76.080	83.146
300	8.500	7.281	11.066	.000	80.701	73.805	53.767
400	10.471	12.509	11.866	.016	80.691	71.504	39.068
500	11.247	15.079	11.666	2.063	80.598	69.217	30.255
600	11.645	16.597	11.506	3.229	80.475	66.953	24.387
700	11.898	17.812	11.366	4.406	80.329	64.710	20.203
800	12.051	18.781	11.241	5.606	80.125	62.484	17.070
900	12.211	19.549	11.125	6.825	80.039	60.271	14.636
1000	12.463	20.153	10.999	8.063	79.966	58.077	12.691
1100	12.648	21.449	10.878	9.318	79.905	55.877	11.102
1200	12.839	22.593	10.760	10.586	79.850	53.652	9.771
1300	13.037	23.625	10.646	11.866	79.800	51.393	8.670
1400	13.237	24.567	10.538	13.200	79.754	49.148	7.672
1500	13.443	25.487	10.434	14.534	79.712	46.915	6.836
1600	13.654	26.361	10.331	15.868	79.672	44.682	6.105
1700	13.867	27.193	10.230	17.202	79.637	42.453	5.465
1800	14.084	27.983	10.130	18.536	79.609	40.228	4.891
1900	14.304	28.733	10.030	19.870	79.584	38.000	4.381
2000	14.526	30.001	10.000	21.523	79.562	35.754	3.907
2100	14.749	30.715	10.769	22.997	83.705	33.389	3.471
2200	14.972	31.379	20.780	25.942	83.512	30.955	3.075
2300	15.203	32.079	21.265	27.513	83.318	28.559	2.715
2400	15.430	32.729	21.695	29.068	83.072	26.153	2.395
2500	15.659	33.363	21.736	29.068	82.605	23.859	2.083
2600	15.889	33.982	22.195	30.645	82.516	21.477	1.805
2700	16.110	34.576	22.680	32.276	82.205	19.134	1.549
2800	16.332	35.154	23.176	33.869	81.872	16.805	1.312
2900	16.584	35.754	23.507	35.516	81.516	14.484	1.092
3000	16.817	36.320	23.925	37.186	81.139	12.180	.887
3100	17.050	36.875	24.334	38.870	80.738	9.888	.697
3200	17.283	37.425	24.736	40.571	80.316	7.611	.520
3300	17.516	37.970	25.132	42.286	79.871	5.351	.354
3400	17.753	38.482	25.512	44.000	79.402	3.092	.199
3500	17.988	39.000	25.890	45.687	78.911	.857	.054
3600	18.223	39.510	26.261	47.357	78.398	1.630	.099
3700	18.458	40.008	26.625	49.000	77.864	1.407	.139
3800	18.693	40.508	26.985	50.625	77.319	1.186	.172
3900	18.930	40.997	27.338	52.250	76.764	.966	.200
4000	19.167	41.479	27.685	53.875	76.194	.746	.225
4100	19.403	41.955	28.028	55.500	75.619	.526	.246
4200	19.639	42.428	28.367	57.125	75.039	.306	.263
4300	19.876	42.897	28.700	58.750	74.454	.086	.276
4400	20.113	43.350	29.025	60.375	73.864	-.134	.285
4500	20.350	43.805	29.348	62.000	73.269	-.364	.290

ΔH°₀ = -79.8 ± 1 kcal/mol
 ΔH°_{298.15} = -80.7 ± 1 kcal/mol
 ΔH°_m = [16] kcal/mol

S°_{298.15} = 7.23 ± 0.05 gibbs/mol
 T_m = 3220 ± 50°K

Heat of Formation

Humphrey (1) and Neumann et al. (2) determined the heat of combustion of titanium nitride by burning the material in an oxygen bomb calorimeter. For reaction (a) Humphrey obtained ΔH°₂₉₈ = -145.05 ± 0.14 kcal/mol and Neumann et al. ΔH°₂₉₈ = -145.0 kcal/mol. From an examination of the combustion products Humphrey reported that the TiO₂ was >95 per cent rutile and <5 per cent anatase, but made no correction for the anatase. The adopted ΔH°₂₉₈ = -80.7 kcal/mol is the average of three values, two from Humphrey (-80.75, -80.61), one as reported, and one corrected for anatase, and one from Neumann et al. (-80.8). The uncertainty in the adopted heat is due mainly to the uncertainty in the heat of formation of rutile. Hoch et al. (3) determined the vapor pressure of reaction (b), in the temperature range 1987-2241°K, using a Knudsen effusion method. Third law analysis of the data yields a ΔH°₂₉₈ = -79.5 ± 9 kcal/mol. Linevsky (4) obtained the titanium partial pressures of reaction (c) (2088-2141°K) at fixed nitrogen pressures using atomic absorption spectroscopy. Third law analysis of the data gives a ΔH°₂₉₈ = -81 ± 18 kcal/mol. These equilibrium measurements were not considered in deriving the heat of formation due to their large uncertainties in comparison to the calorimetric data.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52-296°K) of Shomate (5). Naylor (6) measured high temperature heat contents (388-1738°K). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 1738°K the heat capacity is graphically extrapolated. The entropy is based on S°₀ - S°₀ = 0.138 eu.

Melting Data

See liquid table.

Reference	Method	Reaction	T°K	ΔH° ₂₉₈ kcal/mol	ΔH° ₂₉₈ kcal/mol
1	Calorimeter	(a) TiN(c) + O ₂ (g) → TiO ₂ (rutile) + 1/2N ₂ (g)	298	-145.05±.14	-80.75
1	Calorimeter	(a) TiN(c) + O ₂ (g) → TiO ₂ (rutile) + 1/2N ₂ (g)	298	-145.05±.14	-80.61*
2	Calorimeter	(a) TiN(c) + O ₂ (g) → TiO ₂ (rutile) + 1/2N ₂ (g)	298	-145.0	-80.80
3	Equilibrium	(b) TiN(c) + Ti(g) → 1/2N ₂ (g)	1987-2241	212±9	-79.5
4	Equilibrium	(c) TiN(c) → Ti(g) + 1/2N ₂ (g)	2088-2141	230±17	-81.2

*Assumes that the product TiO₂ is 95 per cent rutile and 5 per cent anatase.

References

1. G. L. Humphrey, J. Am. Chem. Soc. **73**, 2261 (1951).
2. B. Neumann, C. Kroger and H. Kunz, Z. Anorg. Allgem. Chem. **218**, 379-401 (1938).
3. M. Hoch, D. P. Dingley and H. L. Johnston, J. Am. Chem. Soc. **77**, 304-6 (1955).
4. M. J. Linevsky, General Electric Co., AFML-TR-64-420, February 1965.
5. C. H. Shomate, J. Am. Chem. Soc. **58**, 310 (1946).
6. B. F. Naylor, J. Am. Chem. Soc. **68**, 370 (1946).

(Liquid) GFW = 61.9067

TITANIUM NITRIDE (TiN) (LIQUID) GFW = 61.9067

 $S^{\circ}_{298.15} = [12.603] \text{ gibbs/mol}$ $\Delta H^{\circ}_{298.15} = [-63.531 \pm 1.1] \text{ kcal/mol}$ $\Delta H_m^{\circ} = [16] \text{ kcal/mol}$ $T_m = 3220 \pm 50^{\circ}\text{K}$

Heat of Formation

The heat of formation is obtained from $\Delta H^{\circ}_{298}(c)$ by adding ΔH_m° and the difference between $H_m^{\circ} - H^{\circ}_{298}$ for crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200°K . Below 2200°K the heat capacity is obtained from the heat capacity of the crystal. Above 2200°K it is assumed constant and estimated as 15 gibbs/mol or 7.5 gibbs/g-atom. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

T_m is taken from C. Agte and K. Moers, Z. Anorg. Allgem. Chem. 198, 233-43 (1931). ΔH_m° is derived from an estimated $\Delta S_m = 2.5 \text{ gibbs/g-atom}$ as suggested by O. Kubaschewski, E. L. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, 1967.

T, °K	C_p°	$S^{\circ} - (C_p^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
100						
150						
200						
250						
300	8.462	12.403	.000	-63.531	-58.281	42.721
350		12.603	.016	-63.532	-58.249	42.434
400	10.471	15.456	.993	-63.532	-56.462	36.462
450	11.747	17.886	2.063	-63.429	-54.737	23.725
500		19.474	3.229	-63.306	-53.010	19.309
600	11.445	21.788	4.407	-63.178	-51.304	16.018
700	12.098	23.390	5.606	-63.060	-49.616	13.554
800	12.281	24.426	6.825	-62.956	-47.943	11.642
900	12.463	25.129	8.063	-62.870	-46.289	10.114
1000		26.326	9.316	-62.797	-44.622	8.466
1100	12.439	27.434	10.592	-62.736	-42.935	7.819
1200	13.035	29.470	11.866	-62.686	-41.214	6.929
1300	13.635	30.443	13.200	-62.647	-39.507	6.167
1400	13.237	31.363	14.534	-62.613	-37.811	5.509
1500	13.443	32.238	15.866	-62.579	-36.126	4.935
1600	13.454	33.072	17.264	-62.548	-34.454	4.429
1700	13.467	33.871	18.662	-62.518	-32.791	3.981
1800	14.064	34.638	20.081	-62.474	-31.137	3.582
1900	14.304	35.377	21.523	-62.426	-29.536	3.206
2000	14.526	36.091	22.987	-62.373	-27.971	2.859
2100	14.749	36.783	24.473	-62.313	-25.614	2.545
2200	15.000	37.450	25.973	-62.248	-23.787	2.258
2300	15.000	38.088	27.493	-62.178	-21.927	1.997
2400	15.000	38.700	28.973	-62.103	-20.096	1.757
2500	15.000	39.289	30.473	-62.024	-18.277	1.536
2600	15.000	40.013	31.973	-61.939	-16.464	1.333
2700	15.000	40.400	33.473	-61.846	-14.659	1.144
2800	15.000	40.627	34.973	-61.746	-12.859	.969
2900	15.000	41.435	36.473	-61.653	-11.066	.806
3000		41.927	37.973	-61.559	-9.285	.655
3100	15.000	42.403	39.473	-61.460	-7.510	.513
3200	15.000	42.865	40.973	-61.357	-5.738	.380
3300	15.000	43.313	42.473	-61.250	-3.972	.255
3400	15.000	43.747	43.973	-61.138	-2.216	.138
3500	15.000	44.170	45.473	-61.021	-.000	.012
3600	15.000	44.581	46.973	-60.898	4.376	.258
3700	15.000	44.981	48.473	-60.769	8.944	.514
3800	15.000	45.371	49.973	-60.635	13.513	.757
3900	15.000	45.750	51.473	-60.496	18.072	.967
4000		46.121	52.973	-60.352	22.628	1.206
4100	15.000	46.482	54.473	-60.203	27.178	1.414
4200	15.000	46.835	55.973	-60.048	31.725	1.612
4300	15.000	47.180	57.473	-59.888	36.266	1.801
4400	15.000	47.517	58.973	-59.723	40.811	1.962
4500						

Dec. 30, 1960; June 30, 1968

Monozirconium Mononitride (ZrN)
(Crystal) Mol. Wt. = 105.228

INTERIM TABLE

T, °K.	C _p	S° (cal. mole ⁻¹ deg. ⁻¹)	(S° - H° ₂₉₈)/T	H° - H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	.000	INFINITE	INFINITE	1.575	-86.522	-86.522	INFINITE
100	3.116	1.944	1.944	1.480	-86.522	-86.522	185.526
200	7.970	9.288	9.288	.000	-86.522	-86.522	50.983
300	9.493	9.348	9.288	.018	-87.300	-80.470	56.589
400	10.697	12.265	9.682	1.041	-87.260	-78.142	42.693
500	11.252	14.740	10.455	2.142	-87.161	-75.671	33.162
600	11.630	16.826	11.347	3.287	-87.096	-73.616	26.813
700	11.925	18.642	12.262	4.466	-87.007	-71.377	22.284
800	12.175	20.251	13.162	5.671	-86.911	-69.151	18.690
900	12.400	21.698	14.032	6.900	-86.807	-66.936	16.254
1000	12.608	23.015	14.865	8.150	-86.697	-64.734	14.147
1100	12.806	24.226	15.662	9.421	-86.590	-62.544	12.426
1200	12.997	25.349	16.423	10.711	-86.439	-60.314	10.984
1300	13.182	26.396	17.150	12.020	-86.309	-58.060	9.760
1400	13.364	27.360	17.846	13.348	-86.174	-55.816	8.713
1500	13.544	28.308	18.513	14.693	-86.032	-53.580	7.806
1600	13.721	29.188	19.153	16.056	-85.881	-51.353	7.014
1700	13.896	30.025	19.768	17.437	-85.725	-49.139	6.317
1800	14.071	30.824	20.360	18.835	-85.560	-46.932	5.698
1900	14.244	31.590	20.931	20.251	-85.387	-44.734	5.145
2000	14.417	32.325	21.483	21.684	-85.207	-42.548	4.649
2100	14.573	33.032	22.016	23.136	-85.018	-40.370	4.201
2200	14.760	33.714	22.532	24.601	-84.824	-38.206	3.778
2300	14.931	34.374	23.033	26.086	-84.624	-36.045	3.387
2400	15.102	35.013	23.519	27.587	-84.418	-33.891	3.029
2500	15.272	35.633	23.991	29.106	-84.207	-31.747	2.700
2600	15.443	36.236	24.450	30.642	-83.992	-29.619	2.398
2700	15.612	36.822	24.898	32.194	-83.766	-27.516	2.119
2800	15.782	37.392	25.334	33.764	-83.524	-25.434	1.860
2900	15.952	37.949	25.759	35.351	-83.268	-23.374	1.620
3000	16.121	38.493	26.175	36.954	-82.998	-21.339	1.397
3100	16.290	39.024	26.581	38.575	-82.712	-19.329	1.189
3200	16.459	39.544	26.978	40.212	-82.412	-17.348	1.005
3300	16.626	40.053	27.366	41.867	-82.099	-15.396	.853
3400	16.797	40.552	27.747	43.536	-81.773	-13.472	.720
3500	16.966	41.041	28.120	45.226	-81.438	-11.576	.603
3600	17.135	41.522	28.485	46.931	-81.093	-9.707	.500
3700	17.303	41.993	28.844	48.651	-80.738	-7.863	.407
3800	17.472	42.457	29.196	50.392	-80.374	-6.044	.333
3900	17.641	42.913	29.542	52.148	-80.001	-4.250	.291
4000	17.809	43.362	29.882	53.920	-79.618	-2.483	.269
4100	17.978	43.804	30.216	55.709	-79.226	-0.743	.257
4200	18.146	44.239	30.545	57.516	-78.826	0.957	.250
4300	18.315	44.668	30.868	59.339	-78.418	2.699	.247
4400	18.483	45.091	31.187	61.179	-77.993	4.483	.244
4500	18.652	45.508	31.500	63.035	-77.553	6.312	.241
4600	18.820	45.920	31.809	64.909	-77.098	8.186	.238
4700	18.988	46.326	32.114	66.799	-76.629	10.105	.235
4800	19.157	46.728	32.414	68.707	-76.146	12.067	.232
4900	19.325	47.125	32.710	70.631	-75.649	14.072	.229
5000	19.493	47.517	33.003	72.572	-75.138	16.122	.226

June 30, 1961

NZr

MONOZIRCONIUM MONONITRIDE (ZrN) (crystal)

Mol. Wt. = 105.228
 $\Delta H_f^0 = -86.5 \pm 2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 \text{ 298.15} = -87.3 \pm 2 \text{ kcal. mole}^{-1}$
 $T_m = [3225^\circ\text{K}]$
 $S_{298.15}^0 = 9.29 \pm 0.05 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_m^0 = [16.1] \text{ kcal. mole}^{-1}$

Heat of Formation. The heat of reaction I, $-174.25 \pm 0.30 \text{ kcal. mole}^{-1}$, was measured by A. D. Meh and N. L. Gelbert. The $\Delta H_f^0 \text{ 298.15}$ of ZrN was obtained using $-261.5 \pm 0.2 \text{ kcal. mole}^{-1}$ for $\Delta H_f^0 \text{ 298.15}$ of ZrO_2 . For the same reaction B. Neumann, C. Kroger and H. Kunz, Z. anorg. Chem. 218, 379 (1934) obtain $-176.0 \text{ kcal. mole}^{-1}$ on a sample of unspecified purity. Vapor pressure measurements of M. Hoch, D. P. Dingley and H. L. Johnston, J. Am. Chem. Soc. 77, 304 (1955) lead to $-81 \text{ kcal. mole}^{-1}$ for the $\Delta H_f^0 \text{ 298.15}$ of ZrN. However, this value is uncertain by 10% as evidenced by the work on ZrO_2 by W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 25, 1207 (1957).

(I) $\text{ZrN(c)} + \text{O}_2(\text{g}) = \text{ZrO}_2(\text{c}) + 1/2 \text{ N}_2(\text{g})$

Heat Capacity and Entropy. Low temperature measurements, 53-297°K, of S. S. Todd, J. Am. Chem. Soc. 72, 2914 (1950), were smoothly joined to those of J. P. Coughlin and E. G. Kings, J. Am. Chem. Soc. 72, 2282 (1950), 298-1075°K.

Melting. Estimated by C. B. Henderson and R. S. Scheffer, Atlantic Research Corp., Alexandria, Va., "Survey of Thermochemical Data", January, 1960.

NZr

Monozirconium Mononitride (ZrN)
(Liquid) Mol. Wt. = 105.228

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0								
100	9.666	14.499	14.499	.000	-	64.332	47.155	
200	9.693	14.939	14.939	.014	-	64.300	46.840	
300	10.687	17.906	15.294	1.045	-	62.576	34.188	
400	11.252	20.356	14.069	2.144	-	60.867	26.604	
500	11.630	22.488	14.961	3.289	-	59.174	21.553	
600	11.935	24.259	15.777	4.487	-	57.504	17.920	
700	12.175	25.668	16.467	5.733	-	55.832	15.252	
800	12.360	26.731	17.047	6.902	-	54.179	13.156	
900	12.498	27.563	17.521	8.015	-	52.539	11.482	
1000	12.606	28.100	17.898	9.083	-	50.910	10.114	
1100	12.688	28.466	18.173	10.113	-	49.293	9.048	
1200	12.747	28.666	18.359	11.113	-	47.686	8.268	
1300	12.787	28.766	18.462	12.082	-	46.098	7.760	
1400	12.814	28.796	18.492	13.026	-	44.528	7.439	
1500	12.831	28.766	18.436	13.946	-	42.986	7.260	
1600	12.839	28.666	18.300	14.842	-	41.472	7.210	
1700	12.839	28.466	18.083	15.713	-	40.000	7.260	
1800	12.831	28.173	17.787	16.559	-	38.572	7.439	
1900	12.806	27.798	17.413	17.382	-	37.195	7.760	
2000	12.766	27.346	16.966	18.182	-	35.868	8.268	
2100	12.700	26.819	16.449	18.956	-	34.590	8.910	
2200	12.609	26.219	15.869	19.704	-	33.362	9.700	
2300	12.498	25.546	15.131	20.426	-	32.184	10.640	
2400	12.360	24.798	14.336	21.122	-	31.056	11.740	
2500	12.198	23.976	13.482	21.794	-	30.000	12.990	
2600	12.015	23.082	12.588	22.442	-	29.010	14.390	
2700	11.811	22.126	11.646	23.066	-	28.086	15.940	
2800	11.586	21.106	10.666	23.666	-	27.226	17.640	
2900	11.341	20.026	9.646	24.242	-	26.430	19.490	
3000	11.076	18.886	8.586	24.786	-	25.690	21.500	
3100	10.800	17.686	7.486	25.296	-	25.010	23.670	
3200	10.515	16.426	6.346	25.776	-	24.390	25.990	
3300	10.220	15.106	5.166	26.226	-	23.820	28.460	
3400	9.915	13.726	3.946	26.646	-	23.300	31.080	
3500	9.600	12.286	2.686	27.036	-	22.820	33.850	
3600	9.275	10.786	1.386	27.396	-	22.380	36.770	
3700	8.940	9.226	0.046	27.726	-	21.980	39.840	
3800	8.595	7.606	-0.346	28.026	-	21.620	43.060	
3900	8.240	5.926	-0.746	28.296	-	21.290	46.440	
4000	7.875	4.186	-1.156	28.536	-	21.000	50.000	
4100	7.500	2.386	-1.576	28.746	-	20.740	53.740	
4200	7.115	5.526	-1.996	28.926	-	20.510	57.660	
4300	6.720	8.606	-2.416	29.076	-	20.310	61.760	
4400	6.315	11.626	-2.836	29.206	-	20.140	66.040	
4500	5.900	14.586	-3.256	29.316	-	20.000	70.580	
4600	5.475	17.486	-3.676	29.406	-	19.890	75.380	
4700	5.040	20.326	-4.096	29.476	-	19.800	80.440	
4800	4.595	23.106	-4.516	29.526	-	19.730	85.760	
4900	4.140	25.826	-4.936	29.556	-	19.680	91.340	
5000	3.675	28.486	-5.356	29.566	-	19.650	97.180	
5100	3.200	31.086	-5.776	29.556	-	19.640	103.280	
5200	2.715	33.626	-6.196	29.526	-	19.650	109.640	
5300	2.220	36.106	-6.616	29.476	-	19.680	116.260	
5400	1.715	38.526	-7.036	29.406	-	19.730	123.140	
5500	1.200	40.886	-7.456	29.316	-	19.800	130.280	
5600	0.675	43.186	-7.876	29.206	-	19.890	137.680	
5700	0.140	45.426	-8.296	29.076	-	19.990	145.340	
5800	-0.405	47.606	-8.716	28.926	-	20.100	153.260	
5900	-0.940	49.726	-9.136	28.746	-	20.220	161.440	
6000	-1.465	51.786	-9.556	28.536	-	20.350	169.880	

June 30, 1961

MONOZIRCONIUM MONONITRIDE (ZrN) (Liquid)

Mol. Wt. = 105.228
ΔH_f^o 298.15 = [-59.5] cal. deg.⁻¹ mole⁻¹
T_m = [3225]°K
ΔH_m^o = [16.1] kcal. mole⁻¹

Heat of Formation. Calculated from the solid.

Entropy. Calculated from the solid.

Heat Capacity. The heat capacity function of the solid was assumed to approximate those of the liquid up to the estimated glass point of 2150°K. Above the glass point the heat capacity was estimated.

Monozirconium Mononitride (ZrN)

(Ideal Gas) Mol. Wt. = 105.228

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	4.000	INFINITE	-	2.118	169.418	169.418	INFINITE
100	6.999	47.924	-	1.423	169.770	166.877	- 364.691
200	7.141	52.851	56.448	0.721	170.121	165.849	- 179.037
298	7.567	55.780	55.780	0.000	170.500	165.468	- 119.820
300	7.575	55.827	55.780	0.014	170.497	163.425	- 119.049
400	7.965	58.062	56.082	0.792	170.291	161.098	- 88.016
500	8.243	59.871	56.665	1.603	170.080	158.824	- 69.419
600	8.434	61.392	57.329	2.438	169.854	156.594	- 57.037
700	8.553	62.653	57.860	3.246	169.626	154.404	- 46.860
800	8.664	63.653	58.666	4.150	169.398	152.246	- 41.590
900	8.736	64.478	59.300	5.020	169.114	150.122	- 36.453
1000	8.791	65.002	59.905	5.897	168.849	148.026	- 32.350
1100	8.835	65.642	60.480	6.778	168.566	145.956	- 28.997
1200	8.869	66.372	61.022	7.652	168.272	143.902	- 26.262
1300	8.901	66.123	61.565	8.552	167.922	142.027	- 23.876
1400	8.926	66.784	62.039	9.443	167.521	140.115	- 21.872
1500	8.948	69.400	62.509	10.337	166.412	138.226	- 20.138
1600	8.968	69.978	62.958	11.233	166.095	136.359	- 18.625
1700	8.985	70.525	63.385	12.130	165.738	134.500	- 17.260
1800	9.001	71.037	63.798	13.030	165.336	132.680	- 16.109
1900	9.016	71.524	64.192	13.931	165.093	130.870	- 15.053
2000	9.029	71.986	64.570	14.833	164.872	129.077	- 14.104
2100	9.042	72.427	64.934	15.736	164.384	127.302	- 13.248
2200	9.054	72.841	65.282	16.647	163.826	125.546	- 12.481
2300	9.065	73.231	65.619	17.547	163.206	123.800	- 11.801
2400	9.076	73.637	65.948	18.454	162.559	122.070	- 11.173
2500	9.087	74.008	66.263	19.362	161.889	120.359	- 10.597
2600	9.097	74.364	66.568	20.271	161.166	118.766	- 10.067
2700	9.106	74.699	66.859	21.180	160.389	117.200	- 9.579
2800	9.116	75.039	67.139	22.093	159.562	115.689	- 9.123
2900	9.125	75.359	67.426	23.003	158.663	114.156	- 8.701
3000	9.135	75.669	67.696	23.918	157.693	112.609	- 8.309
3100	9.143	75.968	67.958	24.832	156.704	111.061	- 7.942
3200	9.151	76.259	68.213	25.746	155.685	109.510	- 7.600
3300	9.158	76.541	68.461	26.659	154.646	107.953	- 7.279
3400	9.170	76.814	68.703	27.579	153.567	106.393	- 6.977
3500	9.178	77.080	68.938	28.496	152.459	104.829	- 6.694
3600	9.186	77.339	69.168	29.414	151.310	103.264	- 6.427
3700	9.193	77.591	69.392	30.333	150.132	101.693	- 6.175
3800	9.203	77.831	69.609	31.252	148.926	100.118	- 5.936
3900	9.211	78.075	69.825	32.174	147.693	98.543	- 5.711
4000	9.219	78.308	70.034	33.095	146.434	96.960	- 5.497
4100	9.227	78.536	70.239	34.018	145.152	95.373	- 5.295
4200	9.233	78.759	70.439	34.943	143.848	93.786	- 5.105
4300	9.243	78.976	70.639	35.868	142.523	92.196	- 4.924
4400	9.251	79.188	70.827	36.789	141.179	90.603	- 4.744
4500	9.259	79.396	71.015	37.715	139.826	89.009	- 4.578
4600	9.266	79.600	71.200	38.641	138.454	87.416	- 4.420
4700	9.272	79.799	71.381	39.568	137.066	85.824	- 4.268
4800	9.279	79.993	71.559	40.496	135.663	84.233	- 4.126
4900	9.290	80.186	71.732	41.426	134.248	82.643	- 4.181
5000	9.297	80.374	71.903	42.354	132.823	81.053	- 4.170
5100	9.305	80.558	72.071	43.284	131.389	79.463	- 4.160
5200	9.310	80.739	72.236	44.215	129.946	77.873	- 4.151
5300	9.316	80.916	72.398	45.146	128.494	76.283	- 4.144
5400	9.328	81.091	72.558	46.079	127.033	74.693	- 4.136
5500	9.335	81.262	72.714	47.012	125.564	73.103	- 4.127
5600	9.340	81.430	72.868	47.946	124.089	71.513	- 4.120
5700	9.348	81.596	73.020	48.880	122.609	69.923	- 4.114
5800	9.356	81.766	73.176	49.814	121.124	68.333	- 4.108
5900	9.365	81.918	73.316	50.752	119.634	66.743	- 4.103
6000	9.373	82.076	73.461	51.689	118.139	65.153	- 4.098

June 30, 1963

MONOZIRCONIUM MONONITRIDE (ZrN)

(IDEAL GAS)

MOL. WT. = 105.228

Ground State Configuration [2 Σ] $\Delta H_f^o = [169.4] \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = [55.78] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^o = [170.5] \text{ kcal. mole}^{-1}$
 $S_{298.15}^o = [55.78] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Multiplicities

$$\frac{G_u}{G_l} \text{ cm.}^{-1} \quad \frac{G_u}{G_l} \quad \frac{G_u}{G_l}$$

$$\omega_e = [840] \text{ cm.}^{-1} \quad \omega_e^x = [5] \text{ cm.}^{-1} \quad \epsilon = 1$$

$$r_e = [1.83] \text{ \AA}$$

Heat of Formation.

ΔH_f^o was estimated as 170.7 kcal. mole⁻¹ by J. S. Gordon, AstroSystems International, Livingston, New Jersey, private communication, January 10, 1963. ΔH_f^o 298.15 was then calculated.

Heat Capacity and Entropy.

Molecular constants were estimated by J. S. Gordon, loc. cit. r_e was calculated from the relationship $r_e = (16.858778 / \mu^{1/2} B_e)^{1/2} \text{ \AA}$.

Nitrogen, Diatomic (N₂)
(Reference State - Ideal Gas) Mol. Wt. = 28.0134

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	ΔF _f ^o	Log K _p
0	•000	INFINITE	2.072	•000	•000	•000	•000
100	6.956	38.170	51.957	•000	•000	•000	•000
200	6.957	42.992	46.407	•000	•000	•000	•000
298	6.961	45.776	45.776	•000	•000	•000	•000
300	6.961	45.813	45.770	•013	•000	•000	•000
400	6.990	47.818	46.043	•710	•000	•000	•000
500	7.009	49.386	46.561	1.413	•000	•000	•000
600	7.106	50.685	47.163	2.125	•000	•000	•000
700	7.250	51.806	47.731	2.853	•000	•000	•000
800	7.512	52.798	48.303	3.596	•000	•000	•000
900	7.670	53.692	48.853	4.355	•000	•000	•000
1000	7.815	54.507	49.378	5.129	•000	•000	•000
1100	7.945	55.258	49.879	5.917	•000	•000	•000
1200	8.061	55.955	50.357	6.718	•000	•000	•000
1300	8.162	56.604	50.813	7.529	•000	•000	•000
1400	8.252	57.212	51.248	8.350	•000	•000	•000
1500	8.330	57.784	51.665	9.179	•000	•000	•000
1600	8.398	58.324	52.065	10.015	•000	•000	•000
1700	8.458	58.835	52.448	10.858	•000	•000	•000
1800	8.512	59.320	52.816	11.707	•000	•000	•000
1900	8.559	59.782	53.171	12.560	•000	•000	•000
2000	8.601	60.222	53.513	13.418	•000	•000	•000
2100	8.638	60.642	53.842	14.280	•000	•000	•000
2200	8.672	61.045	54.156	15.144	•000	•000	•000
2300	8.703	61.431	54.468	16.015	•000	•000	•000
2400	8.731	61.802	54.766	16.886	•000	•000	•000
2500	8.756	62.159	55.055	17.761	•000	•000	•000
2600	8.770	62.503	55.325	18.639	•000	•000	•000
2700	8.800	62.835	55.606	19.517	•000	•000	•000
2800	8.820	63.155	55.870	20.398	•000	•000	•000
2900	8.838	63.465	56.127	21.280	•000	•000	•000
3000	8.855	63.765	56.376	22.165	•000	•000	•000
3100	8.871	64.055	56.619	23.051	•000	•000	•000
3200	8.886	64.337	56.856	23.930	•000	•000	•000
3300	8.900	64.611	57.087	24.829	•000	•000	•000
3400	8.914	64.877	57.312	25.719	•000	•000	•000
3500	8.927	65.135	57.532	26.611	•000	•000	•000
3600	8.939	65.387	57.747	27.504	•000	•000	•000
3700	8.950	65.632	57.957	28.399	•000	•000	•000
3800	8.962	65.871	58.162	29.295	•000	•000	•000
3900	8.972	66.104	58.362	30.191	•000	•000	•000
4000	8.983	66.331	58.559	31.089	•000	•000	•000
4100	8.993	66.553	58.751	31.988	•000	•000	•000
4200	9.002	66.770	58.940	32.888	•000	•000	•000
4300	9.012	66.982	59.124	33.788	•000	•000	•000
4400	9.021	67.189	59.305	34.690	•000	•000	•000
4500	9.030	67.392	59.482	35.593	•000	•000	•000
4600	9.039	67.591	59.657	36.496	•000	•000	•000
4700	9.048	67.785	59.827	37.400	•000	•000	•000
4800	9.057	67.976	59.995	38.306	•000	•000	•000
4900	9.066	68.162	60.160	39.212	•000	•000	•000
5000	9.074	68.346	60.322	40.119	•000	•000	•000
5100	9.083	68.525	60.481	41.027	•000	•000	•000
5200	9.091	68.702	60.637	41.935	•000	•000	•000
5300	9.100	68.875	60.791	42.845	•000	•000	•000
5400	9.109	69.045	60.942	43.755	•000	•000	•000
5500	9.118	69.213	61.091	44.667	•000	•000	•000
5600	9.127	69.377	61.238	45.579	•000	•000	•000
5700	9.136	69.539	61.382	46.492	•000	•000	•000
5800	9.145	69.698	61.524	47.406	•000	•000	•000
5900	9.155	69.854	61.664	48.321	•000	•000	•000
6000	9.165	70.008	61.802	49.237	•000	•000	•000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

NITROGEN, DIATOMIC (N₂) (IDEAL GAS - REFERENCE STATE) MOL. WT. = 28.0134

Ground State Configuration $1 \sum^+ g$
 $\Delta H_f^o = 0$
 $S_{298.15}^o = 45.77 \pm 0.01$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^o 298.15 = 0$
 $\omega_e x_e = 14.059$ cm.⁻¹
 $\omega_e = 0.01791 \pm 0.0001$ cm.⁻¹
 $B_e = 1.9825$ cm.⁻¹
 $r_e = 1.08758 \pm 0.0001$ Å
 $\sigma^- = 2$

Heat of Formation.

The heat of formation (ΔH_f^o) for N₂(g) is zero at all temperatures by definition.

Heat Capacity and Entropy.

The functions adopted here are based on the direct summation calculations of L. Glatf, J. Beizer and H. L. Johnston, Ohio State Univ. Res. Found. Proj. 316, Report No. 9, 1953. They calculated the functions for N₂ by a direct summation using spectroscopic data given by G. Herzberg, "Diatomic Molecules", D. Van Nostrand Co., New York, 1950. The entropies were changed by -Ring to remove the effects of nuclear spin included by Glatf, Beizer, and Johnston, and by 0.012 for the difference in spectroscopic constants. J. A. Goff and S. Grotch, Trans. Am. Soc. Mech. Engrs., 72, 741 (1950), calculated a set of functions by a direct summation over the ground state levels only. Agreement with the functions of Glatf, Beizer, and Johnston is within 0.1%.

B. P. Stoicheff, Can. J. Phys. 32, 630 (1954), determined the spectroscopic constants of N₂ by combining his measured rotational spectra with the results of band spectra given in the literature. The constants listed above have been corrected to apply to the naturally occurring isotopic composition listed by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys., 30, 585 (1958).

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	7.015	∞	2.296	20.430	20.430	INFINITE
100	43.988	53.924	1.594	20.084	21.573	-47.145
200	43.988	52.108	0.869	19.766	23.354	-49.354
298	44.230	52.546	0.000	19.010	24.098	-49.248
300	44.230	52.546	0.017	19.008	24.098	-49.248
400	10.201	55.400	2.952	19.530	26.716	-44.596
500	10.953	57.761	5.051	18.520	28.514	-42.463
600	11.565	59.613	6.517	17.558	30.311	-41.040
700	12.070	61.035	8.260	16.623	32.097	-40.021
800	12.486	62.275	9.289	15.873	33.873	-39.253
900	12.830	63.476	10.519	15.280	35.638	-38.654
1000	13.113	64.639	11.960	14.820	37.391	-38.171
1100	13.348	65.779	13.620	14.460	39.132	-37.774
1200	13.544	66.895	15.547	14.180	40.863	-37.442
1300	13.707	67.990	17.764	13.977	42.583	-37.168
1400	13.845	69.069	20.279	13.820	44.293	-36.944
1500	13.961	70.137	23.038	13.700	45.996	-36.761
1600	14.060	71.195	26.040	13.610	47.691	-36.614
1700	14.145	72.245	29.293	13.540	49.377	-36.507
1800	14.218	73.285	32.797	13.480	51.054	-36.428
1900	14.282	74.315	36.553	13.430	52.728	-36.365
2000	14.337	75.337	40.569	13.390	54.399	-36.314
2100	14.385	76.351	44.837	13.360	56.064	-36.272
2200	14.428	77.359	49.360	13.330	57.721	-36.239
2300	14.466	78.362	54.137	13.300	59.371	-36.212
2400	14.499	79.360	59.169	13.270	61.014	-36.189
2500	14.529	80.353	64.456	13.240	62.650	-36.169
2600	14.556	81.342	69.999	13.210	64.282	-36.150
2700	14.580	82.327	75.797	13.180	65.911	-36.132
2800	14.602	83.308	81.850	13.150	67.537	-36.114
2900	14.621	84.285	88.169	13.120	69.160	-36.096
3000	14.639	85.258	94.752	13.090	70.781	-36.078
3100	14.655	86.227	101.609	13.060	72.399	-36.060
3200	14.670	87.192	108.746	13.030	74.014	-36.042
3300	14.684	88.153	116.164	13.000	75.626	-36.024
3400	14.696	89.110	123.871	12.970	77.235	-36.006
3500	14.707	90.063	131.866	12.940	78.841	-35.988
3600	14.718	91.013	140.150	12.910	80.444	-35.970
3700	14.727	91.960	148.723	12.880	82.043	-35.952
3800	14.736	92.904	157.585	12.850	83.639	-35.934
3900	14.745	93.845	166.736	12.820	85.232	-35.916
4000	14.752	94.783	176.176	12.790	86.822	-35.898
4100	14.760	95.718	185.905	12.760	88.409	-35.880
4200	14.766	96.650	195.924	12.730	90.000	-35.862
4300	14.772	97.579	206.233	12.700	91.591	-35.844
4400	14.778	98.505	216.832	12.670	93.179	-35.826
4500	14.784	99.428	227.721	12.640	94.764	-35.808
4600	14.789	100.348	238.900	12.610	96.347	-35.790
4700	14.794	101.265	250.369	12.580	97.927	-35.772
4800	14.798	102.179	262.128	12.550	99.504	-35.754
4900	14.802	103.090	274.176	12.520	101.079	-35.736
5000	14.806	104.000	286.514	12.490	102.651	-35.718
5100	14.810	104.900	299.142	12.460	104.221	-35.700
5200	14.814	105.800	312.060	12.430	105.789	-35.682
5300	14.817	106.699	325.269	12.400	107.354	-35.664
5400	14.820	107.596	338.769	12.370	108.916	-35.646
5500	14.823	108.490	352.560	12.340	110.475	-35.628
5600	14.826	109.381	366.642	12.310	112.031	-35.610
5700	14.829	110.269	380.916	12.280	113.584	-35.592
5800	14.831	111.154	395.383	12.250	115.134	-35.574
5900	14.834	112.037	410.044	12.220	116.681	-35.556
6000	14.836	112.917	424.899	12.190	118.225	-35.538

Dec. 31, 1960; Dec. 31, 1964

DINITROGEN MONOXIDE (N₂O)

(IDEAL GAS)

MOL. WT. = 44.016

$$\Delta H_f^o = 20.43 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta F_f^o = 19.61 \pm 0.1 \text{ kcal. mole}^{-1}$$

Dinitrogen Trioxide (N₂O₃)
(Ideal Gas) Mol. Wt. = 76.016

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	10.247	59.000	0.000	20.501	24.641	- 53.850
100	10.247	59.286	2.659	20.501	24.641	- 53.850
200	10.247	59.571	5.318	20.501	24.641	- 53.850
298	10.247	59.857	7.987	20.501	24.641	- 53.850
300	10.247	59.857	8.000	20.501	24.641	- 53.850
400	17.365	74.771	1.687	19.707	24.641	- 53.850
500	18.751	82.801	5.406	19.707	24.641	- 53.850
600	19.821	89.316	9.274	19.707	24.641	- 53.850
700	20.693	94.939	13.193	19.707	24.641	- 53.850
800	21.386	99.249	16.263	19.707	24.641	- 53.850
900	21.937	102.601	18.774	19.707	24.641	- 53.850
1000	22.376	105.136	20.801	19.707	24.641	- 53.850
1100	22.729	107.286	22.461	19.707	24.641	- 53.850
1200	23.015	109.127	23.801	19.707	24.641	- 53.850
1300	23.250	110.699	24.961	19.707	24.641	- 53.850
1400	23.444	112.059	25.981	19.707	24.641	- 53.850
1500	23.606	113.252	26.891	19.707	24.641	- 53.850
1600	23.742	114.316	27.701	19.707	24.641	- 53.850
1700	23.857	115.266	28.431	19.707	24.641	- 53.850
1800	23.956	116.119	29.091	19.707	24.641	- 53.850
1900	24.041	116.886	29.691	19.707	24.641	- 53.850
2000	24.114	117.576	30.241	19.707	24.641	- 53.850
2100	24.178	118.201	30.751	19.707	24.641	- 53.850
2200	24.234	118.771	31.221	19.707	24.641	- 53.850
2300	24.283	119.296	31.651	19.707	24.641	- 53.850
2400	24.327	119.776	32.051	19.707	24.641	- 53.850
2500	24.366	120.216	32.421	19.707	24.641	- 53.850
2600	24.400	120.616	32.771	19.707	24.641	- 53.850
2700	24.431	120.976	33.101	19.707	24.641	- 53.850
2800	24.459	121.306	33.411	19.707	24.641	- 53.850
2900	24.484	121.606	33.691	19.707	24.641	- 53.850
3000	24.507	121.876	33.951	19.707	24.641	- 53.850
3100	24.527	122.116	34.191	19.707	24.641	- 53.850
3200	24.546	122.326	34.411	19.707	24.641	- 53.850
3300	24.563	122.506	34.611	19.707	24.641	- 53.850
3400	24.579	122.656	34.791	19.707	24.641	- 53.850
3500	24.594	122.786	34.951	19.707	24.641	- 53.850
3600	24.607	122.896	35.091	19.707	24.641	- 53.850
3700	24.619	122.976	35.211	19.707	24.641	- 53.850
3800	24.630	123.026	35.321	19.707	24.641	- 53.850
3900	24.641	123.056	35.421	19.707	24.641	- 53.850
4000	24.651	123.076	35.511	19.707	24.641	- 53.850
4100	24.660	123.096	35.591	19.707	24.641	- 53.850
4200	24.668	123.116	35.661	19.707	24.641	- 53.850
4300	24.676	123.136	35.731	19.707	24.641	- 53.850
4400	24.683	123.156	35.791	19.707	24.641	- 53.850
4500	24.690	123.176	35.851	19.707	24.641	- 53.850
4600	24.696	123.196	35.911	19.707	24.641	- 53.850
4700	24.702	123.216	35.971	19.707	24.641	- 53.850
4800	24.708	123.236	36.031	19.707	24.641	- 53.850
4900	24.713	123.256	36.091	19.707	24.641	- 53.850
5000	24.718	123.276	36.151	19.707	24.641	- 53.850
5100	24.723	123.296	36.211	19.707	24.641	- 53.850
5200	24.728	123.316	36.271	19.707	24.641	- 53.850
5300	24.732	123.336	36.331	19.707	24.641	- 53.850
5400	24.736	123.356	36.391	19.707	24.641	- 53.850
5500	24.739	123.376	36.451	19.707	24.641	- 53.850
5600	24.743	123.396	36.511	19.707	24.641	- 53.850
5700	24.746	123.416	36.571	19.707	24.641	- 53.850
5800	24.749	123.436	36.631	19.707	24.641	- 53.850
5900	24.753	123.456	36.691	19.707	24.641	- 53.850
6000	24.756	123.476	36.751	19.707	24.641	- 53.850

Dec. 31, 1960; Sept. 30, 1963; Dec. 31, 1964

DINITROGEN TRIOXIDE (N₂O₃) (IDEAL GAS)

MOL. WT. = 76.016

Point Group C_{3v}

S_{298.15} = 73.91 ± 0.5 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

(ω, cm. ⁻¹)	(ω, cm. ⁻¹)	(ω, cm. ⁻¹)
1863 (1)	783 (1)	313 (1)
1589 (1)	627 (1)	253 (1)
1297 (1)	407 (1)	[Rotation]

Bond Distances N-N = 2.08 Å N-O (nitroso) = 1.12 Å N-O (nitro) = 1.18 Å

Bond Angles O-N-N (nitroso) = 110° O-N-O = 134°

Product of Moments of Inertia I_AI_BI_C = 4.6201 X 10⁻¹¹⁴ g.³ cm.⁶

Heat of Formation.

Equilibria for the reaction N₂O₃(g) → NO(g) + NO₂(g) have been studied by Beattie and Bell, J. Chem. Soc. 1957, 1681 (1957), Verhoek and Daniels, J. Am. Chem. Soc. 53, 1250 (1931) and Abel and Proia, Z. Elektrochem. 35, 712 (1929).

The results of Beattie and Bell are the most extensive, but they depend on the early analysis of Glaue and Kemp, J. Chem. Phys. 2, 40 (1938), for the simultaneous equilibrium N₂O₄(g) → 2NO₂(g). The JANAF analysis of the tetroxide dissociation has been used to recalculate the data of Beattie and Bell. Non-ideality of N₂O₄ and NO₂ was allowed for by use of the equations of state of Glaue and Kemp, while non-ideality of NO and N₂O₃ was removed by extrapolation of the equilibrium constants to zero pressure in a manner similar to that of Beattie and Bell. The data of Verhoek and Daniels and of Abel and Proia have not been recalculated. Second and third law analyses of the results are summarized below. The heat of formation was obtained from ΔH_f⁰ 298 = 9.70 kcal. mole⁻¹.

Source	Temp. Range °K.	T °K.	Third Law ΔS _T (cal. deg. ⁻¹ mole ⁻¹)	Second Law ΔS ₂₉₈ (kcal. mole ⁻¹)	Third Law ΔH _f ⁰ 298 (kcal. mole ⁻¹)
Beattie - Bell ^a	278 - 318	298	—	33.25 ± 0.35	9.527 ± 0.096
Beattie - Bell ^b	278 - 318	298	33.77	33.04 ± 0.31	9.476 ± 0.093
Beattie - Bell ^c	278 - 318	298	33.77	33.56 ± 0.52	9.642 ± 0.155
Verhoek - Daniels	298 - 318	308	33.78	38.8 ± 1.9	11.1 ± 0.6
Abel - Proia	281 - 308	294	33.77	32.9	9.60

a) Given by authors

b) From author's K_p values

c) From recalculated K_p values

Heat Capacity and Entropy.

The functions are similar to those calculated by I. C. Hirst, J. Phys. Chem. 65, 2249 (1961), based on the analysis of Devlin and Hirst, Spectrochim. Acta 17, 218 (1961), of the Raman and infrared spectra in terms of Urey - Bradley force constants. Devlin and Hirst used observed isotopic shifts in the spectra along with force constants transferred from nitrogen oxides and oxyhalides in order to select the N-N bond distance and the O-N-N bond angle.

The unobserved mode was assumed to be free internal rotation around the N-N bond, leading to S₂₉₈ = 73.91 cal. deg.⁻¹ mole⁻¹ which is in good agreement with 74.15 ± 0.52 cal. deg.⁻¹ mole⁻¹ obtained from the recalculated second law of Beattie and Bell. The principal moments of inertia are I_A = 22.694 X 10⁻³⁹, I_B = 29.577 X 10⁻³⁹, and I_C = 6.883 X 10⁻³⁹ g. cm.², while the reduced moment for internal rotation was calculated as I_r = 0.990 X 10⁻³⁹ g. cm.².

Dinitrogen Tetroxide (N₂O₄)
(Crystal) Mol. Wt. = 92.016



MOL. WT. = 92.016

(CRYSTAL)

DINITROGEN TETROXIDE (N₂O₄)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	5.112	7.263	7.263	INFINITE
100	14.508	13.415	4.339	8.601	2.174	4.750
200	21.917	18.353	2.508	8.693	13.095	14.300
298	29.103	35.820	0.000	8.693	23.185	17.434
300	29.320	36.101	0.054	8.358	23.984	17.471
400	36.720	45.648	3.390	7.141	34.600	18.904
500	40.000	54.271	7.261	5.435	44.844	19.600

$$\Delta H_f^0 = -7.263 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = -8.375 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = 3.502 \pm 0.003 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 35.92 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 261.95 \pm 0.05^\circ \text{K.}$$

Heat of Formation.

The heat of formation was back calculated from that of the liquid using the measured heat of melting and the enthalpy of the crystal and liquid.

Heat Capacity and Entropy.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) measured the low temperature heat capacity from 15-295°K. The entropy was obtained by integration of this data using $S_{15} = 0.34 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The temperature and heat of melting were also measured by Giauque and Kemp, loc. cit.



Dinitrogen Tetroxide (N_2O_4)
(Liquid) Mol. Wt. = 92.016

N_2O_4
MOL. WT. = 92.016

DINITROGEN TETROXIDE (N_2O_4) (LIQUID)

T, °K.	C_p°	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S^\circ - (F^\circ - H_{298}^\circ)/T}$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _f
0	0.000	INFINITE	6.034	4.488	-	INFINITE
100	26.980	17.417	6.034	6.599	3.775	8.249
200	30.560	17.417	6.034	2.759	3.296	13.446
298	34.060	17.417	6.034	4.488	2.346	17.065
300	34.140	50.218	50.008	4.652	23.455	17.086
400	38.440	60.628	51.598	3.692	32.607	17.615
500	42.740	68.668	54.165	3.142	41.333	18.066

$\Delta H_f^\circ = -4.488 \pm 0.4 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -4.676 \pm 0.4 \text{ kcal. mole}^{-1}$
 $\Delta H_m^\circ = 3.502 \pm 0.003 \text{ kcal. mole}^{-1}$
 $\Delta H_v^\circ = 9.11 \pm 0.1 \text{ kcal. mole}^{-1} \text{ (to } N_2O_4 + NO_2)$
 $\Delta H_v^\circ = [6.79] \text{ kcal. mole}^{-1} \text{ (to } N_2O_4)$

$S_{298.15}^\circ = 50.007 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 261.95 \pm 0.05^\circ K.$
 $T_b = 294.25^\circ K. \text{ (to } N_2O_4 + NO_2)$
 $T_b = [301.4^\circ K.] \text{ (to } N_2O_4)$

Heat of Formation.

The heat of formation was back calculated from that of the gas using the calorimetrically measured heat of vaporization to the equilibrium mixture, in conjunction with a dissociation constant $\alpha_c = 0.161$.

Heat Capacity and Entropy.

W. F. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) measured the low temperature heat capacity from 15° to $295^\circ K.$, above $295^\circ K.$ the heat capacity was smoothly extrapolated.

Melting and Vaporization Data.

Giauque and Kemp, loc. cit. measured the temperature and heat of melting and also the boiling point and the calorimetric value of the heat of vaporization to the equilibrium mixture. The heat of vaporization to a hypothetical pure N_2O_4 gas at $294.25^\circ K.$ was calculated to be $6.91 \text{ kcal. mole}^{-1}$.

N_2O_4

Dinitrogen Tetroxide (N₂O₄)
(Ideal Gas) Mol. Wt. = 92.016

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg. ⁻¹	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	-	3.919	4.473	INFINITE	4.473	INFINITE
100	11.77	57.39	96.759	2.762	3.319	9.721	9.721	-21.244
200	13.107	68.017	88.461	2.462	2.860	13.654	13.654	-17.110
298	18.465	72.724	72.724	0.000	0.000	23.395	23.395	-17.110
300	18.520	72.836	72.724	0.034	2.165	23.406	23.406	-17.109
400	21.157	75.484	75.484	2.023	30.619	30.619	30.619	-16.728
500	23.233	83.496	75.002	4.247	2.094	37.761	37.761	-16.505
600	24.860	87.881	76.790	6.655	2.280	44.880	44.880	-16.347
700	26.127	91.813	78.650	9.207	2.548	51.959	51.959	-16.222
800	27.113	95.369	80.530	11.871	2.873	58.994	58.994	-16.116
900	27.884	98.609	82.361	14.623	3.238	65.988	65.988	-16.023
1000	28.492	101.579	84.137	17.443	3.630	72.942	72.942	-15.941
1100	28.977	104.318	85.848	20.317	4.038	79.852	79.852	-15.864
1200	29.367	106.857	87.495	23.235	4.459	86.726	86.726	-15.794
1300	29.684	109.221	89.076	26.188	4.887	93.564	93.564	-15.729
1400	29.946	111.430	90.595	29.170	5.320	100.369	100.369	-15.667
1500	30.163	113.504	92.054	32.176	5.755	107.143	107.143	-15.610
1600	30.345	115.457	93.466	35.201	6.190	113.888	113.888	-15.556
1700	30.499	117.301	94.805	38.244	6.626	120.607	120.607	-15.504
1800	30.630	119.048	96.104	41.300	7.055	127.299	127.299	-15.455
1900	30.743	120.707	97.355	44.369	7.481	133.970	133.970	-15.409
2000	30.840	122.287	98.563	47.448	7.902	140.612	140.612	-15.365
2100	30.925	123.794	99.728	50.537	8.319	147.238	147.238	-15.323
2200	30.999	125.234	100.855	53.633	8.725	153.843	153.843	-15.282
2300	31.064	126.613	101.945	56.736	9.127	160.430	160.430	-15.244
2400	31.121	127.937	103.001	59.845	9.521	167.002	167.002	-15.207
2500	31.172	129.208	104.024	62.960	9.905	173.553	173.553	-15.171
2600	31.218	130.432	105.016	66.080	10.284	180.092	180.092	-15.137
2700	31.259	131.611	105.980	69.204	10.653	186.617	186.617	-15.105
2800	31.295	132.748	106.915	72.331	11.013	193.128	193.128	-15.074
2900	31.329	133.847	107.825	75.463	11.367	199.629	199.629	-15.044
3000	31.358	134.906	108.710	78.597	11.710	206.116	206.116	-15.015
3100	31.386	135.938	109.572	81.734	12.047	212.589	212.589	-14.987
3200	31.410	136.935	110.412	84.874	12.375	219.050	219.050	-14.960
3300	31.433	137.902	111.230	88.016	12.695	225.502	225.502	-14.934
3400	31.454	138.841	112.029	91.161	13.008	231.947	231.947	-14.909
3500	31.473	139.753	112.808	94.307	13.314	238.378	238.378	-14.884
3600	31.490	140.639	113.569	97.455	13.612	244.811	244.811	-14.861
3700	31.506	141.502	114.312	100.605	13.904	251.229	251.229	-14.839
3800	31.521	142.343	115.039	103.756	14.189	257.640	257.640	-14.817
3900	31.535	143.162	115.749	106.909	14.470	264.039	264.039	-14.796
4000	31.547	143.960	116.445	110.063	14.742	270.434	270.434	-14.775
4100	31.559	144.730	117.125	113.218	15.008	276.826	276.826	-14.755
4200	31.570	145.500	117.782	116.375	15.271	283.206	283.206	-14.736
4300	31.580	146.243	118.445	119.532	15.528	289.589	289.589	-14.718
4400	31.590	146.969	119.085	122.691	15.779	295.953	295.953	-14.699
4500	31.599	147.679	119.713	125.850	16.025	302.320	302.320	-14.682
4600	31.607	148.376	120.328	129.011	16.269	308.686	308.686	-14.665
4700	31.615	149.054	120.932	132.172	16.506	315.036	315.036	-14.648
4800	31.623	149.719	121.525	135.334	16.740	321.391	321.391	-14.633
4900	31.630	150.371	122.107	138.496	16.970	327.723	327.723	-14.616
5000	31.636	151.011	122.679	141.660	17.197	334.062	334.062	-14.601
5100	31.642	151.637	123.240	144.824	17.419	340.402	340.402	-14.586
5200	31.648	152.252	123.792	147.988	17.639	346.726	346.726	-14.572
5300	31.654	152.854	124.335	151.153	17.856	353.055	353.055	-14.558
5400	31.659	153.446	124.869	154.319	18.070	359.377	359.377	-14.544
5500	31.664	154.027	125.394	157.485	18.282	365.706	365.706	-14.531
5600	31.668	154.598	125.910	160.652	18.489	372.011	372.011	-14.518
5700	31.673	155.158	126.418	163.819	18.695	378.325	378.325	-14.505
5800	31.677	155.709	126.918	166.986	18.898	384.640	384.640	-14.493
5900	31.681	156.251	127.411	170.154	19.099	390.935	390.935	-14.480
6000	31.685	156.783	127.896	173.322	19.297	397.243	397.243	-14.469

Dec. 31, 1960; June 30, 1961; Sept. 30, 1964

DINITROGEN TETROXIDE (N₂O₄) (IDEAL GAS)

MOL. WT. = 92.016

Point Group V_h ΔH_f^o = 4.47 ± 0.4 kcal. mole⁻¹

S_{298.15} = 72.72 cal. deg.⁻¹ mole⁻¹ ΔH_f^o 298.15 = 2.17 ± 0.4 kcal. mole⁻¹

Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies
ω_g, cm.⁻¹ ω_u, cm.⁻¹ (ω_g, cm.⁻¹)

1373 (1) 1710 (1) 1748 (1)
823 (1) 480 (1) 385 (1)
260 (1) 430 (1) 1281 (1)
[50](1) 675 (1) 750 (1)

Bond Distances: N-N = 1.750 Å N-O = 1.180 Å

Bond Angles: O-N-O = 133.7°

Product of the Moments of Inertia: I_AI_BI_C = 9.9304 X 10⁻¹¹⁴ g.³ cm.⁶

σ = 4

Heat of Formation.

W. P. Giauque and J. D. Kemp, J. Chem. Phys. 6, 40 (1938) calculated idealized equilibrium constants for the reaction N₂O₄(g) = 2NO₂(g) from the work of Bodenstein and Bode (1), Zeits. fur physik. Chem. 100, 75 (1922), Verboek and Daniels (2), J. Am. Chem. Soc. 53, 1250 (1931) and Woutzel (3), Compt. Rend. 169, 1397 (1919). The second and third law analysis of these equilibrium constants has been reported using more recent functions. The results are shown below.

Ref.	Third Law ΔH ₂₉₈	Second Law ΔH ₂₉₈
1.	13.644	13.634 ± 0.015*
2.	13.672	14.429 ± 0.126
3.	13.657	13.599 ± 0.019**

* Ten points rejected because of statistically significant scatter.

** One point rejected.

The second law value of Verboek and Daniels was not considered significant due to the extremely small temperature range and the use of only three temperatures. The adopted value was 13.65 ± 0.03 kcal. which leads to 2.17 kcal. mole⁻¹ for the heat of formation of N₂O₄(g).

Heat Capacity and Entropy.

The structural parameters were taken from the electron diffraction measurements of D. W. Smith and K. Hedberg, J. Chem. Phys. 25, 1282 (1956). The vibrational frequencies are those chosen by I. C. Hataatune, J. P. Devlin and Y. Wada, J. Chem. Phys. 33, 714 (1960). The torsional frequency of 50 cm.⁻¹ was estimated in order to bring the entropy of the gas into agreement with that determined by Giauque and Kemp loc. cit. From low temperature heat capacities and heats of fusion and vaporization. The individual moments of inertia were I_A = 12.508 X 10⁻³⁹ g. cm.², I_B = 22.809 X 10⁻³⁹ g. cm.², and I_C = 35.117 X 10⁻³⁹ g. cm.²

N₂O₄

Point group C_{2v} $\Delta F_f^0 = \text{Unknown}$ $S_{298.15}^\circ = 82.8 \pm 1.0 \text{ cal. deg. mole}^{-1}$ $\Delta H_f^\circ = 298.15 = 2.7 \pm 0.3 \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = 1

Dinitrogen Pentoxide (N₂O₅)
(Ideal Gas) Mol. Wt. = 108.016

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0							
100	18.691	74.506	84.772	-2.053	3.036	19.848	-21.688
200	23.017	87.801	87.801	.000	2.700	28.186	-20.660
300	23.089	82.944	82.801	.043	2.697	28.343	-20.647
400	24.494	90.077	83.751	.243	2.710	36.898	-20.159
500	28.965	96.270	85.649	5.311	2.960	45.421	-19.852
600	30.684	101.713	87.882	8.298	3.348	53.979	-19.624
700	31.971	106.856	90.210	11.431	4.808	62.594	-19.450
800	32.921	111.657	92.431	14.431	6.259	71.259	-19.315
900	33.365	114.750	94.782	17.971	7.634	79.834	-19.163
1000	33.806	118.280	96.958	21.331	8.934	88.332	-19.020
1100	34.137	121.527	99.047	24.728	9.846	95.176	-18.909
1200	34.412	124.456	101.096	28.077	10.375	101.335	-18.808
1300	34.612	127.271	103.096	31.407	10.845	106.810	-18.716
1400	34.782	129.882	104.787	34.677	11.250	111.650	-18.631
1500	34.913	132.246	106.558	38.562	7.818	117.335	-18.552
1600	35.027	134.503	108.216	42.000	8.287	122.849	-18.479
1700	35.117	136.558	109.857	45.266	8.786	128.193	-18.410
1800	35.177	138.459	111.485	48.366	9.186	133.373	-18.346
1900	35.232	140.552	112.857	52.601	9.619	138.403	-18.286
2000	35.302	142.351	114.287	56.129	10.038	143.283	-18.229
2100	35.336	144.074	115.664	59.660	10.445	148.061	-18.176
2200	35.398	145.729	116.993	63.196	10.835	152.740	-18.126
2300	35.428	147.292	118.278	66.725	11.210	157.263	-18.079
2400	35.428	148.779	119.518	70.275	11.570	161.643	-18.033
2500	35.455	150.246	120.718	73.820	11.929	165.893	-17.990
2600	35.480	151.637	121.881	77.366	12.268	170.025	-17.950
2700	35.480	152.968	123.008	80.916	12.594	174.041	-17.911
2800	35.526	154.249	124.093	84.466	12.908	177.946	-17.873
2900	35.546	155.513	125.143	88.021	13.208	181.746	-17.839
3000	35.565	156.720	126.165	91.576	13.496	185.446	-17.806
3100	35.576	157.886	127.168	95.133	13.775	189.046	-17.774
3200	35.587	159.016	128.175	98.692	14.040	192.546	-17.743
3300	35.597	160.114	129.153	102.251	14.290	195.946	-17.713
3400	35.607	161.174	130.103	105.811	14.537	199.246	-17.686
3500	35.617	162.206	130.957	109.372	14.771	202.446	-17.658
3600	35.625	163.209	131.819	112.944	14.994	205.546	-17.633
3700	35.634	164.185	132.690	116.516	15.206	208.546	-17.609
3800	35.642	165.135	133.540	120.091	15.416	211.446	-17.585
3900	35.649	166.061	134.362	123.676	15.612	214.246	-17.562
4000	35.656	166.964	135.166	127.161	15.799	216.946	-17.539
4100	35.661	167.844	135.953	130.757	15.979	219.546	-17.518
4200	35.666	168.704	136.723	134.323	16.153	222.046	-17.498
4300	35.670	169.544	137.477	137.874	16.320	224.446	-17.479
4400	35.676	170.363	138.214	141.457	16.477	226.746	-17.461
4500	35.680	171.165	138.937	145.025	16.630	228.946	-17.441
4600	35.684	171.949	139.646	148.593	16.777	231.046	-17.422
4700	35.689	172.710	140.342	152.162	16.917	233.046	-17.403
4800	35.692	173.450	141.026	155.730	17.050	234.946	-17.385
4900	35.696	174.203	141.693	159.300	17.178	236.746	-17.367
5000	35.699	174.924	142.330	162.870	17.309	238.446	-17.350
5100	35.702	175.631	142.996	166.440	17.428	240.046	-17.334
5200	35.708	176.324	143.650	170.011	17.546	241.546	-17.318
5300	35.713	176.997	144.296	173.582	17.657	242.946	-17.302
5400	35.717	177.671	144.866	177.152	17.767	244.246	-17.287
5500	35.713	178.326	145.466	180.723	17.874	245.446	-17.270
5600	35.715	178.970	146.090	184.295	17.973	246.546	-17.254
5700	35.719	179.604	146.740	187.867	18.072	247.546	-17.239
5800	35.721	180.237	147.417	191.439	18.169	248.446	-17.224
5900	35.721	180.834	147.781	195.010	18.259	249.246	-17.210
6000	35.722	181.434	148.337	198.582	18.348	250.046	-17.200

Dec. 31, 1960; Dec. 31, 1964

Vibrational Frequencies and Degeneracies

ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹	ω , cm. ⁻¹
1728 (1)	614 (1)	[614] (1)	[Rotation]
1358 (1)	353 (1)	[Rotation]	1728 (1)
743 (1)	[85] (1)	577 (1)	1247 (1)
			353 (1)

Bond Distance: O-N = 1.21 Å

Bond Angle: O-N-O = 134°

N-O-N = 95°

O-N-O planes perpendicular to N-O-N plane

Product of the Moments of Inertia: $I_A I_B I_C = 2.066 \times 10^{-113} \text{ g.}^3 \text{ cm.}^6$ $\sigma = 2$

Heat of Formation.

The heat of formation was obtained by recalculation of the calorimetric data of Ray and Ogg for the reaction of $\text{N}_2\text{O}_5(\text{g})$ with NO. The stoichiometry of the reaction products, originally based on the results for $\text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2$ from Diaque and Kemp, J. Chem. Phys. 5, 40 (1938), was based on the JANAF analysis of this simultaneous equilibrium. A correction of 0.29 kcal. was made in the heat of reaction because of the additional formation of N_2O_3 from NO and NO_2 .

Confirmation of the heat of formation was obtained by combination of the heats of hydrolysis and sublimation of $\text{N}_2\text{O}_5(\text{c})$. The results are summarized below. Second law values are given for the heats of sublimation, but third law analyses suggest that the value from Russ and Pokorny is more reliable. Most of the uncertainty in this path, however, arises from the heat of hydrolysis.

Source	Method	Reaction	ΔH_f° 298.15 (kcal. mole ⁻¹)	ΔH_f° 298.15 (kcal. mole ⁻¹)
1	Calorimetric	$\text{N}_2\text{O}_5(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g}) + \text{NO}_2(\text{g}) + 1.138 \text{ N}_2\text{O}_4(\text{g})$	-16.05 ± 0.20	2.67
2	Calorimetric	$\text{N}_2\text{O}_5(\text{c}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{HNO}_3(\text{aq})$	-20.2 ± 0.5	—
3	Vapor Pressure	$\text{N}_2\text{O}_5(\text{c}) \rightarrow \text{N}_2\text{O}_5(\text{g})$	13.37 ± 0.06	2.79*
4	Vapor Pressure	$\text{N}_2\text{O}_5(\text{c}) \rightarrow \text{N}_2\text{O}_5(\text{g})$	13.25 ± 0.12	2.67*

*Using reaction 2 and ΔH_f° 298.15 = -68.35 (H₂O, l), -49.55 (HNO₃, aq)

1) J. D. Ray, R. A. Ogg, J. Phys. Chem. 61, 1087 (1957).

2) R. A. Ogg, J. Chem. Phys. 15, 337 (1947).

3) Russ and Pokorny, Monatsh. 53, 1027 (1913), dynamic vapor pressures.

4) F. Daniels, A. C. Bright, J. Am. Chem. Soc. 42, 1131 (1920).

Heat Capacity and Entropy.

Ray and Ogg, J. Chem. Phys. 25, 384 (1957) reported $S_{298.15}^\circ = 85 \pm 0.5 \text{ cal. deg. mole}^{-1}$ from combination of kinetic and thermochemical values. This entropy was recalculated as follows. The rate data of Ray and Ogg, loc. cit., and of Daniels and Johnston, J. Am. Chem. Soc. 43, 53 (1921) give for the reaction $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ at 25°C the equilibrium constant $K = 5.15 \times 10^{-7} \text{ mole}^2 \text{ liter}^{-2} = 3.08 \times 10^{-4} \text{ atm}^2$. The resulting value of ΔH_f° 298.15 = 4.79 kcal. mole⁻¹ leads to $S_{298.15}^\circ = 82.8 \text{ cal. deg. mole}^{-1}$ for $\text{N}_2\text{O}_5(\text{g})$ when combined with the JANAF entropies and heats of formation of the components of the reaction.

The molecular structure is the nonplanar configuration derived from the electron diffraction study of Akinin, Vilkov and Resolovskii, Zhur. Strukt. Khim. 1, 1 (1960). A planar model (also point group C_{2v}) was assumed by Hasteau, Devlin and Wada, Spectrochim. Acta 18, 1641 (1962) in their approximate normal coordinate analysis of the infrared and Raman spectra. The frequency assignments of these authors are listed above in the order for the planar model, although the vibrations for the nonplanar form will separate differently into the species 5A₁, 3A₂, 3B₁ and 4B₂. Hasteau, et al., estimated the N-O-N deformation frequency (85 cm.⁻¹) from combination bands in the solid and gas phase spectra. The JANAF thermodynamic functions were obtained using these frequencies and assuming the two NO₂ groups to be hindered internal rotators. Barriers to internal rotation of 4.4 kcal. (corresponding to torsional vibrations of about 55 cm.⁻¹) were selected in order to give the observed entropy at room temperature. The principal moments of inertia for the nonplanar model were taken as $I_A = 30.60 \times 10^{-39}$, $I_B = 40.15 \times 10^{-39}$ and $I_C = 16.82 \times 10^{-39} \text{ g. cm.}^2$, while $I_A = 4.693 \times 10^{-39} \text{ g. cm.}^2$ was used for the reduced moment of inertia of the O₂ tops.

Silicon Nitride, Alpha (α -Si₃N₄)
(Crystal) GFW = 140.2848

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	23.789	27.000	27.000	.000	-178.000	-154.734	113.423
300	23.830	27.147	27.000	.044	-178.009	-154.590	112.619
400	26.430	38.387	27.987	2.560	-178.408	-146.721	80.165
500	28.830	40.531	29.677	5.327	-178.079	-139.753	60.693
600	31.000	45.989	32.116	8.324	-178.810	-130.766	47.631
700	33.000	50.920	34.456	11.525	-178.820	-122.756	38.326
800	34.830	55.430	36.800	14.920	-178.711	-114.755	31.350
900	36.400	59.688	39.109	18.485	-178.500	-106.769	25.927
1000	37.830	63.536	41.360	22.196	-178.259	-98.815	21.576
1100	39.120	67.222	43.546	26.044	-177.842	-90.893	18.059
1200	40.270	70.677	45.665	30.014	-177.409	-83.008	15.118
1300	41.236	73.939	47.715	34.091	-176.919	-75.161	12.636
1400	42.046	77.026	49.700	38.256	-176.391	-67.354	10.514
1500	42.700	79.930	51.620	42.495	-175.835	-59.583	8.661
1600	43.132	82.720	53.478	46.788	-175.269	-51.850	7.082
1700	43.540	85.348	55.276	51.123	-174.684	-44.337	5.636
1800	43.946	87.846	57.017	55.493	-174.082	-36.943	4.133
1900	44.106	90.284	58.702	59.891	-173.462	-28.289	2.794
2000	44.320	92.492	60.335	64.313	-172.824	-19.572	1.592
2100	44.402	94.656	61.919	68.749	-172.172	-9.999	.510
2200	44.482	96.724	63.434	73.193	-171.500	4.731	.471
2300	44.558	98.703	64.944	77.645	-170.816	14.341	1.363
2400	44.630	100.601	66.390	82.104	-170.120	23.916	2.178
2500	44.700	102.424	67.795	86.571	-169.412	33.453	2.924
2600	44.766	104.178	69.161	91.044	-168.693	42.968	3.611
2700	44.830	105.869	70.490	95.524	-167.961	52.441	4.245
2800	44.890	107.500	71.783	100.010	-167.217	61.895	4.831
2900	44.946	109.077	73.042	104.502	-166.462	71.318	5.375
3000	45.000	110.601	74.268	108.999	-165.699	80.712	5.860

SILICON NITRIDE, ALPHA (α -Si₃N₄)

(CRYSTAL)

OPW = 140.2848

ΔHf° = Unknown

ΔHf°_{298.15} = -178 ± 7 kcal/mol

S°_{298.15} = [27 ± 4] gibbs/mol

T₀ = [2151]°K

Heat of Formation.

The equilibria (A) Si₃N₄(c) = 3 Si(l) + 2 N₂(g) and (B) Si₃N₄(c) = 3 Si(c) + 2 N₂(g) have been investigated by three groups. R. D. Pehlke and J. P. Elliott, Trans. Met. Soc. AIME 215, 781 (1959), made four series of measurements which mainly concerned reaction (A). W. B. Hinke and L. R. Banniley, J. Amer. Chem. Soc. 52, 48 (1930), made a single series of measurements which covered reactions (A) and (B). C. Matignon, Bull. Soc. Chim. France 13, 791 (1913), also gave a single equilibrium point for reaction (C) 3 SiO₂(c) + 6 C + 2 N₂ = Si₃N₄(c) + 6 CO(g). Below are shown 2nd and 3rd law analyses of the data. It should be noted that these analyses are based on the estimated heat capacities above 900°K, and on an estimated entropy. The uncertainty due to these estimates is estimated as ± 7 kcal in ΔHf°₂₉₈.

Reference	Points	Range °K	Reaction	2nd law ΔHf° ₂₉₈ kcal/mol	3rd law ΔHf° ₂₉₈ kcal/mol	Drift eu	*ΔHf° ₂₉₈ kcal/mol
Pehlke - 1	9	1699-1934	A	190.17.6	211.79	11.844.3	-177.04
Pehlke - 2	9	1691-1959	A	210.749.6	215.29	1.844.9	-178.53
Pehlke - 3	10	1692-1966	A	212.43.3	212.61	0.11.9	-177.85
Pehlke - 4	6	1690-1872	A	207.07.5	212.47	2.644.3	-177.71
Pehlke	30**	1690-1966	A	212.83.2	212.67	-0.21.8	-177.91
Hinke	4	1709-1802	A	196.018.5	213.43	10.310.4	-178.67
Pehlke	4	1653-1666	B		177.41		-177.41
Matignon	1	1700	C		177.82	22.811.8	-177.82
					318.9		-175.1

*Calculated from the third law ΔHf°₂₉₈ values.

**Four points rejected due to failure of a statistical test; this set is a combination of the first four sets.

The adopted ΔHf°₂₉₈(α -Si₃N₄) = -178.7 kcal/mol.

L. A. McClaire and C. P. Coppel, A. D. Little, Inc., "Equilibrium Studies of Refractory Nitrides," Tech. Rept. APWL-TR-65-99, Part 11, Dec. 1966, have investigated the decomposition reaction(B). They conclude that at 1618°K the equilibrium pressure is roughly 0.15 mm. This corresponds to ΔHf°₂₉₈ = -182.3 kcal, and was not given any weight in the adopted value.

Heat Capacity and Entropy.

The enthalpy of α -Si₃N₄ has been measured at three temperatures, in the range 373° - 858°K, by S. Sato, Bull. Chem. Soc. Japan 13, 41 (1938). The heat capacity is calculated from the data assuming that a limit of 45 gibbs/mol is attained by 3000°K. The entropy is obtained from the equilibrium data of Pehlke and Elliott, loc. cit.

Decomposition Data.

The temperature of decomposition is calculated as the point at which the decomposition pressure of nitrogen reaches 1 atm.

Triphosphorus Pentanitride (P_3N_5)
(Crystal) GFW = 162.9549

T, °K	C_p	$\frac{gibbs/mol}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	$\frac{kcal/mol}{\Delta H^\circ}$	ΔG°	Log Kp
0							
100							
200							
298	35.600	44.000	44.000	0.000	64.000	38.129	27.949
300	35.900	44.221	44.001	.066	63.993	37.967	27.659
400	46.000	56.017	45.540	4.191	63.210	29.364	16.056
500	52.000	66.963	48.748	9.108	61.764	21.089	9.218
600	56.000	74.813	52.620	10.514	59.938	13.420	4.779
700	59.000	85.684	56.720	20.374	57.499	5.474	1.710
800	61.000	91.698	60.850	26.574	54.001	1.564	3.563
900	62.500	100.975	64.910	32.459	51.027	1.375	.334
1000	63.400	107.609	68.853	38.755	510.882	10.976	2.399
1100	64.027	113.482	72.457	45.128	107.002	23.023	4.574
1200	64.500	117.275	75.912	55.155	104.400	44.296	7.783
1300	64.920	124.451	79.818	58.023	101.699	46.563	8.986
1400	64.987	129.262	83.180	64.515	98.594	57.563	9.997
1500	65.000	133.747	86.403	71.015	95.504	68.611	

Dec. 31, 1960; Sept. 30, 1952; Mar. 31, 1967

TRIPHOSPHORUS PENTANITRIDE (P_3N_5)

(CRYSTAL)

GFW = 162.9549

$S^\circ_{298.15} = [44 \pm 6]$ gibbs/mol
Td = [730]°K
 $\Delta H^\circ_{298.15} = -64 \pm 5$ kcal/mol
 ΔH°_0 = Unknown

Heat of Formation.

The heat of formation is based on the work of A. Stock and P. Wrede, Chem. Ber. 40, 2923 (1907), who burned P_3N_5 in oxygen. They report a $\Delta H^\circ_{298} = -949.4$ kcal for the reaction $2 P_3N_5(c) + 7.5 O_2(g) = 1.5 P_4O_{10}(amorph) + 5 N_2(g)$. In NBS Technical Note 270-1, "Selected Values of Chemical Thermodynamic Properties," Washington, D.C. (1965), a value of -947.7 kcal is used for the above reaction and we adopt this value. Using the JANAF value for $P_4O_{10}(c)$ and correcting this to $P_4O_{10}(amorph)$ by adding -13.8 kcal/mol, from Technical Note 270-1, we obtain $\Delta H^\circ_{298} P_4O_{10}(amorph) = -716.5$ kcal/mol. Thus, we derive $\Delta H^\circ_{298} P_3N_5(c) = -63.525$ kcal/mol; however, because of the uncertainties in the heat of reaction and correction for amorphous P_4O_{10} we round the value to -64 ± 5 kcal/mol.

Heat Capacity and Entropy.

S. Sato, Sci. Papers Inst. Phys. Chem. Res. (Tokyo) 34, 584 (1958), gave an equation for the heat capacity in the range $273^\circ - 578^\circ K$. Judging from his results for $Be_3N_2(c)$ in the same paper, we believe his values will be slightly high at the upper end of the range. Thus, taking 8.2 gibbs/g-atom as the limiting value, a curve was drawn through Sato's values at the low end and approaching the limit asymptotically. The entropy was estimated from that of $Si_3N_4(c)$ by assuming that the ratio Op_{298}/S_{298} on a gram atom basis would be the same for $P_3N_5(c)$.

Temperature of Decomposition.

Td is calculated as the point at which the total pressure reaches 1 atm. This corresponds to $\log Kp = -0.76$ for the reaction $P_3N_5(c) = 0.75 P_4(g) + 2.5 N_2(g)$. The temperature of decomposition has been reported by V. F. Postnikov and L. L. Kuzmin, J. Appl. Chem. (USSR) 9, 429 (1955) as $1075^\circ K$. This has been confirmed by H. Moreau and P. Rocquet, Compt. Rend. 199, 1691 (1934) and Bull. Chim. France, 3, 1801 (1936); and E. O. Huffman, G. Tarbutton, G. V. Elmore, A. J. Smith and M. G. Rountree, J. Am. Chem. Soc. 79, 1765 (1957). However, it was also noted that $P_3N_5(c)$ is not reformed on cooling the decomposition products; thus the decomposition is non-equilibrium. It is known that the decomposition of AlN , BN and Be_3N_2 is kinetically limited and the equilibrium pressure is not attained until the average energy is greater than the activation energy. It appears that this is also the case for P_3N_5 and a high activation energy is expected.

N_5P_3

N_5P_3

Sodium (Na)

(Reference State) At. Wt. = 22.991

Na

AT. WT. = 22.991

(REFERENCE STATE)

SODIUM (Na)

0° to 370.98°K Crystal
 370.98° to 1176.9°K Liquid
 1176.9° to 6000°K Ideal Monatomic Gas

See crystal, liquid, and ideal monatomic gas for details.

T, °K.	C _p	$S^{\circ} - (F^{\circ} - H_{298}^{\circ})/T$	$\frac{\text{cal. mole}^{-1}}{T}$	$\frac{\text{cal. mole}^{-1}}{T}$	$\frac{\text{cal. mole}^{-1}}{T}$	ΔF°	Log K _p
0	0.000	0.000	INFINITE	1.541	0.000	0.000	0.000
100	5.366	5.690	17.697	1.221	0.000	0.000	0.000
200	6.211	9.725	12.894	0.634	0.000	0.000	0.000
298	6.730	12.296	12.296	0.000	0.000	0.000	0.000
300	6.781	12.340	12.298	0.12	0.000	0.000	0.000
400	7.531	16.086	12.695	1.356	0.000	0.000	0.000
500	7.302	17.741	13.546	2.097	0.000	0.000	0.000
600	7.124	19.056	14.358	2.818	0.000	0.000	0.000
700	6.916	20.173	15.129	3.519	0.000	0.000	0.000
800	6.682	21.073	15.798	4.219	0.000	0.000	0.000
900	6.492	21.885	16.430	4.909	0.000	0.000	0.000
1000	6.318	22.612	17.012	5.599	0.000	0.000	0.000
1100	6.163	23.274	17.552	6.295	0.000	0.000	0.000
1200	6.026	23.881	18.035	6.995	0.000	0.000	0.000
1300	5.904	24.443	18.472	7.698	0.000	0.000	0.000
1400	5.794	24.967	18.871	8.404	0.000	0.000	0.000
1500	5.694	25.460	19.239	9.112	0.000	0.000	0.000
1600	5.604	25.931	19.580	9.821	0.000	0.000	0.000
1700	5.522	26.381	19.846	10.531	0.000	0.000	0.000
1800	5.448	26.811	20.127	11.241	0.000	0.000	0.000
1900	5.381	27.221	20.422	11.951	0.000	0.000	0.000
2000	5.320	27.611	20.731	12.661	0.000	0.000	0.000
2100	5.264	27.981	21.052	13.371	0.000	0.000	0.000
2200	5.212	28.331	21.383	14.081	0.000	0.000	0.000
2300	5.164	28.661	21.724	14.791	0.000	0.000	0.000
2400	5.120	28.971	22.075	15.501	0.000	0.000	0.000
2500	5.079	29.261	22.436	16.211	0.000	0.000	0.000
2600	5.040	29.531	22.807	16.921	0.000	0.000	0.000
2700	5.003	29.781	23.188	17.631	0.000	0.000	0.000
2800	4.968	30.011	23.579	18.341	0.000	0.000	0.000
2900	4.935	30.221	23.970	19.051	0.000	0.000	0.000
3000	4.904	30.411	24.371	19.761	0.000	0.000	0.000
3100	4.874	30.581	24.782	20.471	0.000	0.000	0.000
3200	4.845	30.731	25.193	21.181	0.000	0.000	0.000
3300	4.817	30.871	25.604	21.891	0.000	0.000	0.000
3400	4.790	31.001	26.015	22.601	0.000	0.000	0.000
3500	4.764	31.121	26.426	23.311	0.000	0.000	0.000
3600	4.739	31.231	26.837	24.021	0.000	0.000	0.000
3700	4.714	31.331	27.248	24.731	0.000	0.000	0.000
3800	4.690	31.421	27.659	25.441	0.000	0.000	0.000
3900	4.666	31.501	28.070	26.151	0.000	0.000	0.000
4000	4.643	31.571	28.481	26.861	0.000	0.000	0.000
4100	4.620	31.631	28.892	27.571	0.000	0.000	0.000
4200	4.598	31.681	29.303	28.281	0.000	0.000	0.000
4300	4.576	31.721	29.714	28.991	0.000	0.000	0.000
4400	4.554	31.761	30.125	29.701	0.000	0.000	0.000
4500	4.532	31.791	30.536	30.411	0.000	0.000	0.000
4600	4.510	31.811	30.947	31.121	0.000	0.000	0.000
4700	4.488	31.831	31.358	31.831	0.000	0.000	0.000
4800	4.466	31.841	31.769	32.541	0.000	0.000	0.000
4900	4.444	31.851	32.180	33.251	0.000	0.000	0.000
5000	4.422	31.851	32.591	33.961	0.000	0.000	0.000
5100	4.399	31.841	33.002	34.671	0.000	0.000	0.000
5200	4.377	31.821	33.413	35.381	0.000	0.000	0.000
5300	4.354	31.791	33.824	36.091	0.000	0.000	0.000
5400	4.332	31.751	34.235	36.801	0.000	0.000	0.000
5500	4.309	31.701	34.646	37.511	0.000	0.000	0.000
5600	4.287	31.641	35.057	38.221	0.000	0.000	0.000
5700	4.264	31.571	35.468	38.931	0.000	0.000	0.000
5800	4.242	31.491	35.879	39.641	0.000	0.000	0.000
5900	4.219	31.411	36.290	40.351	0.000	0.000	0.000
6000	4.196	31.321	36.701	41.061	0.000	0.000	0.000

June 30, 1962

Na

Sodium (Na)

(Crystal) At. Wt. = 22.991

T, °K.	C_p	$\frac{\text{cal. mole}^{-1}\text{deg.}^{-1}}{S} = \frac{-(F^{\circ}-H_{298}^{\circ})/T}{S}$	$H^{\circ}-H_{298}^{\circ}$	ΔH_f°	ΔF_f°	Log K _P
0	.000	INFINITE	1.541	.000	.000	INFINITE
100	5.690	17.837	1.221	.000	.000	.000
200	8.211	12.894	.634	.000	.000	.000
298	8.730	12.296	.000	.000	.000	.000
300	8.741	12.294	.012	.000	.000	.000
400	12.338	12.572	.738	.000	.000	.000
500	16.194	11.124	1.935	.562	.211	.092
600	8.000	17.653	11.761	.483	.359	.131
700	8.000	18.886	14.408	.389	.491	.157
800	8.000	19.454	15.036	.274	.715	.174
900	8.000	20.674	16.000	.064	.806	.177
1000	8.000	21.740	16.205			

Na

SODIUM (Na)

(CRYSTAL)

AT. WT. = 22.991

$$\Delta H_f^{\circ} 298.15 = 0$$

$$\Delta H_g^{\circ} 298.15 = 25.755 \text{ kcal. mole}^{-1} \text{ (Monatomic gas)}$$

$$\Delta H_g^{\circ} 298.15 = 32.87 \text{ kcal. mole}^{-1} \text{ (Diatomic gas)}$$

$$S_{298.15}^{\circ} = 12.296 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_{\text{m}}^{\circ} = 0.622 \text{ kcal. mole}^{-1}$$

$$T_m = 370.98 \pm 0.02^{\circ}\text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

D. L. Martin, Proc. Roy. Soc. A254, 433 (1960) reports that the low temperature heat capacity of sodium depends on the thermal history of the sample and ascribes this to a martensitic transformation. The effect is most pronounced in the range 40-80°K., where the graph of C_p against T increases continually for some samples and rises to a peak at 55°K. for others. Martin lists heat capacities obtained in several runs on "high purity" sodium at 21° to 300°K. and the higher values, those defining the peak at 55°K., have been selected here. The heat capacities reported by T. M. Dauphinee, D. L. Martin, and H. Preston-Thomas, Proc. Roy. Soc. A233, 214 (1955), have not been used, since one of the authors in a later publication (Martin, loc. cit.) questions the accuracy of the measurements above 100°K. and at lower temperatures there is no rise to a peak at 55°K. In the range 1.5° to 20°K., L. M. Roberts, Proc. Phys. Soc. B70, 744 (1957) and D. H. Parkinson and J. E. Quarrington Proc. Phys. Soc. A62, 762 (1955) have measured the heat capacity of very high purity sodium. The values of Parkinson and Quarrington are somewhat higher than those of Roberts and have been given greater weight, since they show better continuity with Martin's results. The results of G. L. Picard and P. E. Simon, Proc. Phys. Soc. B1, 1 (1948) have been rejected below 10°K., since they show a peak between 5° and 8°, a feature not verified by other workers; between 10° and 25°K. they agree exactly with the results of Parkinson and Quarrington. J. Rayne, Phys. Rev. 95, 1428 (1954) states that the graph of C_p against T has a small peak at about 0.9°K. This peak has not been observed in the work of W. H. Liden and N. E. Phillips, Phys. Rev. 118, 958 (1960) from 0.15° to 1°K. R. E. Gnaumer and C. V. Heer, Phys. Rev. 118, 955 (1960) from 0.4° to 2°K. and D. L. Martin, Phys. Rev. 124, 438 (1961) from 0.4 to 1.5°K.

T. B. Douglas, A. P. Ball, D. C. Ginnings, and W. D. Davis, J. Am. Chem. Soc. 74, 2472 (1952) report heat capacities in the range 273° to 1173°K. on a sample of not less than 99.9% purity. These values agree to within 1% with those of Martin in the range 273° to 300°K. and the two sets of data have been smoothly joined.

Melting.

Douglas et al. (loc. cit.) have determined the triple point to be $97.82 \pm 0.02^{\circ}\text{C.}$, from which the melting point is calculated to be $97.63 \pm 0.02^{\circ}\text{C.}$, and have measured the heat of fusion.

Heat of Sublimation.

At the boiling point and higher temperatures sodium vapor contains an appreciable proportion of diatomic molecules. G. W. Thompson and E. Garrels "Sodium - Its Manufacture, Properties and Uses," Ed. M. Sittig, Chapter 3, Reinhold Publishing Corporation, Inc., New York (1956), have made a careful analysis of the available vapor pressure data. Their results are consistent with the free energy functions calculated in the present work and have been adopted.

June 30, 1962

Na

Sodium (Na)

(Liquid) At. Wt. = 22.991

Na

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	Log K _f
0						
100	7.617	13.827	13.827	.000	.575	.119
200						
298	7.617	13.827	13.827	.014	.577	.117
300	7.612	13.875	13.875	.014	.577	.117
400	7.531	13.583	13.583	.074	.000	.085
500	7.402	13.236	13.236	1.522	.000	.000
600	7.124	12.053	12.053	2.283	.000	.000
700	6.596	10.143	10.143	3.684	.000	.000
800	6.092	8.528	8.528	4.864	.000	.000
900	5.692	7.182	7.182	4.334	.000	.000
1000	5.416	6.009	6.009	5.024	.000	.000
1100	5.093	5.272	5.272	5.710	.000	.000
1200	4.720	4.895	4.895	6.405	.000	.000
1300	4.403	4.566	4.566	7.105	.000	.000
1400	4.143	4.289	4.289	7.804	.000	.000
1500	3.933	4.063	4.063	8.504	.000	.000
1600	3.763	3.886	3.886	9.205	.000	.000
1700	3.623	3.759	3.759	9.906	.000	.000
1800	3.503	3.669	3.669	10.601	.000	.000
1900	3.403	3.603	3.603	11.292	.000	.000
2000	3.323	3.553	3.553	11.981	.000	.000
				12.670	.000	.000

SODIUM (Na)

(LIQUID)

At. Wt. = 22.991

 ΔH_f^o 298.15 = 0.575 kcal. mole⁻¹ $S_{298.15}^o$ = 13.827 cal. deg.⁻¹ mole⁻¹ ΔH_m = 0.622 kcal. mole⁻¹ T_m = 370.98 ± 0.02°K T_b = 1156°K (Equilibrium mixture) T_b (Monatomic gas) = 1176.9°K ΔH_v 1176.9 = 23.285 kcal. mole⁻¹

Heat of Formation.

Obtained from the heat of fusion by adding $H_{370.98} - H_{298.15}$ for the solid and subtracting $H_{370.98} - H_{298.15}$ for the liquid.

Heat Capacity.

The heat capacity data of T. B. Douglas, A. F. Ball, D. C. Ginnings and W. D. Davis, J. Am. Chem. Soc. **74**, 2472 (1952) were used and were extrapolated below T_m and above 1173°K in a reasonable manner.

Entropy.

Back calculated from the entropy of the liquid at the melting point and the extrapolated heat capacity from the melting point to 298°K.

Vaporization.

Sodium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1156°K. The vapor pressure of the monatomic gas reaches 1 atm. at 1176.9°K and the heat of vaporization to monatomic gas is 23.285 kcal. mole⁻¹ [See Na(crystal)].

Na

Sodium, Monatomic (Na)

(Ideal Gas) At. Wt. = 22.991

Na

AT. WT. = 22.991

(IDEAL GAS)

SODIUM, MONATOMIC (Na)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(H°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰ kcal. mole ⁻¹	Log K _f
0	.000	INFINITE	1.481	25.815	25.815	INFINITE
100	4.966	31.266	1.131	25.992	23.432	51.208
200	4.966	34.730	.944	25.991	20.900	72.838
298	4.966	36.714	.800	25.755	18.475	13.542
300	4.966	36.745	.809	25.752	18.431	13.426
400	4.966	38.176	.506	24.905	16.070	8.780
500	4.966	39.282	.377	24.661	13.890	6.071
600	4.966	40.188	.309	24.537	11.757	4.262
700	4.966	40.958	.262	24.427	9.660	3.062
800	4.966	41.617	.230	24.329	7.593	2.274
900	4.966	42.203	.209	24.246	5.550	1.348
1000	4.966	42.726	.193	24.176	3.529	.771
1100	4.966	43.200	.178	24.118	1.524	.303
1200	4.966	43.632	.165	24.069	.000	.000
1300	4.966	44.030	.153	24.027	.000	.000
1400	4.966	44.398	.142	23.991	.000	.000
1500	4.966	44.740	.132	23.960	.000	.000
1600	4.966	45.061	.123	23.934	.000	.000
1700	4.966	45.362	.115	23.912	.000	.000
1800	4.966	45.646	.108	23.893	.000	.000
1900	4.966	45.915	.102	23.876	.000	.000
2000	4.966	46.170	.096	23.861	.000	.000
2100	4.966	46.413	.091	23.847	.000	.000
2200	4.966	46.646	.086	23.834	.000	.000
2300	4.966	46.868	.082	23.822	.000	.000
2400	4.966	47.078	.078	23.811	.000	.000
2500	4.966	47.276	.074	23.801	.000	.000
2600	4.966	47.463	.071	23.792	.000	.000
2700	4.966	47.639	.068	23.784	.000	.000
2800	4.966	47.804	.065	23.777	.000	.000
2900	4.966	47.958	.063	23.771	.000	.000
3000	4.966	48.101	.061	23.766	.000	.000
3100	4.966	48.234	.059	23.761	.000	.000
3200	4.966	48.357	.057	23.757	.000	.000
3300	4.966	48.470	.055	23.753	.000	.000
3400	4.966	48.574	.054	23.750	.000	.000
3500	4.966	48.669	.053	23.747	.000	.000
3600	4.966	48.755	.052	23.744	.000	.000
3700	4.966	48.832	.051	23.741	.000	.000
3800	4.966	48.900	.050	23.738	.000	.000
3900	4.966	48.959	.049	23.735	.000	.000
4000	4.966	49.009	.048	23.732	.000	.000
4100	4.966	49.050	.047	23.729	.000	.000
4200	4.966	49.083	.046	23.726	.000	.000
4300	4.966	49.108	.045	23.723	.000	.000
4400	4.966	49.125	.044	23.720	.000	.000
4500	4.966	49.134	.043	23.717	.000	.000
4600	4.966	49.136	.042	23.714	.000	.000
4700	4.966	49.130	.041	23.711	.000	.000
4800	4.966	49.116	.040	23.708	.000	.000
4900	4.966	49.094	.039	23.705	.000	.000
5000	4.966	49.064	.038	23.702	.000	.000
5100	4.966	49.027	.037	23.699	.000	.000
5200	4.966	48.983	.036	23.696	.000	.000
5300	4.966	48.932	.035	23.693	.000	.000
5400	4.966	48.875	.034	23.690	.000	.000
5500	4.966	48.812	.033	23.687	.000	.000
5600	4.966	48.743	.032	23.684	.000	.000
5700	4.966	48.669	.031	23.681	.000	.000
5800	4.966	48.590	.030	23.678	.000	.000
5900	4.966	48.506	.029	23.675	.000	.000
6000	4.966	48.418	.028	23.672	.000	.000

June 30, 1962

ΔH_f⁰ = 25.815 kcal. mole⁻¹
 ΔH_f⁰ = 25.755 kcal. mole⁻¹
 S_{298.15} = 36.714 cal. deg.⁻¹ mole⁻¹

Ground State Configuration 2s_{1/2}

Electronic Levels and Multiplicities

E ₁ cm. ⁻¹	E ₁ cm. ⁻¹	E ₁ cm. ⁻¹	E ₁ cm. ⁻¹
0	2	34,549	10
16,956	2	34,589	14
16,973	4	35,042	6
25,740	2	36,373	2
29,173	10	37,057	10
30,267	2	37,058	14
30,273	4	37,060	18
33,201	2	37,237	6

Heat of Formation.

Same as the heat of sublimation to the monatomic species, see notes on Na(crystal)

Heat Capacity and Entropy.

The energy levels have been taken from C. E. Moore, "National Bureau of Standards Circular 487," U. S. Government Printing Office, Washington (1949) p. 83-81. Closely spaced levels have been averaged and the appropriate multiplicities assigned to the averages.

Na

Na⁺

Sodium Unipositive Ion (Na⁺)
(Ideal Gas) At. Wt. = 22.991

SODIUM UNIPosITIVE ION (Na⁺) (IDEAL GAS)

At. Wt. = 22.991

Ground State Configuration 1s² 2s² 2p⁶ 3s¹
S^{298.15} = 35.336 cal. deg.⁻¹ mole⁻¹
ΔH_f⁰ = 144.334 kcal. mole⁻¹
ΔH_f⁰ 298.15 = 145.755 kcal. mole⁻¹

Electronic Levels and Multiplicities

ε, cm. ⁻¹	g _i
0	1
266192	12
298614	36
331860	72
358298	27

Heat of Formation

The heat of formation at 0°K. was obtained from that of the ideal monatomic sodium gas by adding the enthalpy of ionization, calculated from the ionization limit given by C. E. Moore "Atomic Energy Levels" Natl. Bur. Standards Circ. 467 (1949). This was converted to 298°K. by using the formation equation Na(ref. state) - e⁻(ref. state) = Na⁺(monatomic gas), thus Na⁺ involves the difference in enthalpies of the two reference states as well as its own enthalpy.

Heat Capacity and Entropy

These were calculated using the electronic energy levels tabulated above, taken from C. E. Moore loc. cit.

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0						
100	4.968	35.336	0.000	145.755	137.309	-100.711
200						
298	4.968	35.336	0.000	145.755	137.309	-100.711
300	4.968	35.336	0.000	145.755	137.309	-100.711
400	4.968	35.336	0.000	145.755	137.309	-100.711
500	4.968	35.336	0.000	145.755	137.309	-100.711
600	4.968	35.336	0.000	145.755	137.309	-100.711
700	4.968	35.336	0.000	145.755	137.309	-100.711
800	4.968	35.336	0.000	145.755	137.309	-100.711
900	4.968	35.336	0.000	145.755	137.309	-100.711
1000	4.968	35.336	0.000	145.755	137.309	-100.711
1100	4.968	35.336	0.000	145.755	137.309	-100.711
1200	4.968	35.336	0.000	145.755	137.309	-100.711
1300	4.968	35.336	0.000	145.755	137.309	-100.711
1400	4.968	35.336	0.000	145.755	137.309	-100.711
1500	4.968	35.336	0.000	145.755	137.309	-100.711
1600	4.968	35.336	0.000	145.755	137.309	-100.711
1700	4.968	35.336	0.000	145.755	137.309	-100.711
1800	4.968	35.336	0.000	145.755	137.309	-100.711
1900	4.968	35.336	0.000	145.755	137.309	-100.711
2000	4.968	35.336	0.000	145.755	137.309	-100.711
2100	4.968	35.336	0.000	145.755	137.309	-100.711
2200	4.968	35.336	0.000	145.755	137.309	-100.711
2300	4.968	35.336	0.000	145.755	137.309	-100.711
2400	4.968	35.336	0.000	145.755	137.309	-100.711
2500	4.968	35.336	0.000	145.755	137.309	-100.711
2600	4.968	35.336	0.000	145.755	137.309	-100.711
2700	4.968	35.336	0.000	145.755	137.309	-100.711
2800	4.968	35.336	0.000	145.755	137.309	-100.711
2900	4.968	35.336	0.000	145.755	137.309	-100.711
3000	4.968	35.336	0.000	145.755	137.309	-100.711
3100	4.968	35.336	0.000	145.755	137.309	-100.711
3200	4.968	35.336	0.000	145.755	137.309	-100.711
3300	4.968	35.336	0.000	145.755	137.309	-100.711
3400	4.968	35.336	0.000	145.755	137.309	-100.711
3500	4.968	35.336	0.000	145.755	137.309	-100.711
3600	4.968	35.336	0.000	145.755	137.309	-100.711
3700	4.968	35.336	0.000	145.755	137.309	-100.711
3800	4.968	35.336	0.000	145.755	137.309	-100.711
3900	4.968	35.336	0.000	145.755	137.309	-100.711
4000	4.968	35.336	0.000	145.755	137.309	-100.711
4100	4.968	35.336	0.000	145.755	137.309	-100.711
4200	4.968	35.336	0.000	145.755	137.309	-100.711
4300	4.968	35.336	0.000	145.755	137.309	-100.711
4400	4.968	35.336	0.000	145.755	137.309	-100.711
4500	4.968	35.336	0.000	145.755	137.309	-100.711
4600	4.968	35.336	0.000	145.755	137.309	-100.711
4700	4.968	35.336	0.000	145.755	137.309	-100.711
4800	4.968	35.336	0.000	145.755	137.309	-100.711
4900	4.968	35.336	0.000	145.755	137.309	-100.711
5000	4.968	35.336	0.000	145.755	137.309	-100.711
5100	4.968	35.336	0.000	145.755	137.309	-100.711
5200	4.968	35.336	0.000	145.755	137.309	-100.711
5300	4.968	35.336	0.000	145.755	137.309	-100.711
5400	4.968	35.336	0.000	145.755	137.309	-100.711
5500	4.968	35.336	0.000	145.755	137.309	-100.711
5600	4.968	35.336	0.000	145.755	137.309	-100.711
5700	4.968	35.336	0.000	145.755	137.309	-100.711
5800	4.968	35.336	0.000	145.755	137.309	-100.711
5900	4.968	35.336	0.000	145.755	137.309	-100.711
6000	4.968	35.336	0.000	145.755	137.309	-100.711

Na⁺

Mar. 31, 1965

Ground State Configuration [$^2\Pi$]
 $S_{298.15}^\circ = [54.7 \pm 0.5] \text{ gibbs/mol}$
 $\Delta H_f^\circ = [20.3 \pm 10] \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = [20.0 \pm 10] \text{ kcal/mol}$

Electronic Levels and Quantum Heights

E_i , cm $^{-1}$	E_i	σ
0	[4]	$\sigma = 1$
$\omega_e X_e = [3.0] \text{ cm}^{-1}$		$r_e = [2.0] \text{ \AA}$
$\omega_e = [440] \text{ cm}^{-1}$		
$B_e = [0.4467] \text{ cm}^{-1}$		

Heat of Formation

Bawn and Evans (1) have studied the reaction rate of sodium vapor with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite, using the diffusion flame method. On the evidence of reaction rate measurements they estimated the value, $\Delta H_{298}^\circ < 0$, for the reaction $\text{Na(g)} + \text{NO(g)} = \text{NaO(g)} + \text{NO(g)}$. Based on this result, we calculate $\Delta H_{298}^\circ(\text{NaO, g}) > 12 \text{ kcal/mol}$, using $\Delta H_{298}^\circ = 25.8, 7.9$ and 21.6 kcal/mol for $\text{Na(g)}, \text{NO}_2(\text{g})$ and NO(g) , respectively.

Assuming that $D_0(\text{NaO}) = 1/2 D_0(\text{Na}_2) + D_0(\text{O}_2)$, or $\Delta H_0^\circ = 68.1 \text{ kcal/mol}$ for the reaction $\text{NaO(g)} = \text{Na(g)} + \text{O(g)}$, we derive $\Delta H_0^\circ = 16.7$ and $\Delta H_{298}^\circ = 16.4 \text{ kcal/mol}$, using $\Delta H_0^\circ = 25.8$ and 59.0 kcal/mol for Na(g) and O(g) , respectively. Somayajulu (2) found that in a sequence of similar diatomic molecules the force constant (k_e), dissociation energy (D_0) and equilibrium bond distance (r_e) are related by the expression $k_e r_e^3/D_0 = \text{constant}$. Using $r_e = 1.62 \text{ \AA}$, $D_0 = 77.9 \text{ kcal/mol}$ for LiO(g) , $r_e = 2.0 \text{ \AA}$ for NaO(g) and $k_e(\text{NaO})/k_e(\text{LiO}) = 0.4827$, we evaluate $D_0 = 65.4 \text{ kcal/mol}$ for NaO(g) , yielding $\Delta H_{298}^\circ(\text{NaO, g}) = 19.4 \text{ kcal/mol}$. The value k_e is calculated from the relation $k_e = 4\pi^2 \nu^2 \mu$ where ν is the vibrational frequency of the diatomic molecule and μ is the reduced mass.

The value of $\Delta H_{298}^\circ(\text{NaO, g})$ is tentatively adopted as $20 \pm 10 \text{ kcal/mol}$. The corresponding $D_0^\circ(\text{NaO})$ is $65 \pm 10 \text{ kcal/mol}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for OH(g) which has the same number of valence electrons as NaO(g) . The values of ω_e and $\omega_e X_e$ are estimated by comparison with those for LiO(g) , LiF(g) and NaF(g) . The value of r_e is estimated from those for OH(g) , HF(g) and NaF(g) . B_e and a_e are derived from r_e , ω_e and $\omega_e X_e$ by the method suggested by Herzberg (3).

References

1. C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.* **33**, 1571 (1937).
2. G. R. Somayajulu, *J. Chem. Phys.* **33**, 1541 (1960).
3. G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950.

T, K	C_p°	$\frac{g^\circ}{S^\circ}$	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	0.000	INFINITE	2.253	20.326	20.326	INFINITE
100	7.113	46.297	61.869	1.554	20.356	19.365	40.137
200	7.915	51.475	55.492	0.803	20.173	16.495	17.970
298	8.400	54.737	50.000	0.000	20.000	14.552	10.740
300	8.407	54.737	50.000	0.000	20.000	14.552	10.740
400	8.656	57.245	55.071	-0.870	19.152	12.906	7.052
500	8.798	59.194	55.707	-1.743	18.519	11.173	4.971
600	8.888	60.806	56.026	-2.626	18.705	9.884	3.400
700	8.952	62.145	56.195	-3.520	18.792	8.929	2.662
800	9.002	63.380	57.058	-4.416	18.708	7.704	1.913
900	9.042	64.443	58.531	-5.320	18.111	5.603	1.361
1000	9.077	65.397	59.171	-6.225	17.914	4.224	0.923
1100	9.108	66.284	59.777	-7.135	17.707	2.844	0.569
1200	9.135	67.120	60.356	-8.063	17.490	1.464	0.341
1300	9.163	67.900	60.906	-8.993	17.265	0.084	0.211
1400	9.188	68.670	61.413	-9.930	17.036	3.270	0.130
1500	9.213	69.405	61.905	-10.800	16.800	3.916	0.081
1600	9.236	69.700	62.373	-11.723	16.563	4.563	0.053
1700	9.257	70.100	62.820	-12.690	16.326	5.210	0.036
1800	9.276	70.500	63.240	-13.693	16.089	5.857	0.026
1900	9.304	71.293	63.659	-14.735	15.852	6.504	0.019
2000	9.325	71.771	64.053	-15.835	15.615	7.151	0.015
2100	9.347	72.226	64.432	-16.990	15.378	7.799	0.013
2200	9.369	72.658	64.797	-18.202	15.141	8.446	0.011
2300	9.389	73.076	65.149	-19.469	14.904	9.093	0.010
2400	9.410	73.486	65.483	-20.794	14.667	9.740	0.009
2500	9.431	73.883	65.813	-22.178	14.430	10.387	0.008
2600	9.452	74.233	66.130	-23.620	14.193	11.034	0.007
2700	9.473	74.568	66.435	-25.120	13.956	11.681	0.006
2800	9.493	74.895	66.730	-26.678	13.719	12.328	0.005
2900	9.514	75.269	67.023	-28.293	13.482	12.975	0.004
3000	9.534	75.592	67.303	-29.965	13.245	13.622	0.003
3100	9.555	75.905	67.575	-31.695	13.008	14.269	0.002
3200	9.575	76.208	67.840	-33.483	12.771	14.916	0.001
3300	9.595	76.500	68.098	-35.328	12.534	15.563	0.000
3400	9.616	76.790	68.350	-37.230	12.297	16.210	0.000
3500	9.636	77.069	68.595	-39.188	12.060	16.857	0.000
3600	9.656	77.341	68.834	-41.202	11.823	17.504	0.000
3700	9.676	77.606	69.068	-43.270	11.586	18.151	0.000
3800	9.696	77.866	69.298	-45.392	11.349	18.798	0.000
3900	9.717	78.116	69.519	-47.568	11.112	19.445	0.000
4000	9.737	78.362	69.737	-49.799	10.875	20.092	0.000
4100	9.757	78.603	69.950	-52.084	10.638	20.739	0.000
4200	9.776	78.839	70.159	-54.424	10.401	21.386	0.000
4300	9.796	79.070	70.362	-56.818	10.164	22.033	0.000
4400	9.816	79.294	70.564	-59.266	9.927	22.680	0.000
4500	9.836	79.515	70.760	-61.768	9.690	23.327	0.000
4600	9.854	79.711	70.953	-64.324	9.453	23.974	0.000
4700	9.874	79.902	71.137	-66.936	9.216	24.621	0.000
4800	9.894	80.152	71.322	-69.602	8.979	25.268	0.000
4900	9.914	80.356	71.510	-72.322	8.742	25.915	0.000
5000	9.938	80.557	71.699	-75.074	8.505	26.562	0.000
5100	9.958	80.754	71.885	-77.918	8.268	27.209	0.000
5200	9.978	80.946	72.068	-80.858	8.031	27.856	0.000
5300	9.998	81.136	72.247	-83.893	7.794	28.503	0.000
5400	10.019	81.325	72.422	-87.024	7.557	29.150	0.000
5500	10.239	81.509	72.594	-90.259	7.320	29.797	0.000
5600	10.359	81.690	72.761	-93.598	7.083	30.444	0.000
5700	10.479	81.869	72.917	-97.046	6.846	31.091	0.000
5800	10.599	82.053	73.070	-100.594	6.609	31.738	0.000
5900	10.719	82.216	73.171	-104.242	6.372	32.385	0.000
6000	10.839	82.386	73.323	-107.990	6.135	33.032	0.000

Dec. 31, 1950; Dec. 31, 1967

Sodium Monoxide Uninegative Ion (NaO⁻)

(Ideal Gas)

GFW = 38.98975

NaO⁻

T, °K	C _p ^o	gibbs/mol S ^o	-(G ^o -H ^o ₂₉₈)/T	H ^o -H ^o ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0							
100							
200							
298	8.840	51.954	51.954	0.000	-29.000	-32.031	23.479
300	8.887	52.006	51.954	0.016	-29.012	-32.049	23.368
400	8.584	56.457	52.286	0.668	-30.356	-32.907	17.979
500	8.791	56.403	52.922	1.741	-31.087	-33.450	14.625
600	8.995	56.015	53.640	2.625	-31.794	-33.965	12.336
700	9.252	55.390	54.366	3.517	-32.497	-34.156	10.664
800	9.543	54.611	55.042	4.419	-33.190	-34.346	9.664
900	9.793	54.552	55.740	5.317	-33.882	-34.468	8.365
1000	9.981	55.607	56.343	6.224	-34.575	-34.474	7.534
1100	9.114	53.074	56.949	7.133	-35.279	-34.432	6.841
1200	9.143	64.268	57.563	8.046	-35.927	-33.867	6.168
1300	9.171	65.001	58.107	8.962	-36.723	-33.151	5.514
1400	9.198	65.684	58.584	9.881	-37.554	-32.386	4.885
1500	9.222	66.317	59.116	10.801	-38.429	-31.570	4.285
1600	9.247	66.913	59.545	11.725	-39.348	-30.706	3.712
1700	9.270	67.474	60.033	12.651	-40.310	-29.796	3.165
1800	9.294	68.005	60.491	13.579	-41.315	-28.843	2.642
1900	9.316	68.514	60.928	14.510	-42.354	-27.850	2.141
2000	9.339	68.986	61.265	15.442	-43.426	-26.819	1.670
2100	9.361	69.442	61.644	16.377	-44.530	-25.752	1.230
2200	9.383	69.878	62.008	17.314	-45.666	-24.650	0.818
2300	9.405	70.296	62.360	18.254	-46.833	-23.506	0.425
2400	9.426	70.697	62.699	19.197	-48.031	-22.322	0.057
2500	9.449	71.082	63.026	20.139	-49.259	-21.100	-0.321
2600	9.470	71.453	63.343	21.085	-50.517	-19.843	-0.745
2700	9.492	71.811	63.650	22.033	-51.804	-18.552	-1.218
2800	9.513	72.156	63.948	22.983	-53.120	-17.228	-1.737
2900	9.534	72.488	64.237	23.934	-54.464	-15.873	-2.300
3000	9.556	72.814	64.517	24.889	-55.835	-14.489	-2.907
3100	9.577	73.128	64.790	25.847	-57.232	-13.076	-3.561
3200	9.598	73.432	65.055	26.806	-58.655	-11.637	-4.262
3300	9.619	73.728	65.314	27.767	-60.104	-10.174	-5.010
3400	9.639	74.016	65.568	28.730	-61.578	-8.689	-5.805
3500	9.661	74.293	65.811	29.695	-63.077	-7.185	-6.646
3600	9.682	74.568	66.050	30.662	-64.599	-5.664	-7.531
3700	9.703	74.833	66.284	31.631	-66.143	-4.128	-8.461
3800	9.724	75.092	66.513	32.602	-67.708	-2.579	-9.435
3900	9.745	75.346	66.738	33.575	-69.293	-1.018	-10.452
4000	9.766	75.592	66.958	34.551	-70.896	0.553	-11.510
4100	9.787	75.834	67.168	35.529	-72.517	2.067	-12.608
4200	9.808	76.070	67.377	36.509	-74.154	3.524	-13.744
4300	9.829	76.301	67.582	37.491	-75.806	4.933	-14.916
4400	9.849	76.526	67.783	38.475	-77.473	6.294	-16.123
4500	9.870	76.748	67.979	39.460	-79.154	7.607	-17.364
4600	9.891	76.966	68.172	40.449	-80.849	8.872	-18.639
4700	9.912	77.179	68.362	41.439	-82.558	10.091	-19.947
4800	9.933	77.397	68.548	42.431	-84.280	11.263	-21.287
4900	9.954	77.611	68.730	43.424	-86.014	12.388	-22.658
5000	9.975	77.796	68.909	44.422	-87.760	13.466	-24.059
5100	9.995	77.991	69.085	45.420	-89.517	14.497	-25.490
5200	10.016	78.186	69.259	46.421	-91.284	15.481	-26.950
5300	10.037	78.377	69.423	47.423	-93.061	16.417	-28.439
5400	10.057	78.566	69.586	48.426	-94.848	17.304	-29.957
5500	10.079	78.749	69.761	49.435	-96.644	18.142	-31.504
5600	10.099	78.931	69.923	50.444	-98.449	18.931	-33.079
5700	10.120	79.110	70.083	51.455	-100.262	19.671	-34.681
5800	10.141	79.286	70.240	52.468	-102.083	20.363	-36.309
5900	10.162	79.461	70.396	53.482	-103.911	21.007	-37.963
6000	10.182	79.631	70.547	54.500	-105.745	21.603	-39.643

Dec. 31, 1967

SODIUM MONOXIDE UNINEGATIVE ION (NaO⁻)

(IDEAL GAS)

GFW = 38.98975

Ground State Configuration [1²]ΔH_f^o = [-29 ± 20] kcal/molS_{298.15}^o = [52.0 ± 0.5] gibbs/molΔH_f^o_{298.15} = [-29 ± 20] kcal/mol

Electronic Levels and Quantum Weights

 $\frac{g_i}{\sum_i g_i} \frac{\text{cm}^{-1}}{0}$ $\omega_e X_e = [3.2] \text{ cm}^{-1}$
 $\omega_e = [0.00493] \text{ cm}^{-1}$
 $\sigma = 1$
 $r_e = [2.0] \text{ Å}$

Heat of Formation

The electron affinity (E. A.) of NaO⁻(g) is unavailable, therefore the value of ΔH_f^o(NaO⁻, g) is estimated. We first assume that the enthalpy change (ΔH_r^o) of the reaction (1) NaO⁻(g) = Na(g) + O⁻(g) is close to the average of the ΔH_r^o values for the reactions (2) NaO(g) = Na(g) + O(g) and (3) NaF(g) = Na(g) + F(g). The atom F(g) is isoelectronic with O⁻(g). In other words, the ΔH_r^o for reaction (1) is approximately 1/2(64.8 + 113.4) = 89.3 kcal/mol. Then we compare the ΔH_r^o values for the reactions (4) HO(g) = H(g) + O(g), (5) HO⁻(g) = H(g) + O⁻(g), and (6) HF(g) = H(g) + F(g), and find that ΔH_r^o for reaction (5) is experimentally determined as 109.7 kcal/mol which is about 8 kcal/mol more negative than the average of ΔH_r^o values for reactions (4) and (6). Based on this fact we estimate ΔH_r^o = 80 kcal/mol for reaction (1), yielding ΔH_f^o₂₉₈(NaO⁻, g) = -29 kcal/mol which is tentatively adopted. The uncertainty of this value may be ±20 kcal/mol. Based on this ΔH_f^o₂₉₈ value we calculate E. A. = 2.1 ± 0.9 eV for NaO(g). The corresponding value for HO(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of NaF(g) which is isoelectronic with NaO⁻(g). The values of ω_e, ω_eX_e and r_e are estimated by comparison with the observed data for NaF(g). The values of B_e and g_e are calculated from r_e, ω_e and ω_eX_e using the method recommended by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950. The enthalpy at 0°K is -2.248 kcal/mol.

NaO⁻

Sodium Dioxide (NaO₂)

(Crystal) Mol. Wt. = 54.991

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	0.000	0.000	0.000	63.070	63.070	INFINITE
100	10.850	7.310	26.359	3.537	1.606	62.574	48.865	26.659
200	17.222	27.700	27.700	0.000	62.100	52.282	52.282	38.332
300	17.260	27.807	27.700	0.032	62.293	52.219	52.219	38.040
400	18.230	32.905	28.389	1.606	62.574	48.865	48.865	26.659
500	19.210	37.078	29.721	3.678	62.174	45.461	45.461	19.579
600	20.190	40.667	31.253	5.648	61.680	42.187	42.187	15.366
700	21.167	43.852	32.859	7.716	61.096	38.985	38.985	12.171
800	22.140	46.752	34.531	9.881	60.424	35.871	35.871	9.799
900	23.121	49.407	35.913	12.145	59.864	32.846	32.846	7.976
1000	24.100	51.894	37.388	14.506	59.820	29.710	29.710	6.536
1100	25.078	54.236	38.814	16.964	57.897	27.065	27.065	5.377
1200	26.055	56.460	40.193	19.521	80.128	23.428	23.428	4.343
1300	27.031	58.584	41.526	22.176	78.827	19.210	19.210	3.259
1400	28.008	60.623	42.818	24.927	77.437	14.576	14.576	2.291
1500	28.986	62.589	44.071	27.777	75.955	10.244	10.244	1.493
1600	29.957	64.490	45.288	30.728	74.382	5.914	5.914	.808
1700	30.935	66.336	46.472	33.768	72.716	1.684	1.684	.217
1800	31.913	68.132	47.626	36.911	70.959	2.443	2.443	-.297
1900	32.891	69.883	48.751	40.151	69.111	6.472	6.472	-.784
2000	33.870	71.595	49.851	43.489	67.171	10.398	10.398	-1.156

NaO₂SODIUM DIOXIDE (NaO₂)

MOL. WT. = 54.991

(CRYSTAL)

$$\Delta H_f^o = -63.1 \pm 0.7 \text{ kcal. mole}^{-1}$$
$$\Delta H_f^o 298.15 = -62.3 \pm 0.7 \text{ kcal. mole}^{-1}$$
$$\Delta H_f^o = 350 \text{ cal. mole}^{-1}$$
$$\Delta H_{t1}^o = 196.5^\circ \text{K.}$$
$$\Delta H_{t2}^o = 223.5^\circ \text{K.}$$
$$\Delta H_m^o = \text{Unknown}$$

Heat of Formation.

$\Delta H_f^o 298.15$ was obtained from National Bureau of Standards Report 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Element and Some Related Compounds," January 1, 1962. P. W. Gilles and J. L. Margrave, J. Phys. Chem. 60, 1333 (1956) measured the heat of decomposition of NaO₂(c) in H₂O, yielding $\Delta H_f^o 298.15 = -62.1 \pm 0.7 \text{ kcal. mole}^{-1}$. From the original experimental data by R. de Forcrand, Compt. rend., 127, 514 (1898), 158, 843, 931 (1914), the value of $\Delta H_f^o 298.15$ was recalculated to be $-65.0 \text{ kcal. mole}^{-1}$ by P. W. Gilles and J. L. Margrave, loc. cit.

Heat Capacity and Entropy.

The low temperature heat capacities, $52.13^\circ \sim 296.46^\circ \text{K.}$, were measured by S. S. Todd, J. Am. Chem. Soc., 75, 1229 (1953). The heat capacities above 298.15°K. were estimated by comparison with those for Na₂O(c). $S_{298.15}$ was given by S. S. Todd, loc. cit., using $S_{51}^o(\text{extrap.}) = 2.23 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_{t1} , T_{t2} , ΔH_{t1}^o and ΔH_{t2}^o were calculated from the data reported by S. S. Todd, loc. cit.

Temperature of Melting.

The melting temperature was obtained from J. L. Margrave, private communication, May 21, 1963.

June 30, 1963

Na₂O
NaO₂

Sodium, Diatomic (Na₂)

(Ideal Gas) Mol. Wt. = 45.982

Na₂

T, °K.	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	Log K _p
0	0.000	INFINITE	2.485	33.467	INFINITE	33.467	INFINITE
100	8.392	45.884	62.844	1.736	33.576	30.166	65.924
200	8.816	51.443	55.810	.873	33.265	26.866	29.356
298	8.963	54.994	54.994	.000	33.670	23.607	17.450
300	8.965	55.050	54.994	.017	32.843	23.742	17.302
400	9.064	55.400	55.347	.917	30.895	20.886	11.412
500	9.101	59.665	56.015	1.825	30.501	18.409	6.046
600	9.150	61.328	56.766	2.737	29.971	16.041	5.843
700	9.195	62.742	57.522	3.654	29.476	13.757	4.295
800	9.237	63.973	58.253	4.576	29.006	11.585	3.154
900	9.276	65.054	58.964	5.502	28.564	9.530	2.354
1000	9.319	66.043	59.611	6.432	28.104	7.265	1.592
1100	9.359	66.933	60.237	7.366	27.646	5.222	1.038
1200	9.399	67.749	60.829	8.303	27.197	4.119	.750
1300	9.439	68.493	61.381	9.245	26.757	3.030	.521
1400	9.479	69.166	61.891	10.191	26.326	2.000	.341
1500	9.516	69.659	62.432	11.141	25.901	1.038	.190
1600	9.555	70.074	62.915	12.094	25.482	11.955	1.633
1700	9.594	71.405	63.379	13.052	25.076	13.822	1.790
1800	9.633	72.659	63.819	14.016	24.682	15.648	1.954
1900	9.672	72.126	64.243	14.978	24.300	17.430	2.054
2000	9.711	72.623	64.649	15.948	23.930	19.169	2.167
2100	9.749	73.098	65.040	16.921	23.572	21.799	2.269
2200	9.786	73.552	65.417	17.897	23.226	23.774	2.362
2300	9.823	73.986	65.780	18.876	22.892	25.686	2.450
2400	9.865	74.407	66.131	19.863	22.569	27.724	2.524
2500	9.904	74.811	66.470	20.851	22.256	29.695	2.596
2600	9.942	75.200	66.799	21.844	21.952	31.673	2.662
2700	9.981	75.576	67.117	22.840	21.660	33.646	2.723
2800	10.019	75.942	67.425	23.842	21.376	35.621	2.780
2900	10.056	76.292	67.725	24.848	21.100	37.594	2.833
3000	10.097	76.634	68.016	25.851	20.831	39.577	2.883
3100	10.135	76.965	68.300	26.863	20.571	41.552	2.929
3200	10.174	77.288	68.576	27.878	20.319	43.530	2.973
3300	10.213	77.601	68.844	28.896	20.076	45.507	3.014
3400	10.251	77.907	69.104	29.916	19.841	47.483	3.052
3500	10.290	78.204	69.362	30.944	19.614	49.467	3.089
3600	10.328	78.495	69.612	31.979	19.395	51.445	3.123
3700	10.367	78.778	69.856	33.014	19.180	53.420	3.155
3800	10.405	79.054	70.094	34.052	18.969	55.392	3.186
3900	10.444	79.326	70.327	35.095	18.762	57.365	3.216
4000	10.482	79.591	70.556	36.141	20.025	59.371	3.244
4100	10.521	79.850	70.779	37.191	20.105	61.361	3.271
4200	10.559	80.104	70.998	38.245	20.201	63.344	3.296
4300	10.598	80.353	71.213	39.303	20.313	65.316	3.321
4400	10.636	80.597	71.425	40.364	20.430	67.287	3.346
4500	10.675	80.837	71.630	41.430	20.604	69.250	3.367
4600	10.713	81.072	71.833	42.500	20.786	71.205	3.389
4700	10.752	81.303	72.032	43.573	20.997	73.159	3.410
4800	10.790	81.529	72.227	44.650	21.242	75.112	3.430
4900	10.829	81.751	72.418	45.731	21.494	77.063	3.449
5000	10.868	81.971	72.608	46.816	21.744	79.013	3.469
5100	10.906	82.187	72.794	47.905	22.209	81.407	3.488
5200	10.945	82.399	72.977	48.997	22.623	83.441	3.507
5300	10.983	82.608	73.156	50.093	23.091	85.485	3.525
5400	11.021	82.814	73.330	51.194	23.564	87.528	3.543
5500	11.060	83.016	73.508	52.298	24.206	89.598	3.560
5600	11.099	83.216	73.679	53.406	24.862	91.674	3.578
5700	11.137	83.413	73.848	54.516	25.590	93.764	3.595
5800	11.175	83.608	74.013	55.630	26.385	95.863	3.612
5900	11.214	83.798	74.179	56.753	27.243	97.963	3.629
6000	11.253	83.987	74.341	57.878	28.258	100.113	3.646

June 30, 1962

SODIUM, DIATOMIC (Na₂)

(IDEAL GAS)

MOL. WT. = 45.982

ΔH_f^o = 33.467 kcal. mole⁻¹ΔH_f^o 298.15 = 32.87 kcal. mole⁻¹Ground State Configuration = 1Σ⁺g_{298.15} = 54.994 cal. deg.⁻¹ mole⁻¹ω_e = 159.23 cm.⁻¹ω_ex_e = 0.726 cm.⁻¹

σ = 2

B_e = 0.15471 cm.⁻¹α_e = 0.00079 cm.⁻¹r_e = 3.076(6) Å

Heat of Formation.

Same as the heat of sublimation for the diatomic gas; see notes on Na(crystal)

Heat Capacity and Entropy.

Spectroscopic data from G. Hertzberg, "Spectra of Diatomic Molecules," 2nd Edn., D. Van Nostrand Co., Inc., New York (1950).

Na₂

(CRYSTAL)

DISODIUM MONOXIDE (Na₂O)

GFW = 61.979

$\Delta H_f^\circ = -98.74 \pm 1.0 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = -99.90 \pm 1.0 \text{ kcal/mol}$
 $\Delta H_f^\circ (\gamma + \beta) = 0.42 \text{ kcal/mol}$
 $\Delta H_f^\circ (\beta + \alpha) = 2.85 \text{ kcal/mol}$
 $\Delta H_m^\circ = 11.4 \text{ kcal/mol}$

$S_{298.15}^\circ = 17.935 \text{ gibbs/mol}$
 $T_f(\gamma + \beta) = 1023.2^\circ\text{K}$
 $T_f(\beta + \alpha) = 1243.2^\circ\text{K}$
 $T_m = 1405.2^\circ\text{K}$

GFW = 61.979

Disodium Monoxide (Na₂O)

(Crystal)

T, °K	Cp ^a	S ^b	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔH ^c	ΔG ^d	Log Kp
0	∞	∞	INFINITE	∞	∞	∞	∞	∞	INFINITE
100	7.28	3.979	30.827	-2.668	-2.668	-98.744	-98.744	-98.744	21.212
200	14.233	11.761	19.357	-1.505	-1.505	-96.842	-96.842	-96.842	21.212
298	16.516	17.855	17.855	-1.000	-1.000	-95.900	-95.900	-95.900	66.418
300	16.550	18.038	17.936	-1.031	-1.031	-95.900	-95.900	-95.900	65.966
400	18.111	23.017	18.604	-1.765	-1.765	-101.209	-101.209	-101.209	47.714
500	19.478	27.212	19.917	-3.648	-3.648	-101.174	-101.174	-101.174	36.654
600	20.885	30.854	21.483	-5.648	-5.648	-100.993	-100.993	-100.993	29.289
700	22.336	34.073	23.022	-7.735	-7.735	-100.707	-100.707	-100.707	24.041
800	21.819	36.948	24.586	-9.889	-9.889	-100.342	-100.342	-100.342	20.118
900	22.281	39.546	26.166	-12.095	-12.095	-99.923	-99.923	-99.923	17.078
1000	22.666	41.915	27.570	-14.345	-14.345	-99.467	-99.467	-99.467	14.656
1100	23.028	44.504	29.004	-17.051	-17.051	-98.572	-98.572	-98.572	12.492
1200	23.534	46.521	30.380	-19.369	-19.369	-97.832	-97.832	-97.832	10.687
1300	23.611	50.693	31.795	-21.567	-21.567	-96.783	-96.783	-96.783	8.500
1400	23.687	52.452	33.209	-25.941	-25.941	-95.835	-95.835	-95.835	7.215
1500	24.106	54.107	34.547	-28.339	-28.339	-94.584	-94.584	-94.584	5.744
1600	24.336	55.630	35.810	-31.743	-31.743	-93.874	-93.874	-93.874	4.504
1700	24.556	57.152	37.031	-34.206	-34.206	-93.668	-93.668	-93.668	3.400
1800	24.755	58.561	38.198	-36.472	-36.472	-93.637	-93.637	-93.637	2.476
1900	24.949	59.906	39.296	-39.159	-39.159	-93.792	-93.792	-93.792	1.561
2000	25.169	61.192	40.359	-41.666	-41.666	-93.731	-93.731	-93.731	.749

Heat of Formation

The enthalpy change of the reaction $\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(aq)$ has been determined by Matsui (1, 2), Roth (3, 4) and Rengade (5). Based on their reported ΔH_f° values, the corresponding ΔH_f° for $\text{Na}_2\text{O}(c)$ are calculated, using ΔH_f° for $\text{H}_2\text{O}(l)$ = -68.315 kcal/mol obtained from U. S. Natl. Bur. Std. Tech. Note 270-1, 1965, and ΔH_f° for NaOH derived from JANAF ΔH_f° (NaOH, c) and ΔH_{soln} and ΔH_{dil} reported by V. B. Parker, U. S. Natl. Bur. Std. NSRDS-NBS 2, 1965. The sample employed by Matsui was prepared by the method of Rengade (2) and contains $\text{Na}_2\text{O}_2(c)$ and $\text{Na}(c)$ as impurities. The sample used by Roth also contains 3.96 per cent (by weight) $\text{Na}_2\text{O}_2(c)$. Corrections in the reported results for such impurities have been made by the authors. However, in order to obtain better results, more measurements using purer samples are necessary. The enthalpy change of the reaction $2\text{Na}(c) + \text{H}_2\text{O}(l) = \text{Na}_2\text{O}(c) + \text{H}_2(g)$ was calculated by Rengade (5) from his measurements (5) incorporating with ΔH_f° = -86.2 kcal/mol for the reaction $2\text{Na}(c) + 2\text{H}_2\text{O}(l) = 2\text{NaOH}(aq) + \text{H}_2(g)$ determined by Joannis (6). The value ΔH_f° = -94.9 kcal/mol is derived from the data of Forcand (6) using ΔH_f° ($\text{Na}_2\text{O}_2, c$) = -122.66 kcal/mol. The results are presented in the table below.

Brewer (11) determined the equilibrium constants, 918-1467°K, for the vaporization of $\text{Na}_2\text{O}(c)$, using an effusion method. The Na_2O vapor consists predominately of $\text{Na}(g)$ and $\text{O}_2(g)$ molecules with any oxide molecules being not important. The Na/O ratio was not measured and assumed to be 2/1 in all calculations on Na_2O . Based on the reported data, we derive the equilibrium constants for the reaction $\text{Na}_2\text{O}(c) = 2\text{Na}(g) + 1/2\text{O}_2(g)$ and evaluate the third law ΔH_f° for $\text{Na}_2\text{O}(c)$. From this ΔH_f° value, we obtain ΔH_f° ($\text{Na}_2\text{O}, c$) = -65.6 ± 10 kcal/mol, employing ΔH_f° = 25.76 kcal/mol for $\text{Na}(g)$. The value -65.6 kcal/mol is not consistent with the other values determined above. This may be caused by an invalid assumption used in the calculation.

The heat of formation at 298°K for $\text{Na}_2\text{O}(c)$ is tentatively selected as -99.90 ± 1.0 kcal/mol.

Investigator	Reaction	ΔH_f° , kcal/mol	ΔH_f° , kcal/mol
1. Matsui (1929)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(7890 \text{ H}_2\text{O})$	-56.61 ± 0.16	-100.08
2. Matsui (1929)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(4600 \text{ H}_2\text{O})$	-56.70 ± 0.07	-99.89
3. Roth (1947)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(825 \text{ H}_2\text{O})$	-56.03 ± 0.13	-100.55
4. Roth (1948)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(825 \text{ H}_2\text{O})$	-55.98 ± 0.13	-100.60
5. Rengade (1907)	$\text{Na}_2\text{O}(c) + \text{H}_2\text{O}(l) = 2\text{NaOH}(aq)$	-56.50	-100.09
6. Forcand (1900)	$2\text{Na}(c) + \text{H}_2\text{O}(l) = \text{Na}_2\text{O}(c) + \text{H}_2(g)$	-28.70	-97.02
	$\text{Na}_2\text{O}(c) + 1/2\text{O}_2(g) = \text{Na}_2\text{O}_2(c)$	-27.76	-94.90

Heat Capacity and Entropy

The low temperature heat capacities, 15-380°K, were obtained from Furukawa (9). We make the corrections in the reported Cp values for impurity $\text{Na}_2\text{CO}_3(c)$ 2.33 per cent (by weight), analyzed by Grimley (10). The effect on heat capacity due to the presence of Na_2O_2 (0.91 per cent) impurity is insignificant. Using the smoothed low temperature Cp data the $S_{298.15}^\circ$ is calculated, based on $S_{15}^\circ = 0.0122 \text{ eu}$.

Grimley (10) measured the high temperature enthalpies, 380.1-1174.6°K, with a copper block drop-type calorimeter. The enthalpies for the γ phase, 380.1-980.4°K, are joined smoothly with the low temperature data and extrapolated to 1023.2°K (the $\gamma + \beta$ transition temperature). The enthalpies above 1023.2°K are obtained by extrapolation. The enthalpies measured at 1078.3 and 1174.6°K by Grimley are unreasonably large, and are not adopted.

Transition Data

The transition temperature and heats of transition were determined calorimetrically by Bouaziz (12) who used a very pure sample. The adopted $\Delta H^\circ = 0.42$ and 2.85 kcal/mol, are averages of the derived values, 0.36 - 0.48 and 2.7 - 3.0 kcal/mol, respectively.

Melting Data

T_m and ΔH_m° were obtained from Bouaziz (12). The adopted ΔH_m° is an average of the reported 10.8-12.0 kcal/mol. T_m has been reported as 1193 and 1190 ± 10°K by Bunzel (13) and Brewer (11), respectively, which are not adopted.

References

1. M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929).
2. M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 83 (1929).
3. W. A. Roth and H. L. Kaula, Z. Anorg. Chem. 253, 352 (1947).
4. W. A. Roth, Z. Anorg. Chem. 255, 324 (1948).
5. E. Rengade, Compt. Rend. 145, 236 (1907).
6. De Forcand, Compt. Rend. 130, 1465 (1800).
7. E. Rengade, Compt. Rend. 112, 372 (1860).
8. Joannis, Compt. Rend. 112, 372 (1860).
9. G. T. Furukawa, private communication, National Bureau of Standards, November 13, 1967.
10. R. T. Grimley and J. L. Margrave, J. Phys. Chem. 64, 1763 (1960).
11. L. Brewer and J. Margrave, J. Phys. Chem. 59, 421 (1955).
12. R. Bouaziz, G. Papin and A. P. Rollet, Compt. Rend. Ser. C 262, 1051 (1966).
13. E. G. Bunzel and E. J. Kohlmeier, Z. Anorg. Chem. 234, 1 (1947).

June 30, 1962; June 30, 1968

Disodium Monoxide (Na₂O)

(Liquid)

GFW = 61.979

T, °K	C _p ^a	S ^b	-(C _p ^a -H ₂₉₈)/T	H ^c -H ₂₉₈	ΔH ^c	ΔG ^f	Log K _p
kcal/mol							
100							
200							
298	25.000	21.895	21.895	.000	- 89.112	- 81.001	59.376
300	25.000	21.900	21.895	.046	- 89.094	- 80.950	58.972
400	25.000	22.242	22.476	2.546	- 89.640	- 78.249	42.753
500	25.000	34.420	24.728	5.046	- 88.987	- 75.476	35.990
600	25.000	39.378	26.801	7.546	- 88.307	- 72.837	26.531
700	25.000	43.232	28.880	10.046	- 87.667	- 67.853	21.544
800	25.000	46.115	30.797	12.546	- 87.054	- 62.868	16.548
900	25.000	48.951	32.597	15.046	- 86.477	- 57.883	11.552
1000	25.000	51.748	34.303	17.546	- 85.937	- 52.898	6.556
1100	25.000	54.532	36.008	20.046	- 85.439	- 47.913	1.560
1200	25.000	57.318	37.618	22.546	- 84.978	- 42.928	- 3.435
1300	25.000	60.101	39.142	25.046	- 84.554	- 37.943	- 8.439
1400	25.000	62.884	40.682	27.546	- 84.165	- 32.958	- 13.443
1500	25.000	65.668	42.255	30.046	- 83.811	- 27.973	- 18.447
1600	25.000	68.459	43.858	32.546	- 83.492	- 22.988	- 23.451
1700	25.000	71.251	45.493	35.046	- 83.208	- 17.993	- 28.455
1800	25.000	74.042	47.161	37.546	- 82.959	- 12.998	- 33.459
1900	25.000	76.834	48.861	40.046	- 82.744	- 7.993	- 38.463
2000	25.000	79.628	50.593	42.546	- 82.562	- 2.998	- 43.467
2100	25.000	82.422	52.357	45.046	- 82.413	2.003	- 48.471
2200	25.000	85.216	54.151	47.546	- 82.298	7.008	- 53.475
2300	25.000	88.010	55.974	50.046	- 82.217	12.013	- 58.479
2400	25.000	90.804	57.824	52.546	- 82.170	17.018	- 63.483
2500	25.000	93.598	59.704	55.046	- 82.156	22.023	- 68.487
2600	25.000	96.392	61.614	57.546	- 82.173	27.028	- 73.491
2700	25.000	99.186	63.554	60.046	- 82.220	32.033	- 78.495
2800	25.000	101.980	65.531	62.546	- 82.298	37.038	- 83.499
2900	25.000	104.774	67.541	65.046	- 82.407	42.043	- 88.503
3000	25.000	107.568	69.589	67.546	- 82.548	47.048	- 93.507

DISODIUM MONOXIDE (Na₂O)

(LIQUID)

GFW = 61.979

S_{298.15} = [21.895] gibbs/molΔH_{298.15}^a = [-89.112] kcal/mol

Tm = 1405.2°K

Td = 2223°K

Heat of Formation

The heat of formation is obtained from ΔH_{298.15}^a(c) by adding ΔH_m^a and the difference between H_{1405.2}^a - H₂₉₈^a for Na₂O(c) and Na₂O(l).

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for Na₂SiO₃(l) and SiO₂(l). The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

See the Na₂O(c) table.

Decomposition Temperature

Td is the temperature at which the Gibbs energy change of the decomposition reaction Na₂O(l) = 2Na(g) + 1/2O₂(g) approaches zero.

June 30, 1962; June 30, 1968



(Crystal)

$$GFW = 122.0738$$

$$GEW = 122.0738$$

(CRYSTAL)

SODIUM METASILICATE (Na_2SiO_3)

$$\Delta H_{\text{f}}^{\circ} = -370.75 \pm 1.0 \text{ kcal/mol}$$

$$\Delta H_{\text{f}}^{\circ} \text{C}_2\text{H}_2 = -373.19 + 1.0 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 12.38 \text{ kcal/mol}$$

$$\Delta G_{\text{f}}^{\circ} = 27.21 \pm 0.3 \text{ gibbs/mol}$$

$$T_m = 1362 \pm 0.5^\circ\text{K}$$

Heat of Formation

The heats of solution of $\text{NaCl}(\text{c})$, $\text{Na}_2\text{SO}_4(\text{c})$, $\text{SiO}_2(\text{quartz})$, $\text{Na}_2\text{SiO}_3(\text{c})$, $\text{HCl}(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ in 20 percent hydrofluoric acid at -74.7°C were measured by F. C. Kraeck, Ann. Rept. of the Geophysical Laboratory, No. 1215, 69 (1953). The author derived two values of $\Delta H_{\text{sol}}(\text{c})$ of $\text{Na}_2\text{O}(\text{c})$ from those of $\text{NaCl}(\text{c})$, $\text{Na}_2\text{SO}_4(\text{c})$ and $\text{H}_2\text{SO}_4(\text{aq})$ presumably employing auxiliary data from U. S. Natl. Bur. Std. Circ. 500, 1952. We recalculate $\Delta H_{\text{sol}}(\text{c})$ of $\text{Na}_2\text{O}(\text{c})$ in the calorimetric solution as -87.50 (chloride scheme, originally -87.66) and -88.74 kcal/mol (sulfate scheme, originally -89.19), using recent $\Delta H_{\text{f}}^{298}$ values for $\text{NaCl}(\text{c})$, $\text{Na}_2\text{SO}_4(\text{c})$, $\text{HCl}(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, and $\text{Na}_2\text{O}(\text{c})$. The corresponding enthalpy changes, $\Delta H_{\text{f}}^{298}$, for the reaction $\text{Na}_2\text{O}(\text{c}) + \text{SiO}_2(\text{quartz}) = \text{Na}_2\text{SiO}_3(\text{c})$ are derived as -55.20 and -56.38 kcal/mol. Adopting the weighted average $\Delta H_{\text{f}}^{298} = -55.59$ kcal/mol with $\Delta H_{\text{f}}^{298}(\text{Na}_2\text{O}, \text{c}) = -99.9$ kcal/mol and $\Delta H_{\text{f}}^{298}(\text{SiO}_2, \text{c}) = -217.7$ kcal/mol, we obtain $\Delta H_{\text{f}}^{298} = -373.19$ kcal/mol for $\text{Na}_2\text{SiO}_3(\text{c})$. This $\Delta H_{\text{f}}^{298}(\text{Na}_2\text{SiO}_3, \text{c})$ value is independent of future changes in $\Delta H_{\text{f}}^{298}$ of $\text{Na}_2\text{O}(\text{c})$ but the values of $\Delta H_{\text{sol}}(\text{c})$ are not independent. The adopted value of $\Delta H_{\text{f}}^{298}(\text{Na}_2\text{O}, \text{c})$ is the average of -100.1 and -99.7 kcal/mol reported by W. A. Roth and H. L. Kaula, Z. Anorg. Chem. 253, 352 (1947); ibid. 255, 329 (1949), and M. Matsui and S. Oka, J. Soc. Chem. (Japan) 32, 79 (1949), respectively.

W. A. Roth and H. Troitzsch, Z. Anorg. Chem. 260, 337 (1949), have measured the heats of solution of $\text{SiO}_2(\text{quartz})$, $\text{Na}_2\text{SiO}_3(\text{c})$ and $\text{Na}_2\text{O}(\text{c})$ in 10.3 percent HF at 22°C to be -32.85 , -67.96 and -88.9 kcal/mol, respectively. Using these results, we calculate the enthalpy change of the reaction $\text{Na}_2\text{O}(\text{c}) + \text{SiO}_2(\text{quartz}) = \text{Na}_2\text{SiO}_3(\text{c})$ as -53.79 kcal/mol and $\Delta H_{\text{f}}^{298}(\text{Na}_2\text{SiO}_3, \text{c}) = -371.39$ kcal/mol.

By use of high temperature reaction calorimetry D. C. Kroger and W. Janetzko, *Z. Anorg. Allgem. Chem.* **284**, 83 (1956), have determined the enthalpy change of the reaction $\text{Na}_2\text{O}_2(\text{c}) + \text{CO}_2(\text{g})$ as 17.99 kcal/mol. Based on $\Delta H_{298}^\circ = -270.26$, -582.92 and -94.05 kcal/mol for $\text{Na}_2\text{CO}_3(\text{c})$, $\text{Na}_2\text{Si}_2\text{O}_5(\text{gl})$ and $\text{CO}_2(\text{g})$, respectively, we evaluate $\Delta H_{298}^\circ = -370.57$ kcal/mol for $\text{Na}_2\text{SiO}_3(\text{c})$.

The heats of solution of $\text{Na}_2\text{CO}_3(\text{c})$, $\text{SiO}_2(\text{quartz})$ and $\text{Na}_2\text{SiO}_3(\text{c})$ in 39 percent HF at 26.5°C were measured to be -244.1 , -564.5 and -673.6 cal/g, by C. Hummel and H. E. Schwiete, *Glastech. Ber.* **32**, 327 (1959). From these results we calculate the enthalpy change to be 22.43 kcal/mol for the reaction $\text{Na}_2\text{CO}_3(\text{c}) + \text{SiO}_2(\text{quartz}) = \text{Na}_2\text{SiO}_3(\text{c}) + \text{CO}_2(\text{g})$, yielding $\Delta H_{298}^\circ(\text{Na}_2\text{SiO}_3, \text{c}) = -371.48$ kcal/mol.

Many other older calorimetric measurements have been made in order to derive the heat of formation for $\text{Na}_2\text{SiO}_2(\text{c})$, but most of these are of questionable accuracy and in some cases the products of the reaction are uncertain. For further details the review by N. W. McCready, *J. Phys. Colloid. Chem.* 52, 1277 (1948).

Heat Capacity and Entropy

The low temperature heat capacities, 53.6 – 294.5°K, were measured by K. K. Kelley, J. Am. Chem. Soc. **63**, 471 (1939), and high temperature enthalpies, 360.5 – 1749°K were determined by B. F. Naylor, J. Am. Chem. Soc. **67**, 466 (1945). The high temperature heat capacities are derived from the measured enthalpy data and joined smoothly with the low temperature Cp values. The entropy at 298°K is calculated using the adopted low temperature heat capacities, based on $S_{298}^{\circ} = 1.195$ eu.

Melting Data

See $\text{Na}_2\text{SiO}_3(l)$ table for details.



Sodium Metasilicate (Na₂SiO₃)

GFW = 122.0738

(Liquid)



GFW = 122.0738

(LIQUID)

SODIUM METASILICATE (Na₂SiO₃)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	26.740	35.967	35.967	.000	- 361.107	- 341.240	250.136
300	26.863	36.132	35.967	.050	- 361.110	- 341.116	248.503
400	30.540	44.397	37.069	7.931	- 362.490	- 334.332	182.670
500	33.154	51.506	39.262	6.122	- 362.421	- 327.293	143.060
600	35.161	57.735	41.833	0.582	- 362.184	- 320.291	116.466
700	36.716	62.586	43.745	13.345	- 362.708	- 313.550	97.832
800	38.181	66.268	45.172	16.492	- 361.145	- 306.480	83.727
900	42.380	72.856	49.776	20.772	- 360.478	- 299.683	72.773
1000	42.380	77.322	52.311	25.010	- 359.484	- 292.982	64.031
1100	42.380	81.361	54.771	29.248	- 358.532	- 286.382	56.899
1200	42.380	85.081	57.422	33.724	- 402.787	- 278.948	50.803
1300	42.380	88.581	59.422	37.724	- 402.787	- 268.573	45.131
1400	42.380	91.581	61.668	41.962	- 401.504	- 258.297	40.322
1500	42.380	94.505	63.705	46.200	- 400.242	- 248.112	36.150
1600	42.380	97.240	65.716	50.438	- 398.998	- 238.000	32.511
1700	42.380	102.812	69.502	54.816	- 408.503	- 237.294	26.794
1800	42.380	104.523	71.295	63.152	- 407.251	- 217.216	26.374
1900	42.380	106.467	73.002	67.390	- 406.009	- 204.622	23.767
2000	42.380	108.795	74.656	71.628	- 404.773	- 196.097	21.428
2100	42.380	112.720	77.792	80.104	- 402.331	- 185.433	19.319
2200	42.380	116.424	79.261	84.342	- 401.124	- 175.523	17.407
2300	42.380	118.424	80.722	88.580	- 399.926	- 164.577	15.667
2400	42.380	116.154			- 398.926	- 154.574	14.076
2500	42.380					- 144.333	12.618

Heat of Formation

 $\Delta H_f^{298}(l)$ is obtained from $\Delta H_f^{298}(c)$ by adding ΔH_m^* and the difference between H_{1362}^* and H_{298}^* for crystal and liquid.

Heat Capacity and Entropy

The heat capacity above 900°K is derived as constant from the high temperature enthalpy data, 1414 - 1747°K, measured by B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945). A glass transition temperature is assumed at 900°K; i.e. the heat capacities below 900°K are taken to be the same as those for Na₂SiO₃(c).

The entropy is obtained in a manner analogous to that of the heat of formation. The low temperature heat capacities, 63.74 - 162.48°K, have been measured by V. V. Tarasov and Y. S. Savitskaya, Dokl. Akad. Nauk SSSR, 82, 1019 (1953); however, these are not adequate to be used to evaluate S_{298}^* .

Melting Data

The adopted $T_m = 1362^\circ K$, determined by F. C. Kracek, J. Phys. Chem. 24, 1583 (1930), is in good agreement with the value 1261°K reported by F. M. Jaeger, J. Wash. Acad. Sci., 1, 49 (1911), and later confirmed by G. W. Morey and N. L. Bowen, J. Phys. Chem. 28, 1167 (1924).

Other reported T_m values are 1280, 1291 and 1379°K by M. V. Kultascheff, Z. Anorg. Chem. 35, 186 (1903); R. C. Wallace, ibid., 53, 1 (1909); and H. S. van Klooster, ibid., 53, 135 (1910), respectively. These values are all lower than the adopted T_m value, probably because the sample compositions were not the exact composition of metasilicate.

The value of ΔH_m^* is evaluated from the adopted heat capacities for Na₂SiO₃(c) and Na₂SiO₃(l), and the enthalpy data reported by B. F. Naylor, loc. cit., assuming the final state of the calorimetric sample to be Na₂SiO₃(c). From the phase diagrams of Na₂SiO₃ with other compounds, K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936, derived the values of ΔH_m^* of 9.8 - 10.5 kcal/mol.



Sodium Sulfate, V (Na₂SO₄)
(Crystal)

GFW = 142.0412



T, °K	Cp	gibbs/mol S	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	5.550	328.815	328.815	INFINITE
100	15.991	10.329	59.049	4.872	330.329	321.648	702.942
200	25.232	24.622	38.407	2.757	331.173	312.596	341.589
298	30.549	35.764	35.764	0.000	331.550	303.383	222.386
300	30.633	35.953	35.765	0.057	331.553	303.308	220.884
400	37.958	43.275	39.061	3.331	333.688	293.615	160.424
500	47.969	53.450	39.511	6.269	333.732	283.610	123.966
600	40.670	60.622	42.443	10.007	333.603	273.592	99.656
700	42.790	67.056	45.508	15.084	333.194	263.596	82.259
800	44.490	72.865	48.571	20.829	332.556	253.690	69.176
900	45.830	78.033	51.533	26.610	331.400	243.541	50.822
1000	46.740	83.093	54.484	33.349	342.174	221.520	44.012
1100	47.820	87.610	57.293	38.166	387.377	209.691	38.190
1200	48.510	91.801	59.996	43.048	385.585	198.352	32.154
1300	49.100	95.708	62.594	47.957	382.092	165.878	24.168
1400	49.540	99.283	65.092				
1500	50.000	102.797	67.492				

SODIUM SULFATE, V (Na₂SO₄)

(CRYSTAL)

OPW = 142.0412

ΔHf° = -328.82 ± 0.2 kcal/mol
ΔHf°_{298.15} = -331.55 ± 0.2 kcal/mol
ΔHf°(V-I) = 2.584 kcal/mol

S°_{298.15} = 35.76 ± 0.1 gibbs/mol
π(V-I) = 521.7°K

Heat of Formation.

P. L. E. Shibata, S. Oda and S. Furukawa, J. Sci. Hiroshima Univ. (Japan) Ser. A, 3, 227 (1933), measured the emf of the cell: Na-amalg. (0.207%) | Na₂SO₄ (sat. soln.) | Hg₂SO₄ | Hg at 33-37°C. Extrapolating their results to 25°C, we obtain the ΔHf°_{298.15} = -153.77 kcal/mol for the reaction 2Na(c) + Hg₂SO₄(c) = 2Hg(l) + Na₂SO₄(c), which yields ΔHf°_{298.15} = -303.36 and ΔHf°_{298.15} = -331.53 kcal/mol for Na₂SO₄(c). The auxiliary value, ΔHf°_{298.15} = -149.59 kcal/mol, for Hg₂SO₄(c) is obtained from D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," Tech. Note 270-1, Natl. Bur. Std., Washington, D.C., 1965.

The heat of formation for Na₂SO₄(∞ H₂O) is evaluated as -332.10 kcal/mol, using ΔHf°_{298.15} = -57.39 and -217.32 kcal/mol for Na⁺(∞ H₂O) and SO₄²⁻(∞ H₂O), respectively, from Tech. Note 270-1, loc. cit. J.F. Coughlin, J. Am. Chem. Soc. 77, 868 (1955), determined the enthalpy change, ΔHf°_{298.15} = -0.301 ± 0.035 kcal/mol for the reaction Na₂SO₄(c, V) = Na₂SO₄(1050 H₂O). Adopting ΔHf°_{298.15} = 0.244 kcal/mol for the reaction Na₂SO₄(∞ H₂O) = Na₂SO₄ (1050 H₂O) from Natl. Bur. Std. Circ. 500, Washington, D.C., 1952, we derive the value, ΔHf°_{298.15} = 0.545 kcal/mol for the reaction Na₂SO₄(∞ H₂O) = Na₂SO₄(c, V), yielding ΔHf°_{298.15} = -331.56 kcal/mol for Na₂SO₄(c, V).

The heat of formation for Na₂SO₄(c, V) is adopted as -331.55 ± 0.2 kcal/mol.

Heat Capacity and Entropy.

The low temperature heat capacities, 13.74 - 313.44°K, have been measured by K. S. Pitzer and L. V. Coulter, J. Am. Chem. Soc. 60, 1310 (1938). The heat capacities in the temperature range 324.61 - 503.05°K were determined by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 5, 1321 (1961), using an adiabatic calorimeter. These two sets of data are joined smoothly and extrapolated graphically to 1500°K. The enthalpy values derived from the adopted Cp data are in fair agreement with those determined by J. P. Coughlin, J. Am. Chem. Soc. 77, 868 (1955). The corresponding Cp values, reported by M. M. Popov and G. L. Galchenko, J. Gen. Chem. USSR, 21, 2489 (1951), seem too high at the high temperature end. S_{298.15} is derived using the low temperature Cp data reported by K. S. Pitzer and L. V. Coulter, loc. cit., based on S°₁₄ = 0.057 eu.

Transition Data.

Polymorphism studies by P. C. Kracek, J. Phys. Chem. 33, 1281 (1929), and P. C. Kracek and R. E. Gibson, J. Phys. Chem. 33, 1304 (1929); ibid., 34, 148 (1930), indicate five distinct modifications, I-e, V, IV, III, II, I, of which only V and I are stable forms. Calorimetric studies of Shmidt and Sokolov, loc. cit., suggest another form, stable at high temperatures, which is labeled as δ.

The transition temperature and heat of transition are from the calorimetric data for thenardite reported by Shmidt and Sokolov, loc. cit.



GFw = 142.0412

(Crystal)

SODIUM SULFATE, III (Na₂SO₄)

(CRYSTAL)

GFw = 142.0412

$\Delta H_f^{\circ}{}_{298.15} = -331.005 \text{ kcal/mol}$
 $\Delta H_f^{\circ}(\text{III} \rightarrow \text{I}) = 1.630 \text{ kcal/mol}$

$S^{\circ}_{298.15} = 36.653 \text{ gibbs/mol}$
 $T_f(\text{III} \rightarrow \text{I}) = 521.7^{\circ}\text{K}$

Heat of Formation.

The $\Delta H_f^{\circ}{}_{298.15}(\text{Na}_2\text{SO}_4, \text{III})$ value is obtained from $\Delta H_f^{\circ}{}_{298.15}(\text{Na}_2\text{SO}_4, \text{I})$ by subtracting $\Delta H_t^{\circ}(\text{III} \rightarrow \text{I})$ and the difference between $H^{\circ}_{521.7} - H^{\circ}_{298.15}$ for $\text{Na}_2\text{SO}_4(\text{III})$ and $\text{Na}_2\text{SO}_4(\text{I})$.

J. P. Coughlin, J. Am. Chem. Soc. 77, 868 (1955), determined the heat of reaction of $\text{Na}_2\text{SO}_4(\text{V}) \rightarrow \text{Na}_2\text{SO}_4(\text{III})$ as $0.735 \pm 0.015 \text{ kcal/mol}$ at 303.16°K by solution calorimetry. This value is in reasonable agreement with 0.55 kcal/mol obtained from the selected heat of formation.

Heat Capacity and Entropy.

The heat capacities in the temperature range $319.02 - 521.65^{\circ}\text{K}$ were measured with an adiabatic calorimeter by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 6, 1321 (1961). The Cp values below 319°K and above 521°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data.

$\text{Na}_2\text{SO}_4(\text{III})$ is the melttable form obtained by cooling $\text{Na}_2\text{SO}_4(\text{I})$ in the absence of moisture. The temperature and heat of transition are taken from the calorimetric data of Shmidt and Sokolov, loc. cit. The value $\Delta H_t^{\circ}(\text{III} \rightarrow \text{I}) = 1.630 + 0.005 \text{ kcal/mol}$ is the average of three determinations.

J. P. Coughlin, loc. cit., reported the heat of transition $(\text{III} \rightarrow \text{I})$ at 514°K to be 1.680 kcal/mol , obtained by drop calorimetry, which is in good agreement with the value adopted.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
100							
200							
298	31.790	36.653	36.653	.000	- 331.005	- 303.104	222.181
300	31.830	36.849	36.653	.059	- 331.006	- 302.929	220.684
400	35.769	46.503	37.944	3.424	- 332.850	- 293.440	160.328
500	41.735	55.087	40.524	7.282	- 332.874	- 283.571	123.949
600	47.130	63.208	41.635	11.748	- 332.221	- 273.221	87.777
700	50.651	70.755	46.977	16.645	- 331.089	- 263.089	62.650
800	52.950	77.679	50.389	21.833	- 342.711	- 255.871	49.901
900	54.480	84.010	53.778	27.209	- 340.781	- 245.130	59.526
1000	55.410	89.801	57.095	32.706	- 338.759	- 234.608	51.273
1100	56.000	95.113	60.313	38.270	- 336.499	- 224.298	44.564
1200	56.300	100.000	63.420	43.697	- 381.101	- 211.255	38.839

Sodium Sulfate, I (Na_2SO_4)
(Crystal)

GFW = 142.0412



T, °K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	38.990	37.733	37.733	+0.00	- 330.094	- 302.517	221.751
300	39.000	37.975	37.734	+0.72	- 330.084	- 302.345	220.258
400	39.868	49.313	39.274	4.015	- 331.350	- 293.064	160.122
500	40.790	58.305	42.211	8.047	- 331.200	- 281.506	123.920
600	41.920	65.890	45.517	12.182	- 330.874	- 273.994	99.602
700	43.243	72.399	48.916	16.438	- 330.386	- 264.529	82.500
800	44.796	78.272	52.224	20.438	- 342.797	- 256.432	70.054
900	46.581	83.649	55.421	24.405	- 341.676	- 243.700	59.664
1000	48.190	88.640	58.496	28.143	- 340.413	- 235.101	51.361
1100	49.570	93.299	61.451	35.033	- 339.036	- 224.641	44.632
1200	50.640	97.659	64.289	40.045	- 384.044	- 213.369	38.863
1300	51.570	101.750	67.014	45.157	- 382.085	- 199.244	33.466
1400	52.300	105.600	69.634	50.351	- 380.060	- 185.254	28.920
1500	52.917	109.230	72.154	55.613	- 377.982	- 171.417	24.975
1600	53.390	112.691	74.580	60.930	- 375.861	- 157.712	21.542
1700	53.696	115.907	76.916	66.285	- 373.711	- 144.141	18.531
1800	53.900	118.983	79.169	71.666	- 371.552	- 130.701	15.869
1900	54.001	121.900	81.341	77.062	- 369.390	- 117.376	13.501
2000	54.000	124.671	83.439	82.463	- 367.236	- 104.174	11.384

SODIUM SULFATE, I (Na_2SO_4)
(CRYSTAL)

OPW = 142.0412

$$\Delta H_{298.15}^\circ = -330.096 \text{ kcal/mol}$$

$$\Delta H^\circ(\text{V} \rightarrow \text{I}) = 2.584 \text{ kcal/mol}$$

$$\Delta H^\circ(\text{I} \rightarrow \delta) = 0.08 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 5.67 \text{ kcal/mol}$$

$$S_{298.15}^\circ = 37.733 \text{ gibbs/mol}$$

$$T_t(\text{V} \rightarrow \text{I}) = 521.7^\circ\text{K}$$

$$T_t(\text{I} \rightarrow \delta) = 980^\circ\text{K}$$

$$T_m = 1157^\circ\text{K}$$

Heat of Formation.

The $\Delta H_{298.15}^\circ(\text{Na}_2\text{SO}_4, \text{I})$ is obtained from $\Delta H_{298.15}^\circ(\text{Na}_2\text{SO}_4, \text{V})$ by adding $\Delta H^\circ(\text{V} \rightarrow \text{I})$ and the difference between $H_{521.7}^\circ - H_{298.15}^\circ$ for $\text{Na}_2\text{SO}_4(\text{V})$ and $\text{Na}_2\text{SO}_4(\text{I})$.

Heat Capacity and Entropy.

The heat capacities in the temperature range 538.65 - 917.65°K were measured with an adiabatic calorimeter by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. 8, 1321 (1961). The Cp values below 538.65°K and above 917.65°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data.

The value $\Delta H^\circ(\text{V} \rightarrow \text{I}) = 2.584 \pm 0.015 \text{ kcal/mol}$ is the average of two determinations from the calorimetric studies of Shmidt and Sokolov, loc. cit. The transition temperature was derived from the heating curve obtained in measuring the heat of transition. It was taken to be the temperature at which the specimen began to show its lowest heating rate. The heat of transition was the difference between the quantity of heat actually dissipated and the sum of the heats calculated from the heat capacity curve of the apparatus and from the specific heat curves of (V) and (I) linearly extrapolated to the transition temperature.

The values of T_t and ΔH° for $\text{Na}_2\text{SO}_4(\text{I}) \rightarrow \text{Na}_2\text{SO}_4(\delta)$ transition were reported by Shmidt and Sokolov, loc. cit. See $\text{Na}_2\text{SO}_4(\delta)$ table for details.

Melting Data.

See $\text{Na}_2\text{SO}_4(\text{I})$ table for details.



Sodium Sulfate, Delta (δ - Na₂SO₄)

GFW = 142.0412

(Crystal)

SODIUM SULFATE, δ (Na₂SO₄) (CRYSTAL) OFW = 142.0412

$$\Delta H_f^{298.15} = 37.741 \text{ gibbs/mol}$$

$$\Delta H_c^{298.15} = -330.083 \text{ kcal/mol}$$

$$\Delta H_c^{\circ} (I \rightarrow \delta) = 0.08 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 5.50 \text{ kcal/mol}$$

$$S_{298.15}^{\circ} = 37.741 \text{ gibbs/mol}$$

$$T_f (I \rightarrow \delta) = 980^{\circ}\text{K}$$

$$T_m = 1157^{\circ}\text{K}$$

Heat of Formation

The heat of formation ($\Delta H_f^{298.15}$) is obtained from $\Delta H_f^{298.15}$ for Na₂SO₄ (I) by adding $\Delta H_c^{\circ} (I \rightarrow \delta)$ and the difference between $H_{980} - H_{298.15}^{\circ}$ for Na₂SO₄ (I) and Na₂SO₄ (δ).

Heat Capacity and Entropy

The heat capacities in the temperature range 930 - 1010°K were measured by N. E. Shmidt and V. A. Sokolov, Russ. J. Inorg. Chem. **5**, 1321 (1961). The Cp values below 900°K are assumed to be the same as those for Na₂SO₄ (I). The heat capacities above 1010°K are obtained by graphical extrapolation. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

A small anomalous region between 690 - 720°C (965.15 - 993.15°K) on the Cp curve for Na₂SO₄ (c) was reported by N. E. Shmidt and V. A. Sokolov, loc. cit. By use of graphical integration of the area between the measured Cp curve and an arbitrary base line over the region 900 - 1100°K, a value of $\Delta H_c^{\circ} (I \rightarrow \delta) = 0.08 \text{ kcal/mol}$ was obtained. It is assumed to be 980°K. This anomalous region was first observed by G. W. Wyrouboff, Z. Krist. **21**, 284 (1933), and later confirmed by Y. F. Simanov and D. P. Kirikina, Zh. Neorg. Khim. **2**, 699 (1957), as a transition from a hexagonal to an orthorhombic structure. This transition was not observed by the earlier investigators because their measurements did not extend to that temperature range.

Melting Data

The temperature and heat of melting of Na₂SO₄ (I) \rightarrow Na₂SO₄ (l) were reported to be 1157°K and 5.67 kcal/mol, respectively, by Coughlin, loc. cit. No mention was made of the δ phase and the enthalpy measurements were probably not sensitive enough to detect this phase. Based on our selected Cp values for δ and liquid Na₂SO₄, we derive $H_m^{\circ} (\delta \rightarrow l) = 5.50 \text{ kcal/mol}$, using Coughlin's enthalpy data on Na₂SO₄ (l). The melting temperature is assumed to be the same as that reported by Coughlin.

T_m was reported to be 880°C (1153°K), 897°C (1170°K) and 888°C (1161°K) by Ruff and Plato, Ber. Deutsch. Chem. Ges. **36**, 2357 (1903); K. Hittner and O. Tammann, Z. Anorg. Chem. **43**, 215 (1905); and H. E. Boeke, Z. Anorg. Chem. **50**, 355 (1906), respectively.

T, °K	Cp°	$\frac{dH}{dT}$ in cal/mole	$-(C_p^{\circ} - H_m^{\circ})/T$	$H^{\circ} - H_m^{\circ}$	ΔH°	ΔG°	Log Kp
0							
100	36.990	37.741	4.000	-330.089	-302.512	221.747	
200	36.990	37.741	4.000	-330.089	-302.512	221.747	
298	36.990	37.741	4.000	-330.089	-302.512	221.747	
300	36.990	37.741	4.000	-330.089	-302.512	221.747	
350	36.990	37.741	4.000	-330.089	-302.512	221.747	
400	36.990	37.741	4.000	-330.089	-302.512	221.747	
450	36.990	37.741	4.000	-330.089	-302.512	221.747	
500	36.990	37.741	4.000	-330.089	-302.512	221.747	
550	36.990	37.741	4.000	-330.089	-302.512	221.747	
600	36.990	37.741	4.000	-330.089	-302.512	221.747	
650	36.990	37.741	4.000	-330.089	-302.512	221.747	
700	36.990	37.741	4.000	-330.089	-302.512	221.747	
750	36.990	37.741	4.000	-330.089	-302.512	221.747	
800	36.990	37.741	4.000	-330.089	-302.512	221.747	
850	36.990	37.741	4.000	-330.089	-302.512	221.747	
900	36.990	37.741	4.000	-330.089	-302.512	221.747	
950	36.990	37.741	4.000	-330.089	-302.512	221.747	
1000	36.990	37.741	4.000	-330.089	-302.512	221.747	

Sodium Sulfate (Na₂SO₄)
(Liquid)

GFw = 142.0412



QFV = 142.0412

(LIQUID)

SODIUM SULFATE (Na₂SO₄)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔHf° kcal/mol	ΔGf°	Log Kp
200							
250	36.990	42.777	42.777	.000	- 324.241	- 294.165	218.561
300	39.000	43.018	42.777	.072	- 324.229	- 295.903	217.095
400	39.868	54.356	44.317	4.015	- 325.495	- 289.226	199.026
500	40.790	63.396	47.294	8.047	- 325.345	- 286.172	122.453
600	41.920	70.894	50.591	12.182	- 325.019	- 271.165	98.772
700	43.243	77.442	53.959	16.438	- 324.531	- 262.204	81.864
800	47.160	83.315	57.268	20.438	- 336.942	- 254.511	69.556
900	47.180	88.872	60.477	25.556	- 335.670	- 244.395	59.347
1000	47.180	93.643	63.569	30.274	- 334.427	- 234.316	51.210
1100	47.180	98.340	66.529	34.992	- 333.222	- 224.372	44.579
1200	47.180	102.645	69.353	39.710	- 332.522	- 215.412	38.904
1300	47.180	106.221	72.046	44.428	- 376.959	- 199.430	33.611
1400	47.180	109.718	74.613	49.146	- 375.410	- 186.374	29.094
1500	47.180	112.973	77.064	53.864	- 373.876	- 172.926	25.195
1600	47.180	116.018	79.404	59.582	- 372.354	- 159.577	21.797
1700	47.180	118.878	81.643	63.300	- 370.841	- 146.322	18.611
1800	47.180	121.575	83.787	69.018	- 369.345	- 133.160	16.168
1900	47.180	124.126	85.844	72.736	- 367.861	- 120.076	13.812
2000	47.180	126.546	87.819	77.454	- 366.390	- 107.078	11.701
2100	47.180	128.858	89.718	82.172	- 364.928	- 94.150	9.798
2200	47.180	131.042	91.547	86.890	- 363.482	- 81.286	8.075
2300	47.180	133.140	93.310	91.608	- 362.045	- 68.496	6.509
2400	47.180	135.148	95.012	96.326	- 360.622	- 55.757	5.077
2500	47.180	137.074	96.656	101.044	- 359.211	- 43.091	3.767
2600	47.180	138.924	98.246	105.762	- 357.813	- 30.468	2.561
2700	47.180	140.705	99.786	110.480	- 356.429	- 17.909	1.450
2800	47.180	142.420	101.278	115.198	- 355.060	- 5.396	.421
2900	47.180	144.076	102.766	119.916	- 353.703	7.074	.533
3000	47.180	145.675	104.131	124.634	- 352.363	19.493	1.420

S_{298.15} = 42.777 gibbs/mol
Tm(δ → 1) = 1157°K

ΔHf°_{298.15} = -324.241 kcal/mol
ΔHm°(δ → 1) = 5.50 kcal/mol

Heat of Formation.
The value of ΔHf°_{298.15}(1) is obtained from ΔHf°_{298.15}(I) by adding ΔHm° and the difference between H°₁₁₅₇ - H°_{298.15} for Na₂SO₄(δ) and Na₂SO₄(I).

Heat Capacity and Entropy.
The enthalpies for Na₂SO₄(l) were measured by drop calorimetry in the temperature range 1157 - 1828°K by J. P. Coughlin, J. Am. Chem. Soc. **77**, 868 (1955); and in the temperature range 1173 - 1290°K by M. M. Popov and D. M. Ginzburg, J. Gen. Chem. USSR **25**, 1107 (1956). The constant heat capacity adopted here is derived from the enthalpy measurements reported by J. P. Coughlin, loc. cit. Below 800°K, the heat capacities are assumed to be the same as those of the δ phase. The entropy is calculated in a manner analogous to that of the heat of formation.

Melting Data.

The temperature and heat of melting of Na₂SO₄(I) → Na₂SO₄(l) were reported to be 1157°K and 5.67 kcal/mol, respectively, by Coughlin, loc. cit. No mention was made of the δ phase, and the enthalpy measurements were probably not sensitive enough to detect this phase. Based on our selected Cp values for δ liquid Na₂SO₄, we derive ΔHm°(δ → 1) = 5.50 kcal/mol, using Coughlin's enthalpy data on Na₂SO₄(l). The melting temperature is assumed to be the same as that reported by Coughlin.

Tm was reported to be 880°c(1153°K), 897°c(1170°K) and 888°c(1161°K) by Ruff and Plato, Ber. Deutch. Chem. Ges. **36**, 2357 (1903); K. Hüttner and G. Tammann, Z. Anorg. Chem. **43**, 215 (1905); and H. E. Boeke, Z. Anorg. Chem. **50**, 355 (1906), respectively.

Sodium Tungstate (Na_2WO_4)(Crystal) $\text{GFW} = 293.8272$

T, °K	C_p^*	$\frac{\text{gibbs/mol}}{S^*}$	$-(G^* - H^*)_{298}/T$	$H^* - H^*_{298}$	$\frac{\text{kcal/mol}}{\Delta H^*}$	ΔG^*	Log Kp
0	0.000	0.000	INFINITE	6.044	-366.823	-366.823	INFINITE
100	16.627	10.322	63.976	5.358	-368.321	-359.714	786.154
200	26.627	16.627	48.627	3.606	-369.820	-360.743	180.505
298	33.407	36.320	38.527	3.000	-369.200	-361.743	250.505
300	33.490	36.527	38.321	.062	-369.199	-341.572	248.635
400	37.126	44.697	39.683	3.606	-370.354	-332.277	181.548
500	40.000	57.301	42.387	7.467	-370.038	-322.788	141.090
600	42.600	64.827	45.496	11.599	-369.469	-313.387	114.151
700	45.100	71.582	48.744	15.284	-368.673	-304.101	94.945
800	47.500	77.761	51.994	20.614	-367.662	-294.945	80.575
900	50.000	83.295	55.600	27.825	-356.081	-286.304	69.524
1000	52.400	88.597	59.633	36.964	-356.650	-278.402	60.665
1100	54.850	103.706	63.409	44.327	-355.021	-270.459	53.775
1200	57.300	108.584	66.972	49.934	-352.665	-262.153	47.705
1300	59.780	113.268	70.354	55.788	-349.205	-256.791	42.162
1400	62.250	117.789	73.582	61.890	-344.522	-249.631	37.408
1500	64.700	122.167	76.676	68.237	-341.619	-226.665	33.316



(CRYSTAL)

SODIUM TUNGSTATE (Na_2WO_4) $\text{GFW} = 293.8272$

$\Delta H^*_{298} = -366.8 \pm 2 \text{ kcal/mol}$
 $\Delta H^*_{298,15} = -369.2 \pm 2 \text{ kcal/mol}$
 $\Delta H^*_{298} = 0.983 \text{ kcal/mol}$
 $\Delta H^*_{298} = 7.373 \text{ kcal/mol}$
 $\Delta H^*_{298} = 5.688 \text{ kcal/mol}$

Heat of Formation

The adopted heat of formation, $\Delta H^*_{298}(\text{Na}_2\text{WO}_4, \text{c}) = -369.2 \text{ kcal/mol}$, is calculated from $\Delta H^*_{298,15} = 19.44 \pm 0.08 \text{ kcal/mol}$ for the reaction $\text{H}_2\text{WO}_4(\text{c}) + 2\text{HCl}(\text{g}) = \text{Na}_2\text{WO}_4(\text{c}) + 2\text{HCl}(\text{g})$, using the JANAF value of $\Delta H^*_{298}(\text{H}_2\text{WO}_4, \text{c}) = -270.5 \text{ kcal/mol}$ and $\Delta H^*_{298}(\text{NaCl}, \text{c}) = -98.26 \text{ kcal/mol}$, and auxiliary data for $\text{HCl}(\text{aq})$ (11). The value of $\Delta H^*_{298,15}$ was determined by solution calorimetry by M. F. Kohler, L. B. Pankratz and R. Barany (1).

J. M. Sherfey and A. Brenner (2) measured by electrochemical calorimetry the heat of reaction $\Delta H^*_{298} = -7 \pm 1.5 \text{ kcal/mol}$ for $\text{W}(\text{c}) + \text{NaOH}(\text{ss}, 55\text{H}_2\text{O}) + 2\text{H}_2\text{O}(\text{l}) = \text{Na}_2\text{WO}_4(\text{c}) + 3\text{H}_2(\text{g})$. This value, combined with the heat of solution (Δ_{sol}), $\Delta H^*_{\text{sol}} = -1.7 \pm 0.1 \text{ kcal/mol}$ for $\text{Na}_2\text{WO}_4(\text{c}) = \text{Na}_2\text{WO}_4(\text{aq})$, gives $\Delta H^*_{298}(\text{Na}_2\text{WO}_4, \text{c}) = -368.4 \text{ kcal/mol}$, which is in good agreement with the value adopted.

The previously accepted value (Δ_{sol}), $\Delta H^*_{298}(\text{Na}_2\text{WO}_4, \text{c}) = -379 \pm 0.5 \text{ kcal/mol}$, was based on the unreliable $\Delta H^*_{298}(\text{H}_2\text{WO}_4, \text{c}) = -280.2 \pm 0.4 \text{ kcal/mol}$. (See JANAF $\text{H}_2\text{WO}_4(\text{c})$ table of March 31, 1967.) The other quoted value (1), $\Delta H^*_{298}(\text{Na}_2\text{WO}_4, \text{c}) = -385 \text{ kcal/mol}$, was obtained from W. G. Mixer's (3) measurement of the heat of reaction of tungsten powder with excess Na_2O_2 . This value was probably in error because the complex tungstate and peroxytungstates were formed in the reaction.

Heat Capacity and Entropy

Low temperature heat capacities ($52-299.87^\circ\text{K}$) were measured calorimetrically by E. G. King and W. W. Weller (4). The heat capacities above 300°K are estimated by extrapolation of the low temperature heat capacity curve to $C_{p,60} = 49.0 \text{ gibbs/mol}$. The latter is obtained from an estimate of C_p equal to 7 gibbs/g-atom at the first transition temperature.

The entropy, $S^*_{298} = 38.32 \pm 0.5 \text{ eu}$, is calculated from low temperature heat capacity data of King and Weller (4), based on an extrapolation of $S^*_{51} = 2.77 \pm 0.5 \text{ eu}$.

Transition Data

Transition temperatures and heats were obtained from differential heating and cooling curves both at atmospheric and higher pressures by R. W. Goranson and F. C. Kracek (7). Existence of three phases is confirmed by the earlier birefringence studies of H. E. Boeke (8).

R. Riccardi and C. Sinistri (10) found only one transition at 864°K with $\Delta H^* = 8.23 \text{ kcal/mol}$ by differential thermal analysis. This heat is apparently the sum of the two adopted heats of transition.

Melting Data

The adopted melting data were measured by the differential heating and cooling curve method by Goranson and Kracek (7). R. Riccardi and C. Sinistri (10) found the melting point at 971°K with $\Delta H^* = 7.52 \text{ kcal/mol}$ by differential thermal analysis.

References

1. M. F. Kohler, L. B. Pankratz and R. Barany, U.S. Bur. Mines RI 5973 (1962).
2. J. M. Sherfey and A. Brenner, J. Electrochem. Soc. **105**, 565 (1958).
3. R. L. Graham and L. G. Hepler, J. Amer. Chem. Soc. **80**, 3538 (1958).
4. U. S. Natl. Bur. Std. Circ. 500, 1952.
5. W. G. Mixer, Am. J. Sci. **26**, 125 (1908).
6. E. G. King and W. W. Weller, U.S. Bur. Mines RI 5791 (1961).
7. R. W. Goranson and F. C. Kracek, J. Chem. Phys. **3**, 87 (1935).
8. H. E. Boeke, Z. Anorg. Allgem. Chem. **50**, 359 (1906).
9. S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
10. R. Riccardi and C. Sinistri, Ric. Sci. Rend. Sez. A **36**, 1026 (1965).
11. V. B. Parker, U.S. Natl. Bur. Std. NBS-RS-2, 1965, and U. S. Bur. Std. Tech. Note 270-1, 1965.

June 30, 1967



Sodium Disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$)

GFW = 182.1586

(Crystal)

T, °K	C_p^0	S^0	$-(G^0 - H^0_{298})/T$	$H^0 - H^0_{298}$	kcal/mol ΔH^0	ΔG^0	Log Kp
0	0.000	INFINITE	-	-	-586.870	-	INFINITE
100	15.590	10.052	44.782	5.673	-586.729	-578.064	1263.357
200	29.656	25.807	42.412	3.321	-586.853	-566.900	619.479
298	37.550	39.210	40.000	0.000	-590.360	-555.509	407.199
300	37.642	39.443	39.211	0.70	-590.365	-555.292	404.530
400	43.834	51.116	41.155	4.155	-591.760	-543.478	296.940
500	48.577	61.467	43.694	8.788	-591.525	-531.418	232.283
600	52.002	70.643	47.602	13.825	-590.952	-519.447	189.208
700	54.455	78.854	51.491	19.154	-590.150	-507.591	158.474
800	56.205	86.246	55.361	24.972	-589.150	-495.825	133.466
900	57.439	92.845	59.164	30.825	-588.150	-484.256	117.553
1000	58.000	99.537	62.884	36.653	-586.571	-472.779	103.376
1100	58.000	106.208	66.524	43.653	-584.330	-461.511	91.694
1200	58.000	112.289	70.059	50.653	-582.620	-449.511	81.871
1300	58.000	117.902	73.554	57.653	-580.961	-437.686	73.278
1400	58.000	123.050	76.100	64.653	-579.346	-426.086	65.578
1500	58.000	127.819	80.151	71.653	-577.772	-414.638	59.101
1600	58.000	132.437	83.279	78.653	-576.229	-403.355	53.437
1700	58.000	136.681	86.297	85.653	-574.702	-392.221	48.468
1800	58.000	140.682	89.208	92.653	-573.196	-381.246	44.066
1900	58.000	144.466	92.016	99.653	-571.716	-370.428	40.197
2000	58.000	148.057	94.731	106.653	-570.266	-359.766	36.190

SODIUM DISILICATE ($\text{Na}_2\text{Si}_2\text{O}_5$)

(CRYSTAL)

GFW = 182.1586

$S^0_{298,15} = 39.21 \pm 1.0$ gibbs/mol
 $T_f(B \rightarrow A\beta) = 951^\circ\text{K}$
 $T_f(A\beta \rightarrow A\alpha) = 980^\circ\text{K}$
 $T_m = 1147^\circ\text{K}$

Heat of Formation

The heats of solution of $\text{NaCl}(c)$, $\text{Na}_2\text{SO}_4(c)$, $\text{SiO}_2(\text{quartz})$, $\text{Na}_2\text{Si}_2\text{O}_5(c)$, $\text{HCl}(aq)$ and $\text{H}_2\text{SO}_4(aq)$, in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek (3). The author derived two values of ΔH_{soln} of $\text{Na}_2\text{O}(c)$ from those of $\text{NaCl}(c)$, $\text{Na}_2\text{SO}_4(c)$, $\text{HCl}(aq)$ and $\text{H}_2\text{SO}_4(aq)$, presumably employing auxiliary data from (2). We recalculate ΔH_{soln} of $\text{Na}_2\text{O}(c)$ in the calorimetric solution as -87.50 (chlorine scheme originally -87.66) and -88.74 kcal/mol (sulfate scheme, originally -89.13), using recent $\Delta H^0_{f,298}$ values (15, 17, 18) for $\text{NaCl}(c)$, $\text{HCl}(aq)$, $\text{H}_2\text{SO}_4(aq)$, $\text{Na}_2\text{SO}_4(c)$, and $\text{Na}_2\text{O}(c)$. The corresponding enthalpy changes, $\Delta H^0_{f,298}$ for the reaction $\text{Na}_2\text{O}(c) + 2\text{SiO}_2(\text{quartz}) = \text{Na}_2\text{Si}_2\text{O}_5(c)$ are derived as -94.65 and -55.89 kcal/mol. Adopting the weighted average $\Delta H^0_{f,298} = -55.06$ kcal/mol with $\Delta H^0_{f,298}(\text{Na}_2\text{O}, c) = -99.9$ kcal/mol and $\Delta H^0_{f,298}(\text{SiO}_2, \text{quartz}) = -217.7$ kcal/mol, we obtain $\Delta H^0_{f,298} = -590.36$ kcal/mol for $\text{Na}_2\text{Si}_2\text{O}_5(c)$. This $\Delta H^0_{f,298}$ ($\text{Na}_2\text{Si}_2\text{O}_5, c$) value is independent of future changes in $\Delta H^0_{f,298}$ of $\text{Na}_2\text{O}(c)$, but the values of ΔH_{soln} and $\Delta H^0_{f,298}$ are not independent.

Stevens et al. (3) measured the heats of solution of $\text{Na}_2\text{Si}_2\text{O}_5(c)$, $\text{Na}_2\text{O}(c)$ and $\text{SiO}_2(\text{quartz})$ in $\text{HF}(aq)$ at 25°C . Based on the reported results, the enthalpy change for the reaction $\text{Na}_2\text{O}(c) + 2\text{SiO}_2(\text{quartz}) = \text{Na}_2\text{Si}_2\text{O}_5(c)$ is calculated as -53.25 ± 0.32 kcal/mol, yielding $\Delta H^0_{f,298}(\text{Na}_2\text{Si}_2\text{O}_5, c) = -588.55$ kcal/mol.

Hummel (4) determined the heats of solution of $\text{Na}_2\text{Si}_2\text{O}_5(c)$, $\text{SiO}_2(\text{quartz})$ and $\text{Na}_2\text{CO}_3(c)$ in 39 percent HF at 26.5°C . From the data reported we derive the enthalpy change to be 70.88 kcal/mol for the reaction $\text{Na}_2\text{CO}_3(c) + 2\text{SiO}_2(\text{quartz}) = \text{Na}_2\text{Si}_2\text{O}_5(c) + \text{CO}_2(g)$. Employing $\Delta H^0_{f,298} = -270.26$, -217.7 and -94.05 kcal/mol for $\text{Na}_2\text{CO}_3(c)$, $\text{SiO}_2(\text{quartz})$ and $\text{CO}_2(g)$, respectively, we obtain $\Delta H^0_{f,298} = -590.73$ kcal/mol for $\text{Na}_2\text{Si}_2\text{O}_5(c)$ which is in good agreement with the adopted one.

Heat Capacity and Entropy

The low temperature heat capacities, $54.3 - 294.7^\circ\text{K}$, have been measured by Kelley (5) and the high temperature enthalpies, $376.8 - 1100.2^\circ\text{K}$, by Naylor (6). The derived high temperature heat capacities are joined smoothly with the low temperature ones at 298°K . An approximate C_p of 70 gibbs/mol is derived from the enthalpies above 980°K ; this value is extrapolated to 2000°K . The value of S^0_{298} is calculated from the adopted low temperature heat capacities based on $S^0_{298} = 2.945$ eu. The entropy extrapolation derives from the Debye-Einstein extrapolation of Kelley (5) which yields a C_p curve with an extra inflection in the region from 15 to 50°K . A more normal extrapolation would lead to a value of S^0_{298} which is lower by 0.5 eu.

There are six slowly inverting polymorphous phases (1, 2-9), namely A, B, C, D, E and F, of which only the first two phases are stable. Two rapid transitions have been reported at 951 and 980°K (1, 10). Phase A, which has two subphases, $A\alpha$ and $A\beta$, is stable above 951°K . The stable phase below 951°K is known as phase B, previously called $\beta\text{-Na}_2\text{Si}_2\text{O}_5$. The two values of $\Delta H^0_{f,298}$ derived from the enthalpy data of Naylor (6) using the adopted C_p values. Three more rapid transitions have been reported at 822 , 846 and 866°K (1, 10) in E, previously called $\gamma\text{-Na}_2\text{Si}_2\text{O}_5$. A recent examination of these transitions was reported by Willgallis and Range (10).

Transition Data

Melting Data

T_m is obtained from Morey (11). The selected value of ΔH^0_m is based on the following ΔH^0_m values derived from four different kinds of measurements.

Investigator	ΔH^0_m , kcal/mol ^a at 298°K	ΔH^0_m , kcal/mol ^a at 1147°K	Method ^b	Reference
Kelley (1936)	(7.51)	8.46	I	12
Kracek (1953)	5.25	(6.20)	II	1
Kröger-Janetzko (1956)	8.81	(9.76)	III	13
Kröger-Kreitlow (1956)	8.83	(9.78)	II	14
Schwiete-Ziegler (1958)	(7.50)	8.45	IV	15
Hummel-Schwiete (1959)	8.09	(9.04)	II	4

^aThe numbers in parentheses are derived from the measured ones at the other listed temperatures.

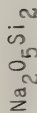
^bI = phase diagram; II = solution calorimetry; III = high temperature reaction calorimetry; and

IV = dynamic-differential calorimetric method.

References

1. F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 58, 69 (1953).
2. U. S. Natl. Bur. Std. Circ. 500, 1957.
3. C. Stevens and E. F. Turkdogan, Trans. Faraday Soc. 53, 356 (1955).
4. C. Hummel, Ann. Chem. Phys. 32, 327 (1959).
5. K. K. Kelley, J. Am. Chem. Soc. 63, 471 (1939).
6. B. F. Naylor, J. Am. Chem. Soc. 62, 466 (1945).
7. G. W. Morey and N. L. Bowen, J. Soc. Glass Technol., 3, 226 (1925).
8. F. C. Kracek, J. Phys. Chem., 34, 1543 (1930).
9. A. Hilla and J. Köffler, Z. Anorg. Allgem. Chem. 32, 134 (1934).
10. G. W. Morey and N. L. Bowen, J. Phys. Chem. 28, 1167 (1924).
11. K. K. Kelley, U. S. Bur. Mines Bull. 393, 1936.
12. C. Kröger and W. Janetzko, Z. Anorg. Allgem. Chem. 284, 84 (1956).
13. C. Kröger and G. Kreitlow, Glasstech. Ber. 29, 393 (1956).
14. C. Kröger and G. Ziegler, Ber. Deut. Keram. Ges. 33, 193 (1958).
15. S. J. JANAF, JANAF Thermochemical Data Tables, 3rd ed., 1973.
16. U. S. Natl. Bur. Std. Tech. Note 270-1, 1965.
17. U. S. Natl. Bur. Std. Note 270-1, 1965.
18. Z. Anorg. Chem. 298, 253, 352 (1947), and M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) 32, 79 (1929).

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967



Sodium Disilicate (Na₂Si₂O₅)
(Liquid) GFW = 182.1586

T, °K	Cp	$\frac{\text{Btu}}{\text{lb}}/\text{mol}$ $S^{\circ} - (G^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	kcal/mol ΔH°	ΔG°	Log Kp
0						
100	37.420	45.101	45.101	.000	- 549.716	4.02.953
200	37.442	45.134	45.102	- 582.816	- 540.510	4.00.318
300	43.434	57.040	46.656	4.154	- 538.281	3.94.103
400	48.577	67.358	46.785	8.786	- 526.615	3.90.270
500	52.002	76.927	53.493	13.820	- 515.432	3.87.746
600	56.750	84.972	57.390	19.304	- 504.172	3.87.409
700	65.050	93.296	61.360	25.548	- 493.098	3.84.708
800	66.020	101.053	65.347	32.135	- 482.249	3.81.106
900	64.000	107.927	69.269	38.658	- 471.616	3.77.071
1000	62.430	113.935	73.062	46.940	- 461.157	3.71.423
1100	62.430	119.367	76.698	55.203	- 450.913	3.64.840
1200	62.430	124.364	80.175	63.546	- 440.724	3.57.259
1300	62.430	128.991	83.498	71.869	- 430.762	3.49.640
1400	62.430	133.298	86.677	80.175	- 421.078	3.41.928
1500	62.430	137.327	89.718	88.461	- 411.608	3.33.833
1600	62.430	141.112	92.631	96.661	- 402.340	3.25.482
1700	62.430	144.680	95.424	104.787	- 393.260	3.16.882
1800	62.430	148.056	98.106	112.849	- 384.367	3.08.099
1900	62.430	151.258	100.684	120.849	- 375.652	3.00.000
2000	62.430	154.302	103.166	128.790	- 367.116	2.91.667
2100	62.430	157.208	105.557	136.666	- 358.748	2.83.191
2200	62.430	159.983	107.863	144.480	- 350.546	2.74.576
2300	62.430	162.640	110.091	152.236	- 342.502	2.65.811
2400	62.430	165.189	112.244	160.000	- 334.616	2.56.906

Dec. 31, 1960; June 30, 1965; Sept. 30, 1967

SODIUM DISILICATE (Na₂Si₂O₅)

(LIQUID)

GFW = 182.1586

$S^{\circ}_{298.15} = 45.101$ gibbs/mol

$\Delta H^{\circ}_{298.15} = -582.811$ kcal/mol

$T_m = 1147^{\circ}\text{K}$

$\Delta H_m^{\circ} = 8.5$ kcal/mol

Heat of Formation

The $\Delta H^{\circ}_{298}(\ell)$ is obtained from $\Delta H^{\circ}_{298}(\text{c})$ by adding ΔH_m° and the difference between $H^{\circ}_{1147} - H^{\circ}_{298}$ for crystal and liquid. The heats of solution of NaCl(c), Na₂SO₄(c), H₂SO₄(aq), SiO₂(quartz) and Na₂Si₂O₅(gl) in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek (1). Following the same procedure as described in the Na₂Si₂O₅(c) table, we derive the enthalpy changes, ΔH°_{298} , for the reaction Na₂O(c) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) as -48.40 and -50.64 kcal/mol using the heats of solution of Na₂O(c) as -87.50 (chloride scheme) and -88.74 kcal/mol (sulfate scheme), respectively. Adopting the weighted average $\Delta H^{\circ}_{298} = -49.81$ kcal/mol with $\Delta H^{\circ}_{298}(\text{Na}_2\text{O}, \text{c}) = -89.9$ kcal/mol and $\Delta H^{\circ}_{298}(\text{SiO}_2, \text{quartz}) = -217.7$ kcal/mol, we obtain $\Delta H^{\circ}_{298} = -585.113$ kcal/mol for Na₂Si₂O₅(gl).

Using high temperature reaction calorimetry, Kröger (2) determined the enthalpy changes as 25.28 ± 0.22 and -18.68 ± 0.36 kcal/mol for the reactions Na₂CO₃(c) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) + CO₂(g) and 2NaOH(c) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) + H₂O(l), respectively. From the given results, we calculate the corresponding values of $\Delta H^{\circ}_{298}(\text{Na}_2\text{Si}_2\text{O}_5, \text{gl})$ to be -586.32 and -589.46 kcal/mol, using $\Delta H^{\circ}_{298} = -270.26$, -217.70, -94.05, -101.90 and -68.32 kcal/mol for Na₂CO₃(c), SiO₂(quartz), CO₂(g), NaOH(c) and H₂O(l), respectively. These two $\Delta H^{\circ}_{298}(\text{Na}_2\text{Si}_2\text{O}_5, \ell)$ values, as well as the value -585.113 kcal/mol based on Kracek's data, are not adopted, because incorporating these $\Delta H^{\circ}_{298}(\text{gl})$ values with the value of $\Delta H^{\circ}_{298}(\text{c})$, gives values if the heat of melting at 298°K which are too low in comparison with the other values (see the Na₂Si₂O₅(c) table).

Hummel (3) measured the heats of solution of Na₂CO₃(c), SiO₂(quartz) and Na₂Si₂O₅(gl) in 39 percent hydrofluoric acid at 25.5°C, as -244.1, -584.5 and -573.7 cal/g, respectively. Based on these results, we derive the enthalpy change for the reaction Na₂CO₃(c) + 2SiO₂(quartz) = Na₂Si₂O₅(gl) + CO₂(g) to be 29.01 kcal/mol, yielding $\Delta H^{\circ}_{298}(\text{Na}_2\text{Si}_2\text{O}_5, \text{gl}) = -582.6$ kcal/mol which is in good agreement with the adopted value.

Heat Capacity and Entropy

Using drop calorimetry, Naylor (4) has measured the enthalpies of Na₂Si₂O₅(gl), 445.5 - 1120.7°K, and Na₂Si₂O₅(ℓ), 1173.2 - 1744°K. Based on the liquid enthalpy data, we evaluate the heat capacity of Na₂Si₂O₅(ℓ) to be 62.43 gibbs/mol. The Cp values below 1147°K are derived from the enthalpies measured at 445.5 - 1120.7°K by Naylor (4). Below 600°K, Cp is identical with that of the crystal. The adopted curve rises rapidly to a maximum in the glass transition region, 650-950°K, then smoothly approaches the value of the real liquid near Tm. The heat capacity of Na₂Si₂O₅(ℓ) is assumed to be constant in the temperature range 1147 to 2500°K.

S°_{298} is obtained in a manner analogous to that of the heat of formation.

Melting Data

See Na₂Si₂O₅(c) table for details.

References

1. F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1216, 69 (1953).
2. C. Kröger and H. Janetzko, Z. Anorg. Allgem. Chem. 284, 84 (1956).
3. C. Hummel and H. E. Schwiete, Glasstech. Ber. 32, 327 (1959).
4. B. F. Naylor, J. Am. Chem. Soc. 67, 466 (1945).

Na₂O₅Si₂

Disodium Sulfide (Na₂S)

INTERIM TABLE

(Solid) Mol. Wt. = 78.048

T, °K.	C _p ^a	S ^b	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^c	ΔF _f ^c	Log K _p
100							
200							
298	18,990	23,400	23,400	4,000	-89,000	-86,368	63.307
300	19,000	23,517	23,400	4,035	-89,000	-86,368	63.307
400	19,300	29,025	24,119	1,687	-85,989	-84,351	62.903
500	19,600	33,353	27,573	3,695	-81,346	-81,903	62.497
600	19,900	36,964	27,180	5,670	-76,670	-77,381	62.086
700	20,200	40,054	26,803	7,675	-71,977	-72,723	61.675
800	20,500	42,771	30,383	9,910	-67,260	-68,038	61.264
900	20,800	45,202	31,897	11,870	-62,530	-63,336	60.853
1000	21,100	47,459	33,339	14,070	-57,796	-58,631	60.442
1100	21,400	49,435	34,712	16,195	-53,058	-53,922	60.031
1200	21,700	51,359	36,018	18,350	-48,315	-49,207	59.620
1300	22,000	53,058	37,262	20,535	-43,568	-44,489	59.209
1400	22,300	54,700	38,484	22,750	-38,815	-39,777	58.797
1500	22,600	56,288	39,585	24,995	-34,058	-35,062	58.386
1600	22,900	57,716	40,673	27,270	-29,298	-30,222	57.975
1700	23,200	59,114	41,717	29,575	-24,535	-25,369	57.564
1800	23,500	60,488	42,721	31,910	-19,768	-20,633	57.153
1900	23,800	61,827	43,687	34,275	-14,998	-15,886	56.742
2000	24,100	63,135	44,620	36,670	-10,225	-11,082	56.331

December 31, 1960.

Na₂SDISODIUM SULFIDE (Na₂S) (Solid)

Mol. Wt. = 78.048

ΔH_f^{298.15} = -89 kcal. mole⁻¹S_{298.15}^{298.15} = 23.4 cal. deg.⁻¹ mole⁻¹T_m = 1223°K.ΔH_m = 16 kcal. mole⁻¹

ΔH_f^{298.15}, T_m^a, and ΔH_m from National Bureau of Standards Circular 500 (1952). S_{298.15} calculated from ΔH_f^{298.15} as reported by N. A. Landiya, Zhur. Fiz. Khim. 24, 257 (1950). C_p estimated.

Na₂S

Disodium Sulfide (Na₂S)

(Liquid) Mol. Wt. = 78.048

INTERIM TABLE

T, °K.	C _p	S°	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	ΔH _f [°]	ΔF _f [°]	Log K _p
0							
100	17.618	24.136		.000	= 87.870	= 85.458	62.639
200	17.666	24.283		1.033	= 87.871	= 85.441	62.291
300	19.445	24.603		3.493	= 87.872	= 85.439	61.943
400	20.341	24.822		5.955	= 87.872	= 85.437	61.595
500	20.648	24.956		8.056	= 87.872	= 85.436	61.247
600	21.162	25.036		10.183	= 87.872	= 85.435	60.899
700	21.366	25.065		12.328	= 87.872	= 85.434	60.551
800	21.511	25.081		14.484	= 87.872	= 85.433	60.203
900	21.614	25.088		16.650	= 87.872	= 85.432	59.855
1000	21.690	25.090		18.822	= 87.872	= 85.431	59.507
1100	21.748	25.091		20.999	= 87.872	= 85.430	59.159
1200	21.788	25.092		23.180	= 87.872	= 85.429	58.811
1300	21.810	25.093		25.365	= 87.872	= 85.428	58.463
1400	21.826	25.094		27.552	= 87.872	= 85.427	58.115
1500	21.838	25.095		29.741	= 87.872	= 85.426	57.767
1600	21.848	25.096		31.933	= 87.872	= 85.425	57.419
1700	21.856	25.097		34.126	= 87.872	= 85.424	57.071
1800	21.863	25.098		36.319	= 87.872	= 85.423	56.723
1900	21.869	25.099		38.515	= 87.872	= 85.422	56.375
2000	21.874	25.100		40.711	= 87.872	= 85.421	56.027
2100	21.878	25.101		42.908	= 87.872	= 85.420	55.679
2200	21.882	25.102		45.105	= 87.872	= 85.419	55.331
2300	21.886	25.103		47.304	= 87.872	= 85.418	54.983
2400	21.889	25.104		49.503	= 87.872	= 85.417	54.635
2500	21.892	25.105		51.702	= 87.872	= 85.416	54.287
2600	21.895	25.106		53.902	= 87.872	= 85.415	53.939
2700	21.898	25.107		56.103	= 87.872	= 85.414	53.591
2800	21.901	25.108		58.304	= 87.872	= 85.413	53.243
2900	21.904	25.109		60.506	= 87.872	= 85.412	52.895
3000	21.907	25.110		62.709	= 87.872	= 85.411	52.547

DISODIUM SULFIDE (Na₂S) (Liquid)

Mol. Wt. = 78.048

ΔH_f[°] 298.15 = [-87.870] kcal. mole⁻¹S_{298.15} = [24.136] cal. deg.⁻¹ mole⁻¹T_m = 1223°K.ΔH_m = 16 kcal. mole⁻¹

T_m and ΔH_m from National Bureau of Standards Circular 500 (1952).
Other data estimated.

Na₂S

December 31, 1960.

Oxygen, Monatomic (0)

(Ideal Gas) At. Wt. = 16.000

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH° _f	ΔF°	Log K _p
0	∞	∞	∞	58,989	58,989	INFINITE
100	5.666	32.466	1,080	58,160	57,989	-126.730
200	5.834	36.340	4,523	56,733	56,177	-61.962
298	5.823	36.468	5,000	56,339	55,339	-40.604
300	5.235	38.501	5,010	55,369	54,369	-40.334
400	5.135	39.981	5,288	53,725	52,725	-29.473
500	5.081	41.131	5,605	52,485	51,485	-22.940
600	5.029	42.034	5,940	51,508	50,508	-18.574
700	5.029	42.631	6,283	50,908	49,908	-15.486
800	5.015	43.501	6,631	50,516	49,516	-13.101
900	5.006	44.092	6,971	50,311	49,311	-11.272
1000	4.999	44.619	7,302	50,167	49,167	-9.807
1100	4.994	45.095	7,624	50,098	49,098	-8.604
1200	4.990	45.529	7,939	50,053	49,053	-7.604
1300	4.987	45.926	8,248	50,023	49,023	-6.755
1400	4.984	46.298	8,548	50,000	49,000	-6.037
1500	4.982	46.642	8,834	50,000	49,000	-5.395
1600	4.981	46.963	9,107	50,012	49,012	-4.822
1700	4.979	47.265	9,367	50,027	49,027	-4.318
1800	4.978	47.550	9,613	50,042	49,042	-3.878
1900	4.978	47.819	9,846	50,058	49,058	-3.509
2000	4.978	48.074	10,066	50,074	49,074	-3.178
2100	4.974	48.317	10,274	50,090	49,090	-2.880
2200	4.974	48.549	10,471	50,106	49,106	-2.611
2300	4.970	48.770	10,657	50,122	49,122	-2.367
2400	4.964	48.974	10,832	50,137	49,137	-2.147
2500	4.954	49.155	11,000	50,151	49,151	-1.947
2600	4.940	49.301	11,152	50,164	49,164	-1.764
2700	4.920	49.509	11,294	50,176	49,176	-1.597
2800	4.900	49.751	11,426	50,187	49,187	-1.454
2900	4.879	49.926	11,548	50,197	49,197	-1.328
3000	4.856	50.036	11,661	50,206	49,206	-1.216
3100	4.830	50.280	11,766	50,214	49,214	-1.116
3200	4.805	50.524	11,862	50,221	49,221	-1.026
3300	4.781	50.724	11,950	50,227	49,227	-0.943
3400	4.758	50.874	12,031	50,232	49,232	-0.867
3500	4.734	51.019	12,106	50,236	49,236	-0.797
3600	4.710	51.152	12,176	50,239	49,239	-0.732
3700	4.686	51.274	12,241	50,241	49,241	-0.671
3800	4.661	51.385	12,301	50,242	49,242	-0.613
3900	4.636	51.487	12,356	50,242	49,242	-0.558
4000	4.611	51.580	12,406	50,241	49,241	-0.506
4100	4.586	51.664	12,451	50,239	49,239	-0.456
4200	4.561	51.739	12,491	50,236	49,236	-0.408
4300	4.536	51.805	12,526	50,232	49,232	-0.363
4400	4.511	51.862	12,556	50,227	49,227	-0.320
4500	4.486	51.910	12,581	50,221	49,221	-0.278
4600	4.461	51.949	12,601	50,214	49,214	-0.237
4700	4.436	51.979	12,616	50,206	49,206	-0.197
4800	4.411	51.999	12,626	50,200	49,200	-0.158
4900	4.386	52.010	12,631	50,193	49,193	-0.120
5000	4.361	52.014	12,633	50,186	49,186	-0.083
5100	4.336	52.012	12,631	50,178	49,178	-0.048
5200	4.311	52.005	12,626	50,169	49,169	-0.015
5300	4.286	51.994	12,616	50,159	49,159	0.016
5400	4.261	51.979	12,601	50,148	49,148	0.041
5500	4.236	51.959	12,581	50,136	49,136	0.066
5600	4.211	51.934	12,556	50,123	49,123	0.091
5700	4.186	51.904	12,526	50,109	49,109	0.116
5800	4.161	51.869	12,491	50,094	49,094	0.141
5900	4.136	51.829	12,451	50,078	49,078	0.166
6000	4.111	51.784	12,406	50,061	49,061	0.191

OXYGEN, MONATOMIC (0) (IDEAL GAS) AT. WT. = 16.000

ΔH°_f = 58.989 kcal. mole⁻¹
 ΔH°_f 298.15 = 59.559 ± 0.03 kcal. mole⁻¹
 S°_{298.15} = 38.47 cal. deg.⁻¹ mole⁻¹

Electronic Levels and Multiplicities	E ₁ , cm. ⁻¹	E ₂ , cm. ⁻¹	E ₃ , cm. ⁻¹	E ₄ , cm. ⁻¹
Ground State Configuration 3P ₂	0.0	5	5	5
	158.5	3	3	3
	226.5	1	1	1
	15,867.7	5	5	5
	33,782.4	1	1	1
				105,000.0

Heat of Formation.

P. Brix and G. Herzberg, Can. J. Phys. 32, 110 (1954), observed 21 bands in the transition $X^3\Sigma^- \rightarrow B^3\Sigma^-$. The Birge-Sponer extrapolation to the dissociation products $3P_2 + 1D_2$ was corrected to the zero levels, $3P_2 + 5P_2$, to give the dissociation energy 41260 ± 15 cm.⁻¹. This is in agreement with the extrapolation of the band heads of the $X^3\Sigma^- \rightarrow A^3\Sigma^+$ transition which goes to the normal products. The extrapolation of the B level is very small, the lowest $\Delta G_{1/2}$ is 34 cm.⁻¹

Heat Capacity and Entropy.

The electronic levels from C. E. Moore, Nat. Bur. Standards, Circ. 467, (1949), were averaged above 80,000 cm.⁻¹

Oxygen Uninegative Ion (O⁻)

(Ideal Gas) Mol. Wt. = 15.99995

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0								
100	37.712	37.712	37.712	0.00	24.300	21.849	-16.015	
200	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
298	37.712	37.712	37.712	0.010	24.294	21.834	-15.905	
300	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
400	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
500	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
600	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
700	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
800	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
900	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1000	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1100	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1200	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1300	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1400	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1500	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1600	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1700	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1800	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
1900	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2000	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2100	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2200	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2300	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2400	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2500	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2600	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2700	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2800	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
2900	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3000	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3100	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3200	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3300	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3400	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3500	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3600	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3700	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3800	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
3900	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4000	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4100	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4200	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4300	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4400	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4500	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4600	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4700	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4800	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
4900	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5000	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5100	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5200	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5300	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5400	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5500	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5600	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5700	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5800	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
5900	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	
6000	37.743	37.743	37.743	0.010	24.294	21.834	-15.905	

June 30, 1965

OXYGEN UNINEGATIVE ION (O⁻)

(IDEAL GAS)

Ground State Configuration $2p^3/2$
 $S_{298.15}^\circ = 37.712 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ = 25.2 \pm .5 \text{ kcal/mole}$
 $\Delta F_f^\circ = 24.3 \pm .5 \text{ kcal/mole}$

Electronic Levels and Quantum Weight

\mathcal{E}_i , cm. ⁻¹	$\frac{\mathcal{E}_i}{4}$
0.0	0.0
[180.0]	2

Heat of Formation.

The heat of formation was calculated from the equation: $O(g) + e^- \rightarrow O^-(g)$ with the JANAP auxiliary value for $O(g)$; using the measured electron affinity = 1.465 e.v. (33.783 kcal/mole) obtained from L. M. Branscomb, D. S. Burch, S. J. Smith and S. Guleman, Phys. Rev. **111**, 504 (1958). Other calculated values for the electron affinity are: 1.22 e.v. E. Clementi and A. D. McLean, Phys. Rev. **133**, 4419 (1964); 1.16 e.v. E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, Phys. Rev. **133**, A1274 (1964); and 1.47 e.v. B. Edlén, J. Chem. Phys. **33**, 98 (1960).

Heat Capacity and Entropy.

The electronic levels and quantum weights were estimated by assuming that the extra electron would produce an electronic structure similar to the next higher atomic numbered element, in this case F(I). An analogy was then made between O^- and F(I) with $O(I)$ and F(II), and $O(II)$ and F(III) in order to estimate the height of the first level above the ground state. The data for F(I), O(I), F(II), O(II) and F(III) were obtained from C. E. Moore, "Atomic Energy Levels", Vol. I, Circular of the National Bureau of Standards 467, June 15, 1949. It is possible that the entropy below 3000°K. could be in error by 0.5 e.v. due to the estimation of the low lying electronic level. The electronic levels above $1 \times 10^5 \text{ cm.}^{-1}$ were omitted because their contribution is negligible below 6000°K. The $H^\circ - H_{298}^\circ$ value at 0°K. is -1.567 kcal/mole.

Phosphorus Monoxide (P0)

INTERIM TABLE

Mol. Wt. = 46.975

(Ideal Gas)	Mol. Wt. = 46.970	cal. mole ⁻¹ deg. ⁻¹						kcal. mole ⁻¹					
T, °K.	C _p ^o	S ^o	(F° - H ₂₉₈ °)/T	H° - H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p						
0	∞	∞	∞	2.285	1.801	∞	∞						
100	7.192	46.781	60.037	1.245	1.510	1.901	INFINITE						
200	7.693	50.177	53.914	.767	1.407	6.096	6.256						
298	7.587	53.219	53.219	.000	1.455	6.096	6.661						
300	7.588	53.266	53.219	.014	1.456	6.096	6.661						
400	7.724	55.404	55.404	.776	1.580	10.742	5.669						
500	7.931	57.210	57.210	1.561	1.734	13.016	5.089						
600	8.126	58.673	58.673	2.364	1.910	15.257	4.557						
700	8.287	59.938	59.938	3.185	2.110	17.465	4.053						
800	8.415	61.054	61.054	4.020	2.332	19.629	3.577						
900	8.516	62.051	62.051	4.867	2.583	21.762	3.130						
1000	8.597	62.953	62.953	5.730	2.862	23.867	2.712						
1100	8.662	63.775	63.775	6.596	3.166	25.953	2.320						
1200	8.715	64.531	64.531	7.455	3.492	28.030	1.952						
1300	8.759	65.230	65.230	8.309	3.839	30.100	1.604						
1400	8.796	65.881	65.881	9.156	4.206	32.161	1.271						
1500	8.827	66.489	66.489	10.000	4.592	34.217	0.952						
1600	8.854	67.059	67.059	10.842	5.000	36.267	0.646						
1700	8.878	67.597	67.597	11.678	5.429	38.312	0.352						
1800	8.899	68.105	68.105	12.513	5.878	40.353	0.069						
1900	8.917	68.587	68.587	13.348	6.346	42.390	-0.212						
2000	8.934	69.044	69.044	14.183	6.834	44.422	-0.496						
2100	8.949	69.481	69.481	15.018	7.342	46.449	-0.784						
2200	8.963	69.897	69.897	15.853	7.870	48.471	-1.074						
2300	8.976	70.296	70.296	16.688	8.418	50.489	-1.366						
2400	8.988	70.678	70.678	17.523	8.986	52.503	-1.660						
2500	8.999	71.045	71.045	18.358	9.574	54.513	-1.956						
2600	9.010	71.399	71.399	19.193	10.182	56.519	-2.254						
2700	9.020	71.739	71.739	20.028	10.810	58.521	-2.552						
2800	9.029	72.067	72.067	20.863	11.458	60.521	-2.850						
2900	9.036	72.384	72.384	21.698	12.126	62.519	-3.148						
3000	9.047	72.691	72.691	22.532	12.814	64.515	-3.446						
3100	9.056	72.987	72.987	23.367	13.522	66.509	-3.744						
3200	9.064	73.275	73.275	24.201	14.250	68.500	-4.042						
3300	9.071	73.554	73.554	25.036	15.000	70.488	-4.340						
3400	9.079	73.825	73.825	25.871	15.770	72.473	-4.638						
3500	9.086	74.088	74.088	26.706	16.560	74.455	-4.936						
3600	9.094	74.344	74.344	27.541	17.370	76.433	-5.234						
3700	9.101	74.594	74.594	28.376	18.200	78.409	-5.532						
3800	9.108	74.836	74.836	29.211	19.050	80.383	-5.830						
3900	9.115	75.073	75.073	30.046	19.920	82.355	-6.128						
4000	9.121	75.304	75.304	30.881	20.810	84.325	-6.426						
4100	9.128	75.529	75.529	31.716	21.720	86.293	-6.724						
4200	9.134	75.749	75.749	32.551	22.650	88.258	-7.022						
4300	9.141	75.964	75.964	33.386	23.600	90.220	-7.320						
4400	9.147	76.174	76.174	34.221	24.570	92.179	-7.618						
4500	9.153	76.380	76.380	35.056	25.560	94.135	-7.916						
4600	9.159	76.581	76.581	35.897	26.570	96.088	-8.214						
4700	9.165	76.778	76.778	36.740	27.600	98.038	-8.512						
4800	9.172	76.971	76.971	37.583	28.650	100.000	-8.810						
4900	9.178	77.161	77.161	38.426	29.720	101.961	-9.108						
5000	9.183	77.346	77.346	39.269	30.810	103.919	-9.406						
5100	9.189	77.528	77.528	40.112	31.920	105.874	-9.704						
5200	9.195	77.704	77.704	40.955	33.050	107.826	-10.002						
5300	9.201	77.882	77.882	41.798	34.200	109.775	-10.300						
5400	9.207	78.054	78.054	42.641	35.370	111.721	-10.598						
5500	9.213	78.223	78.223	43.484	36.560	113.664	-10.896						
5600	9.218	78.389	78.389	44.327	37.770	115.604	-11.194						
5700	9.224	78.552	78.552	45.170	39.000	117.541	-11.492						
5800	9.230	78.712	78.712	46.013	40.250	119.475	-11.790						
5900	9.235	78.870	78.870	46.856	41.520	121.406	-12.088						
6000	9.241	79.026	79.026	47.699	42.810	123.333	-12.386						

December 31, 1950.

Phosphorus Monoxide (P0)

(Ideal Gas)

Mol. Wt. = 46.975

 ΔH_f° 298.15 = -1.46 ± 2 kcal. mole⁻¹ $S_{298.15}^\circ$ = 53.22 cal. deg.⁻¹ mole⁻¹Ground State Configuration 2Π

Electronic Levels and Multiplicities

 ϵ_i , cm.⁻¹ g_i $\omega_e = 1233.42$ cm.⁻¹ $\omega_e x_e = 6.57$ cm.⁻¹ $\alpha_e = 0.0055$ cm.⁻¹ $r_e = 1.475$ Å

Heat of formation based upon a dissociation energy of 49,000 cm.⁻¹, which is the value of two predissociations observed by K. Dressler, Helv. Phys. Acta 29, 563 (1955).

Heat Capacities and Entropies. Molecular and spectroscopic constants based upon measurements of K. Dressler, loc. cit., K. S. Rao, Can. J. Phys. 36, 1526 (1958), and those of N. L. Singh, Can. J. Phys. 37, 136 (1959).

INTERIM TABLE

(Crystal) Mol. Wt. = 223.21

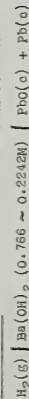
T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈)/T cal. mole ⁻¹	H°-H ₂₉₈ cal. mole ⁻¹	ΔH _f ^o cal. mole ⁻¹	ΔF _f ^o cal. mole ⁻¹	Log K _p
0	0.000	INFINITE	= 2.177	= 51.903	= 51.903	INFINITE
100	0.422	5.916	1.816	= 52.275	= 42.668	23.312
200	1.139	15.552	1.015	= 52.461	= 47.541	51.968
298	10.943	15.552	1.000	= 52.407	= 45.134	33.082
300	10.960	15.552	1.020	= 52.405	= 45.089	32.866
400	11.760	16.928	1.158	= 52.275	= 42.668	23.312
500	12.420	21.626	2.368	= 52.103	= 40.260	17.606
600	12.970	23.940	3.639	= 51.900	= 37.941	13.819
700	13.400	25.974	4.959	= 52.440	= 35.451	11.055
800	13.800	27.769	6.318	= 52.600	= 32.972	9.007
900	14.200	29.438	7.718	= 52.321	= 30.535	7.415
1000	14.600	30.934	9.158	= 52.000	= 28.131	6.166
1100	15.000	32.365	10.638	= 51.639	= 25.761	5.118
1200	15.400	33.687	12.158	= 51.234	= 23.425	4.266
1300	15.800	34.935	13.718	= 50.788	= 21.126	3.551
1400	16.200	36.121	15.318	= 50.305	= 18.863	2.953
1500	16.600	37.252	16.958	= 49.785	= 16.634	2.463
1600	17.000	38.336	18.638	= 49.230	= 14.442	1.973
1700	17.400	39.379	20.358	= 48.640	= 12.285	1.579
1800	17.800	40.385	22.118	= 48.019	= 10.165	1.234
1900	18.200	41.358	23.918	= 47.364	= 8.081	0.929
2000	18.600	42.302	25.758	= 46.677	= 6.031	0.659
2100	19.000	43.219	30.038	= 44.408	= 2.463	0.256
2200	19.400	44.112	30.676	= 42.564	= 1.609	0.160
2300	19.800	44.981	31.280	= 41.703	= 0.583	0.036
2400	20.200	45.834	31.868	= 40.826	= 0.441	0.000
2500	20.600	46.667	32.444	= 40.935	= 13.398	1.169

Lead Monoxide, Red (PbO) (Crystal)

Mol. Wt. = 223.21

 ΔH_f^o 298.15 = -52.41 ± 0.16 kcal. mole⁻¹ $S_{298.15}^o$ = 15.6 ± 0.2 cal. deg.⁻¹ mole⁻¹ ΔH_f^o 298.15 = 63.88 ± 0.22 kcal. mole⁻¹ T_f = 762°K ΔH_f^o = 0.18 ± 0.23 kcal. mole⁻¹

Heat of Formation. Calculated from the cell reaction



reported by D. P. Smith and H. K. Woods, J. Am. Chem. Soc., 45, 2632 (1923), using ΔH_f^o 298.15 for $H_2O(l)$, -68.317 kcal. mole⁻¹, given by Natl. Bur. Standards Circular 500 (1952). ΔH_f^o values reported by other investigators were discussed by R. W. Millar, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. Heat capacity values (51° to 298.15°K) were obtained from E. O. King, J. Am. Chem. Soc., 80, 2400 (1958).

For the higher temperature range, heat capacity given by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960) was used and joined smoothly to data of King at 298.15°K by graphical extrapolation. King obtained entropies below 51°K by empirical extrapolation of the heat capacity curve which fits the measured heat capacities within 1.3%.

Transition Data. Heat of transition recalculated from the data given by E. O. King, loc. cit.

Heat of Sublimation. Calculated from free-energy functions and vapor pressure reported by A. N. Nemeyanov, L. P. Firova and E. P. Isakova, Zhur. Fiz. Khim. 34, 1699 (1960) and R. H6rbe and O. Knacke, Z. Erzhbergbau u. Metallhutenw. 12, 321 (1959).

March 31, 1962

Lead Monoxide, Yellow (PbO)
(Crystal) Mol. Wt. = 223.21

INTERIM TABLE

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	(H° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ^o	ΔH _f ^o	Log K _p
0	0.000	INFINITE	-	-	-	-	-	-
100	6.524	6.352	16.642	2.209	-	51.598	51.598	INFINITE
200	9.720	11.990	17.080	-	1.018	52.013	49.992	108.596
298	10.956	16.114	16.114	0.000	0.000	52.125	47.305	31.650
300	10.970	16.182	16.114	0.020	0.000	52.066	44.949	32.947
400	11.631	19.433	16.533	1.552	52.044	52.044	44.905	32.711
500	12.094	22.080	17.402	2.339	51.991	51.991	42.535	25.239
600	12.469	24.319	18.373	3.568	51.630	37.498	40.202	17.571
700	12.603	26.159	19.352	4.832	51.623	35.822	38.804	13.804
800	12.655	27.657	20.327	6.141	51.623	35.822	37.498	10.002
900	12.631	28.887	21.296	7.453	52.245	30.567	36.156	7.453
1000	12.567	29.956	22.177	8.809	52.009	28.170	34.804	5.126
1100	12.475	30.906	23.039	10.194	51.742	25.800	33.453	4.271
1200	12.355	31.735	23.882	11.607	51.444	23.453	32.104	3.553
1300	12.208	32.481	24.604	13.048	51.114	21.134	30.757	2.931
1400	12.033	33.149	25.211	14.518	50.756	18.866	29.410	2.405
1500	11.833	33.738	25.698	16.015	50.367	16.573	28.067	1.958
1600	11.606	34.254	26.162	17.540	49.957	14.332	26.724	1.588
1700	11.355	34.705	26.604	19.092	49.525	12.116	25.381	1.285
1800	11.082	35.098	27.021	20.672	49.072	9.927	24.038	1.042
1900	10.790	35.431	27.414	22.284	48.600	7.774	22.695	0.842
2000	10.483	35.705	27.780	23.914	48.101	5.622	21.352	0.644
2100	10.156	35.927	28.126	25.576	47.576	3.470	20.009	0.453
2200	9.819	36.092	28.454	27.265	47.026	1.318	18.666	0.272
2300	9.472	36.205	28.762	28.982	46.453	-0.836	17.323	0.107
2400	9.115	36.267	29.048	30.726	45.858	-2.986	15.980	0.000
2500	8.747	36.172	29.172	32.497	45.245	-5.133	14.637	-0.128
2600	8.369	36.025	29.230	34.295	44.618	-7.280	13.294	-0.272
2700	7.981	35.835	29.226	36.120	43.976	-9.422	11.951	-0.428
2800	7.583	35.603	29.158	37.973	43.323	-11.559	10.608	-0.594
2900	7.176	35.331	29.025	39.846	42.558	-13.692	9.265	-0.769
3000	6.759	34.924	28.828	41.736	41.679	-15.819	7.922	-0.951
3100	6.331	34.381	28.564	43.642	40.586	-17.936	6.579	-1.138
3200	5.893	33.705	28.231	45.564	39.281	-20.042	5.236	-1.331
3300	5.445	32.905	27.831	47.500	37.766	-22.136	3.893	-1.528
3400	4.987	31.980	27.262	49.454	36.041	-24.218	2.550	-1.728
3500	4.519	30.931	26.527	51.424	34.106	-26.286	1.207	-1.928
3600	4.041	29.756	25.536	53.408	31.961	-28.339	-0.136	-2.128
3700	3.553	28.454	24.291	55.406	29.606	-30.376	-1.479	-2.328
3800	3.055	27.031	22.796	57.418	27.041	-32.396	-2.822	-2.528
3900	2.547	25.486	21.051	59.444	24.266	-34.399	-4.165	-2.728
4000	2.029	23.821	19.056	61.484	21.281	-36.384	-5.508	-2.928
4100	1.501	22.036	16.801	63.538	18.086	-38.351	-6.849	-3.128
4200	0.963	20.121	14.296	65.606	14.681	-40.291	-8.186	-3.328
4300	0.415	18.086	11.451	67.688	11.066	-42.204	-9.519	-3.528
4400	-0.143	15.931	8.276	69.784	7.251	-44.091	-10.846	-3.728
4500	-0.691	13.656	4.771	71.894	3.236	-45.941	-12.169	-3.928
4600	-1.229	11.271	0.946	74.018	-0.979	-47.761	-13.486	-4.128
4700	-1.757	8.786	-3.199	76.156	-5.004	-49.551	-14.799	-4.328
4800	-2.275	6.201	-6.524	78.308	-9.029	-51.311	-16.106	-4.528
4900	-2.783	3.516	-9.849	80.474	-13.044	-53.041	-17.409	-4.728
5000	-3.281	0.731	-13.164	82.654	-17.049	-54.741	-18.706	-4.928

March 31, 1952

Lead Monoxide, Yellow (PbO) (Crystal)

Mol. Wt. = 223.21
 ΔH_f^o 298.15 = -52.07 ± 0.28 kcal. mole⁻¹
 $S_{298.15}^o$ = 16.1 ± 0.2 cal. deg⁻¹ mole⁻¹
 ΔH_s^o 298.15 = 63.54 ± 0.32 kcal. mole⁻¹
 T_m = 1170 ± 4°K.
 ΔH_m^o = 6.1 ± 0.1 kcal. mole⁻¹

Heat of Formation. Calculated from ΔH_f^o 298.15 for PbO (c, red) and ΔH_m^o 298.15 between PbO (c, red) and PbO (c, yellow).

Heat Capacity, Entropy, and Melting Data. C_p values (51° to 298.15°K.) obtained from E. G. King, J. Am. Chem. Soc., 80, 2400 (1958). For the higher temperature range, the heat capacity reported by E. N. Rodigina, K. Z. Gorn'skii and V. F. Luginina, Zhur. Fiz. Khim., 35, 1799 (1961) was used and joined smoothly to data of King at 298.15°K. by graphical extrapolation. T_m and ΔH_m^o given by E. N. Rodigina, K. Z. Gorn'skii and V. F. Luginina, loc. cit.

Heat of Sublimation. Calculated from ΔH_f^o 298.15 and ΔH_s^o 298.15 for PbO (c, red).

INTERIM TABLE

(Liquid) Mol. Wt. = 223.21

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	$-(F^{\circ}-H_{298}^{\circ})/T$	cal. mole ⁻¹	ΔH_f°	ΔF_f°	Log K _p
100								
200	10.950	20.546		.000	- 46.712	- 40.916		29.991
250		20.614	20.546		- 46.710	- 40.880		29.780
300	10.970	20.614	20.585	1.020	- 46.586	- 40.823		29.583
350	11.000	20.614	20.614	2.040	- 46.437	- 40.740		29.396
400	12.469	28.752	27.805	3.568	- 46.276	- 40.624		29.222
450	12.802	30.700	29.797	4.832	- 47.271	- 41.581		29.059
500	13.535	32.492	31.772	6.117	- 48.048	- 42.418		28.906
550	14.109	34.165	33.258	7.410	- 48.618	- 43.023		28.769
600	14.535	35.758	34.674	8.704	- 48.980	- 43.414		28.646
650	14.850	37.287	36.127	10.000	- 49.147	- 43.599		28.534
700	15.070	38.761	37.539	11.300	- 49.147	- 43.599		28.432
750	15.200	40.185	38.900	12.600	- 48.980	- 43.414		28.339
800	15.335	41.565	40.217	13.900	- 48.618	- 43.023		28.254
850	15.470	42.900	41.490	15.200	- 48.048	- 42.418		28.176
900	15.600	44.185	42.717	16.500	- 47.271	- 41.581		28.104
950	15.735	45.420	43.880	17.800	- 46.276	- 40.624		28.046
1000	15.870	46.614	44.997	19.100	- 45.048	- 39.540		27.999
1050	16.000	47.761	46.070	20.400	- 43.586	- 38.275		27.962
1100	16.135	48.865	47.100	21.700	- 41.922	- 36.832		27.932
1150	16.270	49.920	48.080	23.000	- 40.048	- 35.237		27.906
1200	16.400	50.930	48.920	24.300	- 37.959	- 33.501		27.882
1250	16.535	51.890	49.630	25.600	- 35.693	- 31.666		27.858
1300	16.670	52.800	50.210	26.900	- 33.262	- 29.682		27.834
1350	16.800	53.660	50.670	28.200	- 30.680	- 27.580		27.809
1400	16.935	54.470	51.000	29.500	- 27.959	- 25.299		27.784
1450	17.070	55.230	51.210	30.800	- 25.080	- 22.860		27.759
1500	17.200	55.950	51.300	32.100	- 22.040	- 20.290		27.734
1550	17.335	56.630	51.280	33.400	- 18.840	- 17.610		27.709
1600	17.470	57.260	51.150	34.700	- 15.480	- 14.830		27.684
1650	17.600	57.850	50.900	36.000	- 11.960	- 11.040		27.659
1700	17.735	58.390	50.530	37.300	- 8.290	- 7.250		27.634
1750	17.870	58.880	50.050	38.600	- 4.570	- 3.460		27.609
1800	18.000	59.320	49.460	40.000	- 0.800	- 0.690		27.584
1850	18.135	59.710	48.760	41.400	2.910	1.810		27.559
1900	18.270	60.050	47.950	42.800	5.540	4.440		27.534
1950	18.400	60.340	47.030	44.200	8.170	7.070		27.509
2000	18.535	60.580	46.000	45.600	10.800	9.700		27.484
2050	18.670	60.770	44.860	47.000	13.430	12.330		27.459
2100	18.800	60.920	43.610	48.400	16.060	14.960		27.434
2150	18.935	61.030	42.250	49.800	18.690	17.590		27.409
2200	19.070	61.100	40.780	51.200	21.320	20.220		27.384
2250	19.200	61.130	39.110	52.600	23.950	22.850		27.359
2300	19.335	61.120	37.740	54.000	26.580	25.480		27.334
2350	19.470	61.070	36.570	55.400	29.210	28.110		27.309
2400	19.600	60.980	35.600	56.800	31.840	30.740		27.284
2450	19.735	60.850	34.830	58.200	34.470	33.370		27.259
2500	19.870	60.680	34.260	59.600	37.100	36.000		27.234
2550	20.000	60.470	33.890	61.000	39.730	38.630		27.209
2600	20.135	60.220	33.620	62.400	42.360	41.260		27.184
2650	20.270	60.030	33.450	63.800	45.000	43.900		27.159
2700	20.400	59.800	33.380	65.200	47.630	46.530		27.134
2750	20.535	59.630	33.410	66.600	50.260	49.160		27.109
2800	20.670	59.530	33.540	68.000	52.890	51.790		27.084
2850	20.800	59.400	33.770	69.400	55.520	54.420		27.059
2900	20.935	59.340	34.100	70.800	58.150	57.050		27.034
2950	21.070	59.350	34.630	72.200	60.780	59.680		27.009
3000	21.200	59.420	35.360	73.600	63.410	62.310		26.984

March 31, 1962

Lead Monoxide (PbO) (Liquid)

Mol. Wt. = 223.21
 $\Delta H_f^{\circ} 298.15 = [-46.712] \text{ kcal. mole}^{-1}$
 $S^{\circ} 298.15 = [20.546] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1170 \pm 4^{\circ}\text{K.}$
 $\Delta H_m^{\circ} = 6.1 \pm 0.1 \text{ kcal. mole}^{-1}$
 $T_b = 1789^{\circ}\text{K.}$
 $\Delta H_v^{\circ} = 49.53 \pm 0.22 \text{ kcal. mole}^{-1}$

Heat of Formation. Calculated from that of the crystal.

Heat Capacity, Entropy, and Melting Data. C_p , T_m , and ΔH_m° are obtained from E. N. Rodigina, K. Z. Gmel'skii and V. P. Luginina, Zhur. Fiz. Khim., **35**, 1799 (1961). The reported heat capacity is extrapolated to an assumed glass transition temperature of 780°K., below which the heat capacity is taken to be equal to that of the crystal, PbO (c, red).

Vaporization Phenomena. T_b and ΔH_v° calculated from $\Delta H_f^{\circ} 298.15$ for PbO (c, red) and functions for condensed and gaseous states.

Lead Monoxide (PbO)

(Ideal Gas) Mol. Wt. = 223.21 INTERIM TABLE

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H ₂₉₈)/T	H°-H ₂₉₈ kcal. mole ⁻¹	ΔF° _T	Log K _p
0	4.000	INFINITE	2.142	12.017	INFINITE
100	6.964	49.455	1.946	12.017	21.731
200	7.272	51.916	1.844	11.933	21.731
298	7.366	52.941	1.784	11.877	4.619
300	7.776	57.395	1.742	11.873	4.567
400	8.155	59.687	1.612	11.263	4.566
500	8.400	61.535	1.441	11.053	2.915
600	8.560	63.082	1.249	10.834	1.309
700	8.670	64.410	1.042	9.437	0.022
800	8.748	65.573	0.825	9.186	1.412
900	8.806	66.607	0.600	8.945	2.722
1000	8.850	67.537	0.373	8.709	4.005
1100	8.886	68.383	0.147	8.477	5.266
1200	8.915	69.157	0.000	8.252	6.504
1300	8.940	69.872	-0.166	8.030	7.725
1400	8.962	70.535	-0.331	7.809	8.929
1500	8.980	71.154	-0.494	7.586	10.115
1600	8.997	71.734	-0.654	7.360	11.289
1700	9.013	72.280	-0.807	7.130	12.447
1800	9.027	72.796	-0.952	6.894	13.593
1900	9.040	73.284	-1.089	6.651	14.725
2000	9.052	73.748	-1.219	6.403	15.843
2100	9.064	74.190	-1.343	6.150	16.946
2200	9.075	74.612	-1.462	5.897	18.036
2300	9.086	75.016	-1.576	5.644	19.112
2400	9.096	75.402	-1.684	5.391	20.175
2500	9.106	75.774	-1.787	5.138	21.225
2600	9.116	76.131	-1.884	4.884	22.262
2700	9.126	76.476	-1.976	4.630	23.287
2800	9.135	76.808	-2.062	4.376	24.301
2900	9.144	77.128	-2.143	4.122	25.294
3000	9.153	77.438	-2.219	3.868	26.276
3100	9.162	77.739	-2.290	3.614	27.247
3200	9.171	78.030	-2.356	3.360	28.206
3300	9.180	78.312	-2.418	3.106	29.154
3400	9.188	78.586	-2.476	2.852	30.091
3500	9.197	78.853	-2.530	2.598	31.017
3600	9.205	79.112	-2.580	2.344	31.932
3700	9.214	79.364	-2.626	2.090	32.837
3800	9.222	79.610	-2.669	1.836	33.731
3900	9.230	79.850	-2.709	1.582	34.614
4000	9.238	80.084	-2.745	1.328	35.487
4100	9.247	80.312	-2.777	1.074	36.350
4200	9.255	80.535	-2.806	0.820	37.202
4300	9.263	80.753	-2.832	0.566	38.044
4400	9.271	80.966	-2.856	0.312	38.876
4500	9.279	81.174	-2.875	0.058	39.700
4600	9.287	81.378	-2.890	-0.196	40.515
4700	9.295	81.578	-2.902	-0.450	41.321
4800	9.303	81.774	-2.912	-0.704	42.118
4900	9.311	81.966	-2.919	-0.958	42.906
5000	9.319	82.154	-2.925	-1.212	43.685
5100	9.327	82.338	-2.929	-1.466	44.455
5200	9.335	82.520	-2.931	-1.720	45.216
5300	9.343	82.697	-2.934	-1.974	45.968
5400	9.351	82.872	-2.936	-2.228	46.711
5500	9.359	83.044	-2.937	-2.482	47.445
5600	9.367	83.213	-2.938	-2.736	48.170
5700	9.375	83.378	-2.939	-2.990	48.885
5800	9.382	83.542	-2.940	-3.244	49.590
5900	9.390	83.702	-2.941	-3.498	50.285
6000	9.398	83.860	-2.941	-3.752	50.970

Lead Monoxide (PbO) (Ideal Gas)

Mol. Wt. = 223.21

 $\Delta H_f^\circ 298.15 = 11.48 \pm 0.27 \text{ kcal. mole}^{-1}$ $\Delta G_f^\circ 298.15 = 57.346 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Ground State Configuration $1\sum^+$

Electronic Level and Multiplicity

$\epsilon \text{ cm.}^{-1}$	g_i
0	1

 $\omega_e = 721.8 \text{ cm.}^{-1}$ $\omega_e x_e = 3.70 \text{ cm.}^{-1}$ $\alpha'_e = 0.0019 \text{ cm.}^{-1}$ $r_e = 1.922 \text{ \AA}$ $\sigma = 1$ Heat of Formation. Calculated from $\Delta H_f^\circ 298.15$ for PbO (c, red) and $\Delta H_g^\circ 298.15$.

Heat Capacity and Entropy. The ground state configuration, molecular and spectroscopic constants are obtained from G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950), modified for the natural isotopic abundances reported by J. R. Steim and E. P. Clancy, "Chart of the Nuclides", General Electric Co., N. Y. (1956).

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	(F° - H° ₂₉₈)/T	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	∞	∞	∞	∞	∞
100	6.957	59.290	-1.392	1.640	1.640	∞
200	7.121	53.021	-0.686	1.818	2.510	0.757
298	7.212	53.021	-0.000	1.781	2.510	0.757
300	7.217	53.066	-0.013	1.637	2.510	0.757
400	7.543	53.308	0.751	1.637	2.510	0.757
500	7.846	55.903	1.521	1.637	2.510	0.757
600	8.087	58.356	2.318	1.637	2.510	0.757
700	8.272	59.617	3.137	1.637	2.510	0.757
800	8.413	60.731	3.971	1.637	2.510	0.757
900	8.520	61.728	4.818	1.637	2.510	0.757
1000	8.605	62.631	5.674	1.637	2.510	0.757
1100	8.672	63.454	6.538	1.637	2.510	0.757
1200	8.726	64.211	7.408	1.637	2.510	0.757
1300	8.770	64.911	8.283	1.637	2.510	0.757
1400	8.808	65.563	9.162	1.637	2.510	0.757
1500	8.840	66.171	10.045	1.637	2.510	0.757
1600	8.867	66.743	10.920	1.637	2.510	0.757
1700	8.891	67.281	11.798	1.637	2.510	0.757
1800	8.912	67.790	12.670	1.637	2.510	0.757
1900	8.931	68.272	13.536	1.637	2.510	0.757
2000	8.948	68.731	14.404	1.637	2.510	0.757
2100	8.963	69.168	15.269	1.637	2.510	0.757
2200	8.978	69.585	16.132	1.637	2.510	0.757
2300	8.991	69.984	16.995	1.637	2.510	0.757
2400	9.003	70.367	17.858	1.637	2.510	0.757
2500	9.015	70.735	18.720	1.637	2.510	0.757
2600	9.026	71.089	19.582	1.637	2.510	0.757
2700	9.036	71.430	20.445	1.637	2.510	0.757
2800	9.046	71.759	21.308	1.637	2.510	0.757
2900	9.056	72.076	22.171	1.637	2.510	0.757
3000	9.065	72.383	23.034	1.637	2.510	0.757
3100	9.074	72.681	23.897	1.637	2.510	0.757
3200	9.082	72.969	24.760	1.637	2.510	0.757
3300	9.090	73.248	25.623	1.637	2.510	0.757
3400	9.098	73.520	26.486	1.637	2.510	0.757
3500	9.106	73.784	27.349	1.637	2.510	0.757
3600	9.114	74.040	28.212	1.637	2.510	0.757
3700	9.121	74.290	29.075	1.637	2.510	0.757
3800	9.129	74.534	29.938	1.637	2.510	0.757
3900	9.136	74.771	30.801	1.637	2.510	0.757
4000	9.143	75.002	31.664	1.637	2.510	0.757
4100	9.150	75.228	32.527	1.637	2.510	0.757
4200	9.157	75.449	33.390	1.637	2.510	0.757
4300	9.164	75.664	34.253	1.637	2.510	0.757
4400	9.171	75.875	35.116	1.637	2.510	0.757
4500	9.178	76.081	35.979	1.637	2.510	0.757
4600	9.184	76.283	36.842	1.637	2.510	0.757
4700	9.191	76.481	37.705	1.637	2.510	0.757
4800	9.197	76.674	38.568	1.637	2.510	0.757
4900	9.204	76.864	39.431	1.637	2.510	0.757
5000	9.210	77.050	40.294	1.637	2.510	0.757
5100	9.217	77.232	41.157	1.637	2.510	0.757
5200	9.223	77.411	42.020	1.637	2.510	0.757
5300	9.230	77.587	42.883	1.637	2.510	0.757
5400	9.236	77.760	43.746	1.637	2.510	0.757
5500	9.242	77.929	44.609	1.637	2.510	0.757
5600	9.248	78.096	45.472	1.637	2.510	0.757
5700	9.255	78.259	46.335	1.637	2.510	0.757
5800	9.261	78.420	47.198	1.637	2.510	0.757
5900	9.267	78.579	48.061	1.637	2.510	0.757
6000	9.273	78.735	48.924	1.637	2.510	0.757

Dec. 31, 1980; June 30, 1981; Dec. 31, 1985

SULFUR MONOXIDE (SO)

(IDEAL GAS)

MOL. WT. = 48.0634

Ground State Configuration $3 \sum^-$
 $S_{298.15} = 53.0 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^0 = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 S_{298.15} = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{E_i \text{ cm.}^{-1}}{0} \frac{g_i}{3}$$

$\sigma = 1$
 $r_e = 1.481 \text{ \AA}$

$\omega_e = 1148.19 \text{ cm.}^{-1}$
 $\omega_e x_e = 6.116 \text{ cm.}^{-1}$
 $\alpha_e = 0.00562 \text{ cm.}^{-1}$

Heat of Formation

The dissociation energy of sulfur monoxide has been reported by following investigators:

D ₀ (SO) e.v.	(kcal. mole ⁻¹)	Investigator
5.053	(116.5)	E. V. Martin, Phys. Rev. 41 , 167 (1932).
5.184	(119.5)	A. O. Gaydon, "Dissociation Energies", Chapman & Hall Ltd. London, 1953.
4.001	(92.3)	G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company, Inc. 2nd Ed., 1950.
5.357	(123.5)	R. G. W. Norrish and G. A. Oldershaw, Proc. Roy. Soc. A249 , 498 (1959).
5.510	(127.1)	J. J. McDermott, W. D. McGrath, Proc. Roy. Soc. A278 , 490 (1964).

E. V. Martin, loc. cit., has measured the spectrum of SO(g) in the region 2400-4000 Å, and both Herzberg's and Gaydon's data were based on Martin's spectroscopic measurement. Because of the ambiguity of defining the state of excitation of the atomic products resulting from predissociation, the dissociation energy of SO was in question. Herzberg favored D_0 (SO) = 92.3 kcal. mole⁻¹ but Gaydon D_0 (SO) = 119.5 kcal. mole⁻¹.

Norrish and Oldershaw, loc. cit., redetermined the absorption spectrum of SO by flash photolysis, and also corrected Martin's original vibrational numbering, and then obtained the dissociation energy, D_0 (SO) = 123.5 kcal. mole⁻¹, based on the assumption of predissociation into S(¹D) and O(¹P). This value, D_0 = 123.5 kcal. mole⁻¹, has been selected as the dissociation energy for SO(g) and combination with JANAF values of ΔH_f^0 (S; g) and ΔH_f^0 (O; g) gives the heat of formation of sulfur monoxide, $\Delta H_f^0 S_{298} = 1.64 \pm 0.3 \text{ kcal. mole}^{-1}$, which is adopted in this tabulation.

R. Colby, P. Goldfinger and M. Jeunehomme, Trans. Faraday Soc. **60**, 306 (1964), have confirmed the selected D_0 (SO) = 123.5 kcal. mole⁻¹ in their mass spectrometric studies on the vaporization of CsS, SFS and BS. J. J. McDermott and W. D. McGrath, loc. cit., reported the dissociation energy to be 127.1 kcal. mole⁻¹ based on their ultraviolet spectroscopic studies. This value appears to be the D_0 from the minimum of the potential curve which corresponds to D_0 (SO) = 125 ± 1.5 kcal. mole⁻¹.

Besides the spectroscopic information, G. St. Pierre and J. Chipman, J. Am. Chem. Soc. **76**, 4787 (1954), have reported $\Delta H_f^0 S_{298} = -19 \text{ kcal. mole}^{-1}$ for the reaction $0.5 S_2(g) + 0.5 O_2(g) \rightarrow SO(g)$ in the equilibrium study of lime-iron oxide slags with SO₂ or SO₂-CO mixtures. Using $\Delta H_f^0 S_{298} (S_2f, g) = 30.8 \text{ kcal. mole}^{-1}$, the derived heat of formation, $\Delta H_f^0 S_{298} (SO, g) = -3.6 \text{ kcal. mole}^{-1}$ was obtained. However, this value is doubtful because the reported $\Delta H_f^0 S_{298} = -19 \text{ kcal. mole}^{-1}$ was dependent upon many assumptions and subsidiary data. E. W. Dewing and P. D. Richardson, Trans. Faraday Soc. **54**, 675(1958) have measured the equilibrium constants for the reaction $S_2(g) + 2SO(g) \rightarrow 4SO(g)$ at 1250°C. and $SO_2(g) \rightarrow SO(g) + 1/2 O_2(g)$ at 1500°C. Using the JANAF auxiliary data, the former yields $\Delta H_f^0 S_{298} (SO, g) = -19 \text{ kcal. mole}^{-1}$ and the latter -0.17 kcal. mole⁻¹, respectively. The average of these two values is $\Delta H_f^0 S_{298} = 0 \text{ kcal. mole}^{-1}$. Although D. Meschi and R. Myers, J. Mol. Spectry. **3**, 405 (1959) and U. Blukis and R. Myers, J. Phys. Chem. **69**, 1154 (1965), have certainly concluded in their microwave spectroscopic studies that the SO₂ species was one of the important products in the Sulfur - SO₂ equilibrium which was considered as unimportant by Dewing and Richardson, the value, $\Delta H_f^0 S_{298} (SO, g) = 0 \text{ kcal. mole}^{-1}$, derived from Dewing and Richardson is still very close to the selected value, $\Delta H_f^0 S_{298} (SO, g) = 1.64 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy

The molecular constants ω_e , $\omega_e x_e$ and α_e were obtained from R. Norrish and G. Oldershaw, loc. cit., and the values of r_e and B_e were recently measured in the microwave spectrum by P. X. Powell and D. R. Lide, Jr., J. Chem. Phys. **41**, 1413 (1964).

Disulfur Monoxide (S₂O)

(Ideal Gas) Mol. Wt. = 80.1274

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f kcal. mole ⁻¹	ΔF° kcal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞	∞
100	8.195	53.775	-2.660	-13.016	-13.016	INFINITE
200	9.423	72.481	-1.561	-12.902	-12.902	34.114
300	9.846	84.726	-1.002	-12.810	-12.810	34.114
380	10.344	93.796	-0.800	-12.750	-12.750	15.147
400	10.562	96.024	-0.720	-12.709	-12.709	15.086
500	12.041	69.644	-0.501	-12.572	-12.572	10.883
600	12.477	71.880	-0.408	-12.589	-12.589	9.684
700	12.766	73.828	-0.351	-12.615	-12.615	8.772
800	13.011	75.551	-0.313	-12.659	-12.659	8.066
900	13.177	77.093	-0.288	-12.710	-12.710	7.419
1000	13.303	78.488	-0.272	-12.772	-12.772	6.842
1100	13.399	79.761	-0.262	-12.843	-12.843	6.329
1200	13.475	80.930	-0.256	-12.920	-12.920	5.872
1300	13.536	82.011	-0.252	-13.002	-13.002	5.469
1400	13.585	83.016	-0.250	-13.088	-13.088	5.119
1500	13.625	83.955	-0.248	-13.178	-13.178	4.819
1600	13.658	84.835	-0.247	-13.270	-13.270	4.563
1700	13.686	85.664	-0.246	-13.363	-13.363	4.343
1800	13.709	86.447	-0.245	-13.457	-13.457	4.159
1900	13.729	87.189	-0.244	-13.552	-13.552	3.999
2000	13.747	87.893	-0.243	-13.648	-13.648	3.859
2100	13.761	88.564	-0.242	-13.744	-13.744	3.734
2200	13.774	89.205	-0.241	-13.840	-13.840	3.624
2300	13.786	89.818	-0.240	-13.936	-13.936	3.524
2400	13.796	90.404	-0.240	-14.032	-14.032	3.434
2500	13.805	90.968	-0.239	-14.128	-14.128	3.354
2600	13.813	91.503	-0.238	-14.224	-14.224	3.284
2700	13.820	92.019	-0.237	-14.320	-14.320	3.224
2800	13.826	92.514	-0.236	-14.416	-14.416	3.174
2900	13.832	93.019	-0.235	-14.512	-14.512	3.134
3000	13.837	93.498	-0.234	-14.608	-14.608	3.094
3100	13.841	93.942	-0.233	-14.704	-14.704	3.064
3200	13.846	94.361	-0.232	-14.800	-14.800	3.034
3300	13.849	94.807	-0.231	-14.896	-14.896	3.004
3400	13.853	95.221	-0.230	-14.992	-14.992	2.974
3500	13.856	95.622	-0.229	-15.088	-15.088	2.944
3600	13.859	96.013	-0.228	-15.184	-15.184	2.914
3700	13.862	96.392	-0.227	-15.280	-15.280	2.884
3800	13.864	96.762	-0.226	-15.376	-15.376	2.854
3900	13.867	97.122	-0.225	-15.472	-15.472	2.824
4000	13.869	97.473	-0.224	-15.568	-15.568	2.794
4100	13.871	97.816	-0.223	-15.664	-15.664	2.764
4200	13.873	98.150	-0.222	-15.760	-15.760	2.734
4300	13.875	98.477	-0.221	-15.856	-15.856	2.704
4400	13.876	98.796	-0.220	-15.952	-15.952	2.674
4500	13.878	99.107	-0.219	-16.048	-16.048	2.644
4600	13.879	99.413	-0.218	-16.144	-16.144	2.614
4700	13.880	99.711	-0.217	-16.240	-16.240	2.584
4800	13.882	100.003	-0.216	-16.336	-16.336	2.554
4900	13.883	100.289	-0.215	-16.432	-16.432	2.524
5000	13.884	100.570	-0.214	-16.528	-16.528	2.494
5100	13.885	100.845	-0.213	-16.624	-16.624	2.464
5200	13.886	101.115	-0.212	-16.720	-16.720	2.434
5300	13.887	101.379	-0.211	-16.816	-16.816	2.404
5400	13.888	101.639	-0.210	-16.912	-16.912	2.374
5500	13.889	101.893	-0.209	-17.008	-17.008	2.344
5600	13.889	102.144	-0.208	-17.104	-17.104	2.314
5700	13.890	102.390	-0.207	-17.200	-17.200	2.284
5800	13.891	102.631	-0.206	-17.296	-17.296	2.254
5900	13.891	102.869	-0.205	-17.392	-17.392	2.224
6000	13.892	103.102	-0.204	-17.488	-17.488	2.194

Sept. 30, 1965

DISULFUR MONOXIDE (S₂O)

MOL. WT. = 80.1274

(IDEAL GAS)

Point Group C_{2v}
 $\Delta H_f^0 = 63.8 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = [-13.5 \pm 8] \text{ kcal. mole}^{-1}$
 $\Delta H_f^0 = 298.15 = [-13.5 \pm 8] \text{ kcal. mole}^{-1}$

Ground State Quantum Weight = 1
 Vibrational Frequencies and Degeneracies
 $\nu, \text{ cm.}^{-1}$

679 (1)
 388 (1)
 1165 (1)

Bond Distance: S-S = 1.884 Å S-O = 1.465 Å
 Bond Angle: S-S-O = 118°
 Product of the Moment of Inertia: $I_A I_B I_C = 6.2741 \times 10^{-115} \text{ g. cm.}^2$

Heat of Formation.

There is no direct measurement of the standard enthalpy of formation for S₂O(g). U. Blukis and R. Myers, J. Phys. Chem., **69**, 1154 (1965), have discussed the discrepancy of the values of ΔH_f^0 which vary from -1 to -35 kcal. mole⁻¹. R. Hagemann, Compt. Rend., **225**, 1102 (1962), reported ΔH_f^0 = -17 kcal. mole⁻¹ from his ionization and appearance potential measurements by mass spectrometry. R. Steudel and P. W. Schenk, Z. Physik Chem., **43**, 33 (1964), estimated the enthalpy of formation as -22.7 kcal. mole⁻¹. If the bond dissociation energies D(S-O) = 123.5 kcal. mole⁻¹ and D(S-S) = 101 kcal. mole⁻¹ were used to estimate the dissociation energy of S₂O (i.e. D(S₂O) = 224.5 kcal. mole⁻¹), one will obtain ΔH_f^0 = -35.5 kcal. mole⁻¹. A. V. Jones, J. Chem. Phys., **18**, 1263 (1950), reported the predissociation energy, 91 kcal. mole⁻¹, for sulfur monoxide from the infrared and ultraviolet spectra. [D. Meschi and R. Myers, J. Mol. Spectro., **3**, 405 (1959), have concluded from their experiment that the so called sulfur monoxide is S₂O.] Therefore, if 30(g) + S(g), were the dissociation products, the ΔH_f^0 would be -25.4 kcal. mole⁻¹; and if S₂(g) + O(g) were the products, the ΔH_f^0 would be -1.2 kcal. mole⁻¹. (All JANAP auxiliary data used in calculation.)

E. Dewing and F. Richardson, Trans. Faraday Soc., **54**, 679 (1958), have investigated the gas phase equilibria in the sulfur-oxygen vapor at 1250° and 1500°C respectively. U. Blukis and R. Myers (loc. cit.) recalculated their data based on the assumption that the S₂O (instead of SO) was the major product in the equilibrium, and obtained ΔH_f^0 = -13 kcal. mole⁻¹ for S₂O(g) which is adopted in this table.

Heat Capacity and Entropy.

The bond distance, angle, and vibrational frequencies were obtained from the microwave and infrared spectra measurements by D. Meschi and R. Myers, loc. cit., and U. Blukis and R. Myers, loc. cit. The three principal moments of inertia are $I_A = 2.0219 \times 10^{-39}$, $I_B = 16.6342 \times 10^{-39}$ and $I_C = 18.6580 \times 10^{-39} \text{ g. cm.}^2$

Ground State Configuration $1s^2$
 $S_{298.15}^\circ = 50.54 \text{ gibbs/mol}$
 $\Delta H_f^\circ = -24.3 \pm 2 \text{ kcal/mol}$
 $\Delta H_f^\circ = -24 \pm 2 \text{ kcal/mol}$

OSI

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i
0	1
[30000]	6
42640	2

$$\omega_e X_e = 5.92 \quad \sigma = 1$$

$$\omega_e = 1261.44$$

$$r_e = 1.505 \text{ \AA}$$

$$B_e = 0.7273$$

$$\alpha_e = 0.00508$$

Heat of Formation

The adopted value is based on equilibrium data summarized below. The more reliable results from three different reactions lie in the range from about -23 to -26 kcal/mol. Extreme values, including -20 and -32 kcal/mol, can be discounted on experimental grounds. Margrave (1) recently reported $\Delta H_f^\circ = 82.8 \pm 1.5 \text{ kcal/mol}$ for $0.5510_2(\text{g}) + 0.5510_2(\text{g}) = \text{SiO}(\text{g})$, but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta H_f^\circ = -25.4 \text{ kcal/mol}$. Reaction A involves the nominal composition $\text{SiO}(\text{s})$ which is treated as an intimate mixture of $0.5510_2(\text{c}) + 0.5510_2(\text{high cristobalite})$. X-ray studies (13, 14) suggest that the condensed "SiO" used in (1, 2) is probably a mixture of Si and amorphous or vitreous SiO_2 . The adopted ΔH_f° corresponds to $D_0^\circ = 190 \pm 3 \text{ kcal/mol}$. This may be compared with $D_0^\circ = 179 \text{ kcal/mol}$ obtained by linear Birge-Sponer extrapolation of the ground state vibrational constants and with $D_0^\circ = 185 \pm 7 \text{ kcal/mol}$ obtained by Barrow (15) from $D_0^\circ(\text{LiX}) = 77.5 \text{ kcal/mol}$ for the excited state at 5280 cm^{-1} . Barrow assumed $D_0^\circ/D_0^\circ(\text{LiX}) = 0.456$ based on related molecules.

Source	Reaction	Method	Range, T°K	Points	No. of	ΔH_f° 298	Drift
						$\frac{\text{Kcal/mol}}{\text{Kcal/mol}}$	
1. Ramstad (1961)	A	Carrier gas	1510-1758	6	80.7 ± 2.3	85.08	3.0 ± 1.4
2. Bergman (1959)	A	ΔHs by explosion	---	---	---	87 ± 2	---
3. Gunther (1958)	A*	Knudsen wt. gain	1202-1520	18	97.0 ± 0.7	86.76	-7.6 ± 0.5
4. Porter (1955)	A**	Knudsen mass spec.	1345-1463	2	105.1	87.35	-13
5. Toms (1952)	A	Carrier gas	1573-1920	7	65.4 ± 1.1	84.75	11 ± 1
6. Schaffer (1950)	A	Knudsen wt. loss	1336-1920	21	78.7 ± 1.5	82.74	2.9 ± 1.0
7. Gel'd (1948)	A*	Knudsen wt. loss	1173-1478	11	77.2 ± 1.8	85.87	6.8 ± 1.4
8. Ramstad (1961)	B***	Carrier gas	1698-1873	4	142.6 ± 0.7	133.79	-4.9 ± 0.4
9. Toms (1952)	B***	Carrier gas	1703-1898	---	---	132.3	-2
10. Grube (1949)	B***	Carrier gas	1501-1926	23	88 ± 3	127.3	22 ± 2
11. Nemesyanov (1960)	C**	Knudsen collection	1473-1773	4	112 ± 3	134.4	13 ± 2
12. Yang (1958)	C	Knudsen wt. loss	1653-1739	24	---	---	-20.5
13. Porter (1955)	D	Knudsen mass spec.	1818-1960	15	195.3 ± 3.4	194.5	-241.8
14. Cochran (1962)	D	Knudsen effusion	1800-1900	2	130	184.4	29
15. Cochran (1962)	D	Knudsen effusion	---	---	---	11.5	-32.0
16. A. 0.5510 ₂ (high cristobalite) + 0.5510 ₂ (c) = SiO(g)							
B. SiO ₂ (high cristobalite) + H ₂ (g) = SiO(g) + SiO ₂ (c)							
C. SiO ₂ (high cristobalite) = 0.50 ₂ (g) + SiO(g)							
D. SiO ₂ (c) + Mg(g) = MgO(c) + SiO(g)							

*Starting material was "SiO"
 **Starting material was SiO₂
 ***Starting material was quartz

Heat Capacity and Entropy

All constants for the ground state and the A¹Π state at 42640 cm⁻¹ are taken from the analysis of the A-X system reported by Lagerqvist (16). An intercombination transition has been observed and assigned as $1s^2 3^1\Pi$ by Verma (17). The value of the a-X excitation energy is unknown but is estimated here as 30000 ± 5000 cm⁻¹ by comparison with the A and A states of CO and A¹CL. Several additional excited states are known (18, 19) to lie near or above the A state, but they are omitted because their contribution to the thermal functions is negligible.

References

1. J. L. Margrave, 5th Meeting ICPG Thermochimistry Working Group, Linden, New Jersey, March, 1967.
2. H. F. Ramstad, F. D. Richardson and P. J. Bowles, Trans. AIME 221, 1021 (1961). Data given graphically.
3. G. A. Bergman and V. A. Medvedev, Shornik Trudov Gosudarst. Inst. Priklad. Khim. 1959, 158 (1959).
4. K. G. Gunther, Glasstech. Ber. 31, 9 (1958).
5. R. C. Porter, W. A. Chupka and H. G. Inghram, J. Chem. Phys. 23, 216 (1955).
6. R. C. Porter, W. A. Chupka and H. G. Inghram, J. Chem. Phys. 23, 216 (1955).
7. H. Schaffer and R. A. Hornie, Z. Anorg. Allg. Chem. 263, 161 (1952).
8. P. V. Gel'd and M. I. Kochnev, Zhur. Priklad. Khim. 26, 1249 (1948).
9. G. Grube and H. Speidel, Z. Elektrochem. 53, 341 (1949).
10. A. N. Nemesyanov and L. P. Firsova, Russ. J. Phys. Chem. (English Transl.) 34, 906, 1237, 1279 (1960).
11. A. Lagerqvist and U. Uhler, Arkiv Fysik 8, 95 (1952).
12. C. N. Cochran and L. M. J. Phys. Chem. 66, 380 (1962).
13. A. N. Gusatinskii, K. M. Kolobova and S. A. Nemonov, Izv. Akad. Nauk SSSR, Neorg. Materialy 1 (6), 877 (1965).
14. G. W. Brady, J. Phys. Chem. 63, 1119 (1959).
15. R. F. Barrow and H. C. Rowlinson, Proc. Roy. Soc. (London) A224, 374 (1954).
16. A. Lagerqvist and U. Uhler, Arkiv Fysik 8, 95 (1952).
17. R. D. Verma and R. S. Mulliken, Can. J. Phys. 23, 908 (1961).

OSI

Titanium Monoxide, Alpha (α -TiO)
(Crystal)

GFW = 63.8994

TITANIUM MONOXIDE, ALPHA (α -TiO)

(CRYSTAL)

OPW = 63.8994

T, °K	Cp*	S*	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	3.051	5.259	19.036	1.476	-123.476	-123.476	INFINITE
200	7.333	8.811	13.012	1.378	-123.859	-122.118	266.890
298	9.550	12.200	12.200	∞	-124.128	-120.554	131.408
300	9.574	12.259	12.200	0.018	-124.190	-118.302	86.183
400	10.787	15.192	12.592	1.040	-124.141	-116.344	63.567
500	11.610	17.692	13.368	2.162	-124.030	-114.407	50.007
600	12.238	19.966	14.274	3.355	-123.881	-112.495	40.977
700	12.701	21.925	15.113	4.604	-123.693	-110.535	34.535
800	13.114	23.593	15.896	5.904	-123.516	-108.555	29.710
900	13.502	25.104	17.055	7.244	-123.319	-106.522	25.964
1000	13.970	26.556	17.933	8.623	-123.117	-105.110	22.972
1100	14.314	27.904	18.779	10.037	-122.912	-103.319	20.588
1200	14.560	29.163	19.592	11.483	-122.703	-101.280	18.758
1300	14.810	30.342	20.382	12.962	-122.493	-99.091	16.758
1400	15.255	31.487	21.157	14.475	-122.283	-97.874	15.279
1500	15.548	32.529	21.852	16.016	-122.073	-96.596	14.001
1600	15.835	33.542	22.532	17.585	-121.866	-95.341	12.866
1700	16.317	34.539	23.197	19.186	-121.661	-94.101	11.866
1800	16.663	35.512	23.850	20.808	-121.456	-92.891	11.037
1900	16.931	36.333	24.512	22.460	-121.251	-91.703	10.262
2000	17.197	37.194	25.124	24.140	-121.046	-90.539	9.550
2100	17.197	38.027	25.719	25.847	-120.842	-89.409	8.899
2200	17.760	38.813	26.297	27.587	-120.638	-88.311	8.311
2300	17.760	39.557	26.859	29.339	-120.434	-87.244	7.776
2400	17.940	40.375	27.406	31.124	-120.230	-86.214	7.284
2500	18.237	41.114	27.940	32.934	-120.026	-85.219	6.836

Dec. 31, 1960; Mar. 31, 1967

$$\Delta H_f^\circ = -123.48 \pm 1 \text{ kcal/mol}$$

$$\Delta H_f^{298.15} = -124.19 \pm 1 \text{ kcal/mol}$$

$$\Delta H^\circ = 0.83 \text{ kcal/mol}$$

$$\Delta H_s^{298.15} = 128 \pm 10 \text{ kcal/mol}$$

$$S_{298.15}^\circ = [12.2] \text{ gbbu/mol}$$

$$T_b = 1264^\circ \text{K}$$

Heat of Formation.

G. L. Humphrey, *J. Am. Chem. Soc.* **73**, 1587 (1951), determined the heat of combustion $\Delta H_{298}^\circ = -101.61 \pm 0.12$ kcal/mol for the reaction $\text{TiO}(\alpha) + 1/2\text{O}_2(g) = \text{TiO}_2(\text{rutile})$. Based on this result and on $\Delta H_{298}^\circ(\text{rutile}) = -225.8 \pm 1$ kcal/mol, the adopted $\Delta H_f^{298}^\circ$ for $\text{TiO}(\alpha)$ is calculated to be -124.19 ± 1 kcal/mol. A value of -125.4 ± 0.4 kcal/mol was reported by S. M. Ariya, M. P. Morozova and E. Vol'f, *Russ. J. Inorg. Chem. (English Transl.)* **2**, 16 (1957), who measured the heats of combustion of various compositions in the Ti-O system. Ariya et al. used an estimated correction for the formation of $\text{TiO}_2 \cdot x$, while Humphrey obtained values of $0.2 - 0.4$ kcal/mol by grinding the product and returning it with white oil. Most of the assigned uncertainty arises from this problem of non-stoichiometry [see $\text{TiO}_2(\text{rutile})$ for further details].

Heat Capacity and Entropy.

The low temperature heat capacities, $52.6 - 296.3^\circ \text{K}$, were measured by C. H. Shomate, *J. Am. Chem. Soc.* **68**, 310 (1946). The high temperature enthalpies, $357.0 - 1771^\circ \text{K}$, were determined by B. F. Naylor, *J. Am. Chem. Soc.* **69**, 1077 (1946), by use of drop calorimetry. The high temperature Cp's, $357 - 1200.5^\circ \text{K}$, derived from the enthalpy data, are joined smoothly with the low temperature heat capacities at 298°K . The Cp values above 1200°K are obtained by extrapolation. The entropy is obtained from Cp* using $S_{50}^\circ = 4.13$ eu; this extrapolation includes $0.23, 1.7$ and 2.2 eu for contributions of the lattice, of vacancies and of spin magnetic effects, respectively.

P. W. Dilles, *J. Chem. Phys.* (in press), discussed the inconsistencies in the thermodynamic properties of TiO as derived from widely different measurements. These inconsistencies include (1) a difference of 10 kcal/mol in H_f° values for $\text{TiO}(g)$ obtained from vaporization of TiO and $\text{Ti}_2\text{O}_3(2)$ a difference of about 10 kcal/mol between the calorimetric data for $\text{TiO}(g)$ and a recent re-assessment of the partial free energy of dissociation for the TiO system, and (3) ent. data which suggest that the entropy of $\text{TiO}(g)$ should be increased relative to those of Ti and Ti_2O_3 . In order to minimize these discrepancies, we tentatively increase the experimental value of S_{298}° by addition of estimated contributions due to vacancies in the crystal lattice and to spin-magnetic effects of Ti^{2+} ion.

P. Enrich, *Z. Elektrochem.* **45**, 362 (1959) and Z. Anorg. Chem. **247**, 53 (1941), concluded from the difference in pycnometric and X-ray densities of $\text{TiO}(g)$ that about 25 percent of the Ti and O lattice sites are vacant. This was confirmed later by S. Anderson, B. Gollen, U. Kuylenstierna and A. Magneli, *Acta Chem. Scand.* **11**, 1641 (1957), A. D. Pearson, *J. Phys. Chem. Solids* **5**, 316 (1958), and M. E. Straumanis and H. W. Li, *Z. Anorg. Allgem. Chem.* **305**, 143 (1960). Anderson et al. noted that there may be a "close structural kinship" between the α and β forms, based on the similarity of their densities and the pronounced relationship between their powder diffraction patterns. The authors suggested that the (presumably) random vacancies in $\text{TiO}(g)$ may occur in an ordered way in $\text{TiO}(\alpha)$. Recent electron diffraction studies by J. M. Cowley, *Acta Cryst.* (to be published), may provide an answer to this problem. Assuming the vacancies to be randomly arranged, we estimate the residual entropy of $\text{TiO}(g)$ due to vacancies as $-2R(0.85 \ln 0.85 + 0.15 \ln 0.15) = 1.7$ eu, based on the method proposed by M. Hoch, A. S. Iyer and J. Neiken, *J. Phys. Chem. Solids* **23**, 1463 (1962). An alternative possibility for increasing the entropy of $\text{TiO}(g)$ is discussed in the Transition Data section of the table for $\text{TiO}(g)$.

Metallic-type conductivity of $\text{TiO}(\alpha)$ at temperatures $80 - 1000^\circ \text{K}$ was reported by A. D. Pearson, loc. cit., and P. J. Morin, *Phys. Rev. Letters* **3**, 34 (1959). This led J. B. Goodenough, *Phys. Rev.* **117**, 1442 (1960), to suggest the existence of strong cation-anion interactions and the possibility of a low temperature transformation of the martensitic or antiferromagnetic type. Goodenough noted that the isolectric compound VN becomes superconducting below 8.2°K . We approximate the entropy contribution of these various possibilities at 50°K by a spin-magnetic term of $\text{Rln}3 = 2.2$ eu.

Transition Data.

See $\text{TiO}(g)$ table.

Heat of Sublimation.

The difference between $\Delta H_f^{298}^\circ$ for $\text{TiO}(g)$ and $\text{TiO}(\alpha)$ is ΔH_{298}° .

Titanium Monoxide, Beta (β - TiO)
(Crystal) GFW = 63.8994

T, K	Cp ^a	S ^b	-(G ^c -H ²⁹⁸)/T	H ²⁹⁸ -H ²⁹⁸	ΔH°	ΔG°	Log Kp
100							
200							
298	9.530	12.372	12.372	.000	-123.872	-119.071	86.549
300	9.574	12.372	12.372	.018	-123.872	-119.038	85.989
400	10.787	12.364	12.764	1.040	-123.823	-118.995	83.431
500	11.610	12.364	13.540	2.162	-123.712	-118.175	80.906
600	12.238	20.038	14.446	3.355	-123.563	-117.281	80.888
700	12.755	21.965	15.395	4.606	-123.387	-116.415	34.473
800	13.201	23.697	16.318	5.904	-123.195	-115.575	29.661
900	13.589	25.247	17.214	7.252	-122.987	-114.761	25.044
1000	13.929	26.697	18.114	8.653	-122.763	-113.973	22.042
1100	14.228	28.063	19.014	10.104	-122.525	-113.223	20.509
1200	14.487	29.356	19.914	11.604	-122.275	-112.511	19.480
1300	14.706	30.596	20.814	13.154	-122.015	-111.837	18.761
1400	14.887	31.796	21.714	14.754	-121.745	-111.201	18.210
1500	15.034	32.956	22.614	16.404	-121.465	-110.597	17.807
1600	15.151	34.076	23.514	18.104	-121.175	-110.023	17.521
1700	15.241	35.156	24.414	19.854	-120.875	-109.479	17.341
1800	15.306	36.196	25.314	21.654	-120.565	-108.965	17.261
1900	15.349	37.196	26.214	23.504	-120.245	-108.481	17.281
2000	15.374	38.156	27.114	25.404	-119.915	-108.027	17.391
2100	15.384	39.076	28.014	27.354	-119.575	-107.603	17.501
2200	15.379	39.956	28.914	29.354	-119.225	-107.209	17.611
2300	15.359	40.796	29.814	31.404	-118.865	-106.845	17.721
2400	15.324	41.596	30.714	33.504	-118.495	-106.511	17.831
2500	15.274	42.356	31.614	35.654	-118.115	-106.207	17.941

Mar. 31, 1967

TITANIUM MONOXIDE, BETA (β -TiO) (CRYSTAL) OPW = 63.8994

S₂₉₈^o.15 = [12.372] gbbu/mol $\Delta H^{\circ}_{298.15} = [-123.872]$ kcal/mol

Tt = 1264°K $\Delta H^{\circ} = 0.85$ kcal/mol

Tm = 2023°K $\Delta H^{\circ} = [13]$ kcal/mol

Heat of Formation.

The $\Delta H^{\circ}_{298}(\beta)$ is obtained from $\Delta H^{\circ}_{298}(\alpha)$ by adding ΔH° and the difference between H₁₂₆₄ - H₂₉₈ for TiO(α) and TiO(β).

Heat Capacity and Entropy.

High temperature enthalpies, 1273 - 1771°K, have been measured with a drop calorimeter by B. P. Naylor, J. Am. Chem. Soc. 88, 1077 (1946). The adopted heat capacities are derived from these data, assuming the final state to be TiO(α). This problem is discussed in the Transition Data section. Cp values below 900°K are assumed to be the same as those for TiO(α). The heat capacities at temperatures 900 - 1273°K and above 1771°K are obtained by extrapolation.

The S₂₉₈^o is derived in a manner analogous to that of the heat of formation.

Transition Data.

Tt and ΔH° are derived from the enthalpy data of Naylor, loc. cit., assuming that TiO(α) is the final state of the drop experiment. The X-ray studies of C. C. Wang and N. J. Grant, J. Metals 5, 184 (1956), and A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958), appear to contradict this assumption. These authors found that the α form of stoichiometric TiO was obtained at room temperature only by annealing the β phase for long periods below 1223°K. Samples quenched from temperatures of 1223°K or higher retained the NaCl structure of the β form. Since the drop calorimetric experiment is similar to quenching, it is possible that the final state was mostly the β form. If this is the case, then the derived values of ΔH° and ΔS° are probably much too small. This would be an alternative means for increasing the entropy of TiO(β). It is possible, however, that differences in particle size allowed Naylor's sample to drop to the α form, or that the β form was stabilized by impurities in the X-ray studies. Further experiments are desirable in order to resolve this question. Also related to the question is the fact that the structure of TiO(α) has not been reported, probably because the X-ray diffraction pattern is quite complex.

F. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), reviewed the phase data and presented the most current phase diagram for the Ti-O system. This diagram suggests that stoichiometric TiO(α) starts to transform near 1210°K with formation of the two phases TiO_{1+x}(β) and Ti₂O. Transformation to stoichiometric TiO(β) is complete near 1270°K, which is essentially the Tt chosen by Naylor. This behavior is consistent with Naylor's observation of "pre-transition effects" in the enthalpy between 1224 and 1264°K.

Melting Data.

See TiO(1) table for details.

OTI

OTI

Titanium Monoxide (TiO)

(Liquid)

GFW = 63.8994

OTI

T, °K	C _p ^a	gibbs/mol S ^b - (C _p ^a - H ^c)/T	kcal/mol H ^c - H ²⁹⁸	ΔH ^f	ΔG ^f	Log K _p
0						
100						
200						
298	16,000	16,235	16,235	0.000	-112.801	78.841
300						
300	16,000	16,333	16,235	0.030	-112.769	78.331
400	16,000	16,936	16,862	1.630	-112.162	57.841
500	16,000	22,507	16,047	3,230	-111.574	43.615
600	16,000	25,424	17,374	4,830	-111.017	37.506
700	16,000	27,890	18,705	6,430	-110.492	31.742
800	16,000	30,027	19,990	8,030	-110.001	27.439
900	16,000	31,911	21,212	9,630	-109.544	24.107
1000	16,000	33,597	22,367	11,230	-109.122	21.452
1100	16,000	35,122	23,459	12,830	-108.730	19.288
1200	16,000	36,514	24,490	14,430	-108.366	17.483
1300	16,000	37,795	25,464	16,030	-108.029	15.955
1400	16,000	38,981	26,388	17,630	-107.710	14.651
1500	16,000	40,084	27,265	19,230	-107.400	13.525
1600	16,000	41,117	28,099	20,830	-107.092	12.543
1700	16,000	42,087	28,893	22,430	-106.796	11.680
1800	16,000	43,002	29,652	24,030	-106.500	10.916
1900	16,000	43,867	30,377	25,630	-106.204	10.234
2000	16,000	44,687	31,073	27,230	-105.908	9.605
2100	16,000	45,461	31,740	28,830	-105.612	9.030
2200	16,000	46,212	32,380	30,430	-105.316	8.508
2300	16,000	46,924	32,998	32,030	-105.020	8.034
2400	16,000	47,605	33,592	33,630	-104.724	7.599
2500	16,000	48,258	34,166	35,230	-104.428	7.201
2600	16,000	48,885	34,720	36,830	-104.132	6.834
2700	16,000	49,489	35,256	38,430	-103.836	6.495
2800	16,000	50,071	35,775	40,030	-103.540	6.182
2900	16,000	50,632	36,277	41,630	-103.244	5.890
3000	16,000	51,175	36,765	43,230	-102.948	5.619
3100	16,000	51,699	37,238	44,830	-102.652	5.366
3200	16,000	52,207	37,698	46,430	-102.356	5.129
3300	16,000	52,700	38,145	48,030	-102.060	4.907
3400	16,000	53,177	38,581	49,630	-101.764	4.699
3500	16,000	53,641	39,004	51,230	-101.468	4.503
3600	16,000	54,092	39,417	52,830	-101.172	4.303
3700	16,000	54,530	39,820	54,430	-100.876	4.102
3800	16,000	54,957	40,212	56,030	-100.580	3.902
3900	16,000	55,373	40,596	57,630	-100.284	3.700
4000	16,000	55,778	40,970	59,230	-100.000	3.500
4100	16,000	56,173	41,336	60,830	-99.716	3.300
4200	16,000	56,558	41,696	62,430	-99.432	3.100
4300	16,000	56,935	42,044	64,030	-99.148	2.900
4400	16,000	57,303	42,387	65,630	-98.864	2.700
4500	16,000	57,662	42,722	67,230	-98.580	2.500

TITANIUM MONOXIDE (TiO)

(LIQUID)

OPW = 63.8994

 $\Delta H_f^{298.15} = [-112.801] \text{ kcal/mol}$ $\Delta H_m^{\circ} = [13] \text{ kcal/mol}$ $\Delta H_v^{\circ} = [91.6] \text{ kcal/mol}$ $S_{298.15}^{\circ} = [14.235] \text{ gibbs/mol}$ $T_m = 2023^{\circ}\text{K}$ $T_b = [3934] ^{\circ}\text{K}$

Heat of Formation.

The value of ΔH_f^{298} for TiO(l) is obtained from that of TiO(s) by adding ΔH_m° and the difference between $H_{2023}^{\circ} - H_{298}^{\circ}$ for TiO(s) and TiO(l).

Heat Capacity and Entropy.

The heat capacity for TiO(l) is estimated on the basis of 8 cal/g-atom. S_{298}° is obtained in a manner analogous to that of the heat of formation.

Melting Data.

T_m is taken from W. Dawid and K. Schröter, Z. Anorg. Allgem. Chem. 253, 178 (1957). The heat of melting is estimated by comparison with that of VO(c) reported by C. E. Wicks and P. E. Block, U. S. Bur. Mines Bull. 605, 1963.

T_b has also been reported as 2023 and 2103°K by H. Nishimura and H. Kimura, J. Japan Inst. Metals (Sendai) 20, 589 (1956), and R. DeVries, R. Roy, and E. Osborne, Trans. Brit. Ceram. Soc. 53, 525 (1954), respectively. According to the Ti-O phase diagram reported by P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. 49, 180 (1966), TiO melts incongruently.

Vaporization Data.

T_b is calculated as the temperature at which the Gibbs energy change of the reaction TiO(l) = TiO(g) approaches zero. The difference between ΔH_f° for TiO(g) and TiO(l) at T_b is ΔH_v° .

(Ideal Gas) GFW = 63.8994

TITANIUM MONOXIDE (TiO)

(IDEAL GAS)

OPW = 63.8994

Ground State Configuration $3d^2$ $\Delta H_f^\circ = 3.65 \pm 5.0 \text{ kcal/mol}$ $\Delta H_{298.15}^\circ = 3.75 \pm 5.0 \text{ kcal/mol}$ $S_{298.15}^\circ = 56.0 \text{ gibbs/mol}$

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_1, \text{cm}^{-1}$	g_1	$\epsilon_1, \text{cm}^{-1}$	g_1
0	2	2289.0	1	18502.0	2
66.7	2	11395.4	2	19434.6	2
141.3	2	14242.6	6	19499.4	2
581.0	2	16312.0	6	19565.2	2
$w_e = 1008.4 \text{ cm}^{-1}$		$w_e x_e = 4.61 \text{ cm}^{-1}$		$\sigma = 1$	
$B_e = 0.5355 \text{ cm}^{-1}$		$a_e = 0.0031 \text{ cm}^{-1}$		$r_e = 1.62 \text{ \AA}$	

Heat of Formation

P. W. Gilles, J. Chem. Phys. (to be published), has discussed the difference of about 10 kcal/mol in the dissociation energies of TiO(g) obtained from vaporization of $\text{Ti}_2\text{O}_3(\text{s})$ and TiO(p). By mass spectrometric and Knudsen effusion techniques, P. O. Wahlbeck and P. W. Gilles, J. Chem. Phys. 45, 2465 (1967), studied congruently vaporizing $\text{Ti}_2\text{O}_3(\text{s})$ and derived $D^\circ(\text{TiO}, \text{g}) = 7.26 \pm 0.10 \text{ eV}$. Values of 6.88, 6.93 and 6.8 eV were derived from incongruently vaporizing TiO(p) in earlier studies reported by Q. D. Wheatley, Ph. D. Thesis, University of Kansas, 1964; W. O. Groves, M. Hoch, and H. L. Johnston, J. Phys. Chem. 59, 127 (1955); and J. Berkowitz, W. A. Chupke, and M. O. Inghram, J. Phys. Chem. 61, 1569 (1957). A spectroscopic value of 6.8 eV is obtained by Birge-Sponer extrapolation of the vibrational constants given on this table. Related discrepancies are listed in the Heat Capacity and Entropy section of the table for TiO(c). O. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, 1950, reported $D^\circ = 6.9 \text{ eV}$.

In order to minimize these discrepancies, we tentatively increase the entropy of TiO(c) [see TiO(c) table for details] and re-evaluate the vapor pressure data by the second and third law methods. The results are given in the table below. Values derived from TiO(p) are uncertain due to excess oxygen in the condensed phase; e.g., the sample of Groves et al. contained an excess of about 3%. Our analysis assumes that the activity of TiO is unity in the actual condensed phase. The value of $\Delta H_{298}^\circ(\text{TiO}, \text{g})$ adopted is $3.75 \pm 5 \text{ kcal/mol}$.

Investigator Reaction Temperature, °K No. of Points $\Delta H_{298}^\circ, \text{kcal/mol}$ Drift, eu

Wahlbeck-Gilles	(A)	(B)	(B)	(B)	(B)	(B)	(B)	(B)	(B)
Groves et al.	(B)	(B)	(B)	(B)	(B)	(B)	(B)	(B)	(B)
Berkowitz et al.	(B)	(B)	(B)	(B)	(B)	(B)	(B)	(B)	(B)
(A) $\text{Ti}_2\text{O}_3(\text{s}) = \text{TiO}(\text{g}) + 2\text{O}(\text{g})$									
*Calculation based on the third law ΔH_{298}° value. The corresponding $D^\circ(\text{TiO}, \text{g})$ values are 167.83, 166.75 and 166.05 kcal/mol.									

**Average End law value from ion intensities.

Heat Capacity and Entropy

The electronic spectrum of TiO(g) consists of both singlet and triplet systems with near-degenerate low-lying states. The lowest-lying triplet was originally thought to be $^3\Pi$ by Herzberg, loc. cit., B. Rosen, "Selected Constants," Hermann & Co., Paris, 1951, and J. O. Phillips, J. Astrophys. 115, 567 (1952); *ibid.*, 119, 274 (1954), but has been reidentified as X^3_Σ by U. Uhler, Dissertation, University of Stockholm, Sweden, 1954, and W. Weitzer, Jr. and D. McLeod, Jr., J. Phys. Chem. 69, 3468 (1965). The values of the three lowest electronic levels and quantum weights are obtained from Herzberg. A Δ state lying about 581 cm^{-1} above the ground state was reported by Phillips, loc. cit. A. V. Pettersson and B. Lindgren, Arkiv Fysik 22, 491 (1962); A. V. Pettersson, *ibid.*, 16, 185 (1959), reported two electronic states, $d^1\Sigma$ and $b^1\Pi$, at 1708.0 and 10814.4 cm^{-1} above $^1\Delta$ thus, the values of 2289 and 11395.4 are derived. The next two electronic levels, $^3\Sigma$ and $^3\Pi$, are obtained from Weitzer et al., and the value $1\bar{g} = 18502 \text{ cm}^{-1}$ is obtained from Rosen. The last three levels and the values of w_e , $w_e x_e$, B_e , a_e and r_e are taken from Herzberg, loc. cit. The moment of inertia is $5.226 \times 10^{-39} \text{ g cm}^2$.

The rather thorough studies of the emission spectra of TiO(g) have been summarized by R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," 3rd Ed., John Wiley & Sons, Inc., New York, 1963, and A. Gatterer, J. Junkes, E. W. Salpeter, and B. Rosen, "Molecular Spectra of Metallic Oxides," Vatican Press, Vatican City, 1957.

OTI

T, °K	C_p°	S°	$-(G^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH_f°	ΔG_f°	Log Kp
0	0.000	INFINITE	INFINITE	2.290	3.649	3.649	INFINITE
100	7.801	47.655	62.774	1.512	3.987	1.488	3.164
200	7.551	52.929	56.692	0.732	3.900	1.050	1.448
298	7.810	55.987	55.987	0.000	3.750	0.000	2.531
300	7.816	56.035	55.987	0.014	3.747	3.498	2.348
400	8.127	58.327	56.297	0.612	3.571	5.686	3.216
500	8.374	60.169	56.893	1.638	3.385	8.230	3.597
600	8.558	61.713	57.371	2.488	3.199	10.533	3.637
700	8.707	63.013	57.742	3.152	2.973	12.508	4.110
800	8.874	64.125	58.012	3.682	2.713	14.109	4.169
900	8.974	65.251	58.276	4.106	2.443	15.282	4.189
1000	9.033	66.190	60.193	5.997	2.196	16.431	4.247
1100	9.078	67.043	60.777	6.882	1.883	17.577	4.287
1200	9.113	67.829	61.263	7.765	1.537	18.719	4.306
1300	9.143	68.563	61.657	8.645	1.167	19.858	4.319
1400	9.168	69.250	62.062	9.520	0.782	20.994	4.318
1500	9.188	69.895	62.480	10.507	-0.162	22.128	4.316
1600	9.206	70.502	62.917	11.416	-0.584	23.262	4.315
1700	9.221	71.073	63.373	12.358	-1.000	24.396	4.311
1800	9.234	71.613	63.848	13.334	-1.408	25.530	4.306
1900	9.245	72.125	64.334	14.340	-1.768	26.664	4.296
2000	9.254	72.617	64.835	15.384	-2.100	27.798	4.270
2100	9.261	73.091	65.346	16.464	-2.408	28.932	4.236
2200	9.266	73.546	65.866	17.578	-2.692	30.066	4.203
2300	9.270	73.984	66.396	18.724	-2.952	31.200	4.171
2400	9.274	74.406	66.934	19.900	-3.188	32.334	4.141
2500	9.276	74.815	67.479	21.106	-3.400	33.468	4.112
2600	9.278	75.216	68.030	22.342	-3.588	34.602	4.084
2700	9.279	75.613	68.584	23.608	-3.752	35.736	4.056
2800	9.280	75.996	69.142	24.904	-3.892	36.870	4.030
2900	9.281	76.367	69.704	26.230	-4.008	38.004	3.978
3000	9.282	76.726	70.271	27.586	-4.100	39.138	3.954
3100	9.283	77.076	70.842	28.972	-4.168	40.272	3.930
3200	9.284	77.419	71.417	30.388	-4.212	41.406	3.906
3300	9.285	77.756	71.996	31.834	-4.242	42.540	3.882
3400	9.286	78.088	72.577	33.310	-4.258	43.674	3.858
3500	9.287	78.415	73.162	34.816	-4.262	44.808	3.834
3600	9.288	78.738	73.751	36.342	-4.254	45.942	3.810
3700	9.289	79.057	74.344	37.888	-4.234	47.076	3.786
3800	9.290	79.372	74.939	39.454	-4.200	48.210	3.762
3900	9.291	79.684	75.538	41.040	-4.154	49.344	3.738
4000	9.292	79.992	76.100	42.646	-4.098	50.478	3.714
4100	9.293	80.297	76.667	44.272	-4.032	51.612	3.690
4200	9.294	80.599	77.239	45.918	-3.956	52.746	3.666
4300	9.295	80.898	77.816	47.584	-3.870	53.880	3.642
4400	9.296	81.193	78.398	49.270	-3.774	55.014	3.618
4500	9.297	81.484	78.984	50.976	-3.668	56.148	3.594
4600	9.298	81.772	79.572	52.702	-3.552	57.282	3.570
4700	9.299	82.057	80.164	54.448	-3.426	58.416	3.546
4800	9.300	82.339	80.761	56.214	-3.290	59.550	3.522
4900	9.301	82.618	81.362	58.000	-3.144	60.684	3.498
5000	9.302	82.894	81.970	59.806	-3.000	61.818	3.474
5100	9.303	83.167	82.582	61.632	-2.846	62.952	3.450
5200	9.304	83.437	83.196	63.478	-2.682	64.086	3.426
5300	9.305	83.704	83.816	65.344	-2.508	65.220	3.402
5400	9.306	83.968	84.440	67.230	-2.324	66.354	3.378
5500	9.307	84.229	85.069	69.136	-2.130	67.488	3.354
5600	9.308	84.487	85.702	71.062	-1.926	68.622	3.330
5700	9.309	84.743	86.339	73.008	-1.712	69.756	3.306
5800	9.310	85.000	86.980	75.074	-1.488	70.890	3.282
5900	9.311	85.254	87.626	77.160	-1.254	72.024	3.258
6000	9.312	85.506	88.276	79.276	-1.010	73.158	3.234

Dec. 31, 1960; Mar. 31, 1967

Tungsten Monoxide (W0)
(Ideal Gas)

GFW = 199.8494

T, °K	C _p ^o	gibbs/mol S ^o - (G° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0	∞.000	∞.000	∞.000	∞.000	∞.000	∞.000
100	51.000	51.000	2.093	101.734	101.734	∞.000
200	51.000	51.000	1.876	101.734	101.734	∞.000
298	7.287	58.722	0.013	101.400	93.725	-68.702
300	7.294	58.722	0.013	101.596	93.676	-68.243
400	7.646	60.914	0.761	101.399	91.065	-49.756
500	7.947	62.654	1.241	101.212	88.503	-38.685
600	8.176	64.124	2.348	101.031	85.979	-31.318
700	8.346	65.398	3.174	100.847	83.485	-26.065
800	8.472	66.521	4.015	100.656	81.017	-22.133
900	8.567	67.524	4.867	100.459	78.575	-19.081
1000	8.640	68.431	5.728	100.252	76.154	-16.644
1100	8.698	69.257	6.595	100.036	73.754	-14.654
1200	8.744	70.016	7.467	99.809	71.376	-12.999
1300	8.781	70.717	8.343	99.571	69.016	-11.603
1400	8.813	71.369	9.223	99.322	66.674	-10.408
1500	8.839	71.978	10.106	99.061	64.352	-9.376
1600	8.862	72.549	10.991	98.788	62.047	-8.475
1700	8.881	73.087	11.878	98.503	59.760	-7.683
1800	8.899	73.595	12.767	98.206	57.489	-6.980
1900	8.915	74.077	13.658	97.896	55.235	-6.353
2000	8.930	74.535	14.550	97.573	53.000	-5.791
2100	8.945	74.971	15.444	97.238	50.777	-5.284
2200	8.959	75.387	16.339	96.888	48.572	-4.825
2300	8.974	75.786	17.236	96.527	46.383	-4.407
2400	8.989	76.168	18.134	96.152	44.213	-4.026
2500	9.005	76.535	19.033	95.763	42.056	-3.677
2600	9.022	76.889	19.935	95.363	39.915	-3.355
2700	9.040	77.230	20.838	94.944	37.790	-3.059
2800	9.061	77.559	21.743	94.508	35.683	-2.785
2900	9.082	77.877	22.650	94.057	33.589	-2.531
3000	9.106	78.185	23.554	93.593	31.516	-2.286
3100	9.132	78.484	24.471	93.118	29.459	-2.073
3200	9.161	78.775	25.386	92.634	27.420	-1.873
3300	9.191	79.057	26.304	92.140	25.404	-1.682
3400	9.224	79.332	27.224	91.630	23.410	-1.505
3500	9.259	79.600	28.148	91.100	21.440	-1.339
3600	9.296	79.861	29.076	90.558	19.496	-1.184
3700	9.336	80.116	30.008	90.000	17.628	-1.041
3800	9.377	80.366	30.943	89.430	15.860	-0.918
3900	9.420	80.610	31.883	88.840	14.302	-0.801
4000	9.466	80.844	32.827	88.230	12.954	-0.691
4100	9.513	81.083	33.776	87.600	11.819	-0.587
4200	9.561	81.313	34.730	86.940	10.891	-0.489
4300	9.611	81.539	35.689	86.250	10.064	-0.395
4400	9.663	81.760	36.652	85.530	9.332	-0.306
4500	9.715	81.978	37.616	84.790	8.694	-0.221
4600	9.768	82.192	38.582	84.030	8.149	-0.141
4700	9.822	82.403	39.550	83.250	7.693	-0.064
4800	9.876	82.610	40.520	82.450	7.318	-0.009
4900	9.931	82.814	41.500	81.630	6.924	-0.078
5000	9.985	83.016	42.486	80.790	6.510	-0.145
5100	10.040	83.214	43.475	80.000	6.074	-0.209
5200	10.095	83.409	44.464	79.150	5.616	-0.270
5300	10.149	83.602	45.456	78.250	5.136	-0.328
5400	10.203	83.782	46.450	77.300	4.634	-0.384
5500	10.256	83.960	47.444	76.300	4.100	-0.436
5600	10.309	84.165	48.438	75.250	3.544	-0.489
5700	10.360	84.348	49.434	74.150	2.966	-0.539
5800	10.411	84.519	50.430	73.000	2.366	-0.587
5900	10.460	84.707	51.426	71.800	1.744	-0.632
6000	10.509	84.893	52.422	70.550	1.100	-0.660

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

TUNGSTEN MONOXIDE (W0)

(IDEAL GAS)

OPW = 199.8494

Ground State Configuration [5s²] g_{1/2}⁻
S_{298.15} = [58.7] gibbs/mol
ΔH_{f,0}^o = 101.7 ± 10 kcal/mol
ΔH_{f,298.15}^o = 101.6 ± 10 kcal/mol

Electronic Levels and Quantum Weights

E _i , cm ⁻¹	g _i
[0]	[3]
[14160]	[1]
[17211]	[2]
[19189]	[6]

σ = 1

r_e = [1.81] Å

Heat of Formation

The heat of formation, ΔH_{f,298}^o(W0,g) = 101.6 kcal/mol, was derived from the heat of reaction, ΔH_{r,298}^o = -42.0 kcal/mol for W0(g) → W(c) + O(g) with all JANAF auxiliary data. The value of ΔH_{r,298}^o was calculated by the third law method from the partial pressure data, which were determined mass-spectrometrically in the temperature range 2188° to 2475°K, by G. DeMaris, R. F. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. 32, 1373 (1960). The drift in the third law analysis was -20 ± 7 eu.

Heat Capacity and Entropy

The fundamental vibrational frequency, the ground state configuration, and the probable electronic levels for tungsten monoxide (g) were obtained from the infrared and ultraviolet spectroscopic investigations by matrix isolation by W. Weitzer, Jr., and D. McLeod, Jr., J. Mol. Spectry, 17, 276 (1965). The rotational constant B_e was calculated from an estimated bond distance, W-O = 1.81 Å. The value of x_e was calculated from the relation x_eu²/2 = 0.014 which was given by R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) 219A, 120 (1953). The constant, 0.014, was estimated, based on those for ZrO(g) and VO(g). The value of a_e was calculated from the Morse potential function.

(Ideal Gas) Mol. Wt. = 107.2194

MOL. WT. = 107.2194

ZIRCONIUM MONOXIDE (ZrO)

(IDEAL GAS)

T, °K.	C _p	S°	cal. mole ⁻¹ deg ⁻¹	-(H°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	0.000	INFINITE	INFINITE	INFINITE	2.400	14.255	14.255	INFINITE
100	46.677	46.677	1.771	14.255	1.405	14.255	14.255	10.5132
200	7.048	51.463	54.695	14.255	7.06	14.217	9.937	10.858
298	7.373	54.332	54.332	0.000	0.000	14.000	5.777	5.777
300	7.380	54.378	54.332	0.014	13.996	7.844	7.844	5.714
400	7.754	56.553	57.771	1.771	13.763	3.676	3.676	5.184
500	8.006	58.318	59.184	1.862	13.518	3.673	3.673	4.693
600	8.343	59.813	59.862	2.383	13.257	1.968	1.968	4.717
700	8.644	61.121	56.505	3.232	12.992	1.08	1.08	4.034
800	9.010	62.299	57.157	4.114	12.737	1.717	1.717	4.69
900	9.450	63.385	57.789	5.036	12.507	2.296	2.296	4.852
1000	9.948	64.406	58.000	6.008	12.309	2.878	2.878	4.153
1100	10.471	65.378	58.090	7.027	12.141	7.026	7.026	1.396
1200	10.980	66.311	59.562	8.099	11.951	11.587	11.587	1.587
1300	11.443	67.209	60.116	9.221	10.971	10.359	10.359	1.741
1400	11.853	68.072	60.654	10.386	10.841	11.864	11.864	1.864
1500	12.213	68.899	61.176	11.597	10.697	13.634	13.634	1.966
1600	12.538	69.690	61.683	12.811	10.889	15.268	15.268	2.085
1700	12.844	70.444	62.177	14.054	10.888	16.904	16.904	2.173
1800	13.157	71.160	62.656	15.307	10.888	18.538	18.538	2.251
1900	13.561	71.839	63.122	16.563	10.881	20.172	20.172	2.329
2000	13.957	72.493	63.574	17.817	10.861	21.806	21.806	2.393
2100	14.340	73.092	64.013	19.066	10.827	23.441	23.441	2.439
2200	14.704	73.668	64.439	20.305	5.870	25.066	25.066	2.474
2300	15.056	74.226	64.852	21.533	5.790	26.690	26.690	2.499
2400	15.402	74.762	65.252	22.760	5.686	28.314	28.314	2.524
2500	15.744	75.284	65.632	23.986	5.564	29.938	29.938	2.549
2600	16.086	75.691	66.019	25.217	5.463	31.562	31.562	2.574
2700	16.428	76.137	66.386	26.448	5.325	33.186	33.186	2.598
2800	16.769	76.563	66.742	27.678	5.173	34.810	34.810	2.623
2900	17.109	76.970	67.088	28.908	5.010	36.434	36.434	2.648
3000	17.447	77.360	67.424	29.609	4.834	38.058	38.058	2.673
3100	17.785	77.735	67.750	30.953	4.650	39.682	39.682	2.698
3200	18.123	78.096	68.068	32.090	4.455	41.306	41.306	2.723
3300	18.461	78.444	68.377	33.221	4.253	42.930	42.930	2.748
3400	18.799	78.780	68.678	34.347	4.047	44.554	44.554	2.773
3500	19.137	79.105	68.971	35.469	3.829	46.178	46.178	2.798
3600	19.475	79.421	69.257	36.588	3.609	47.802	47.802	2.823
3700	19.813	79.727	69.536	37.704	3.384	49.426	49.426	2.848
3800	20.151	80.024	69.808	38.819	3.157	51.050	51.050	2.873
3900	20.489	80.313	70.074	39.934	2.927	52.674	52.674	2.898
4000	20.827	80.595	70.333	41.046	2.694	54.298	54.298	2.923
4100	21.165	80.870	70.587	42.160	2.460	55.922	55.922	2.948
4200	21.503	81.138	70.835	43.273	2.225	57.546	57.546	2.973
4300	21.841	81.401	71.078	44.388	1.990	59.170	59.170	2.998
4400	22.179	81.657	71.315	45.504	1.754	60.794	60.794	3.023
4500	22.517	81.908	71.548	46.621	1.518	62.418	62.418	3.048
4600	22.855	82.154	71.776	47.739	1.283	64.042	64.042	3.073
4700	23.193	82.395	71.999	48.860	1.049	65.666	65.666	3.098
4800	23.531	82.631	72.218	49.982	0.815	67.290	67.290	3.123
4900	23.869	82.863	72.433	51.106	0.581	68.914	68.914	3.148
5000	24.207	83.091	72.644	52.233	0.346	70.538	70.538	3.173
5100	24.545	83.314	72.851	53.361	0.112	72.162	72.162	3.198
5200	24.883	83.534	73.054	54.489	-0.122	73.786	73.786	3.223
5300	25.221	83.750	73.254	55.625	-0.357	75.410	75.410	3.248
5400	25.559	83.962	73.451	56.761	-0.592	77.034	77.034	3.273
5500	25.897	84.170	73.644	57.897	-0.827	78.658	78.658	3.298
5600	26.235	84.376	73.833	59.037	-1.062	80.282	80.282	3.323
5700	26.573	84.578	74.023	60.178	-1.297	81.906	81.906	3.348
5800	26.911	84.776	74.204	61.321	-1.532	83.530	83.530	3.373
5900	27.249	84.972	74.385	62.465	-1.767	85.154	85.154	3.398
6000	27.587	85.165	74.566	63.612	-1.997	86.778	86.778	3.423

June 30, 1961; Sept. 30, 1961; Dec. 31, 1965

 $\Delta H_f^0 = 14.26 \pm 12 \text{ kcal. mole}^{-1}$ $\Delta H_f^{298.15} = 14.0 \pm 12 \text{ kcal. mole}^{-1}$ Ground State Configuration $1\Sigma^+$ $S_{298.15}^0 = 54.33 \pm 2 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Electronic Levels and Quantum Weight

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0	1	(18000)	2
[4000]	6	(22000)	6
[6000]	2	(25500)	2
15500	2	27500	1
[15700]	6	(28500)	6
[17500]	6		

 $\omega_e x_e = 4 \text{ cm.}^{-1}$ $\omega_e = 978 \text{ cm.}^{-1}$ $B_e = 0.4142 \text{ cm.}^{-1}$ $r_e = 1.711 \text{ \AA}$ $\sigma = 1$

Heat of Formation.

The $\Delta H_f^{298.15} = 14.0 \pm 12 \text{ kcal. mole}^{-1}$ was calculated from the $\Delta H_f^{298.15} = 290.342 \pm 12.8 \text{ kcal. mole}^{-1}$ for the reaction $\text{Zr}(c) + \text{ZrO}_2(c) = 2\text{ZrO}(g)$. The value of $\Delta H_f^{298.15}$ was obtained by the third law analysis from the mass spectrometric studies of M. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. **28**, 1207 (1957). They observed the variation of the ZrO^+ ion intensity over the system $\text{Zr} + \text{ZrO}_2$ and reported equilibrium constants for the reaction $\text{Zr} + \text{ZrO}_2 \rightarrow 2\text{ZrO}$ in the range 2124-2322°K. The third law drift is $-58 \pm 28 \text{ e.u.}$

Heat Capacity and Entropy.

The ground state of $\text{ZrO}(g)$ was assumed to be $1\Sigma^+$ as determined from the matrix isolation spectra of W. Weltner, Jr., and D. McLeod, Jr., J. Phys. Chem. **69**, 3488 (1965). Previously this had been described as the lower state in the A band system reported by V. Uhler and L. Akerlind, Arkiv Fysik **10**, 431 (1955).

All molecular constants were obtained from Uhler and Akerlind, loc. cit., except $\omega_e = 978 \text{ cm.}^{-1}$ and $\omega_e x_e = 4 \text{ cm.}^{-1}$ which were calculated from ω and $\omega_e = 0.0023 \text{ cm.}^{-1}$ using the equations

$$\omega_e x_e = \frac{6 \sqrt{\omega_e x_e} \cdot B_e^3}{\omega_e} - \frac{6 B_e^2}{\omega_e} \quad \text{and} \quad \omega_e = \omega_e - 2 \omega_e x_e = 969.76 \text{ cm.}^{-1}$$

The higher electronic levels were obtained or estimated from the correlation diagram given by Weltner and McLeod, loc. cit.

Oxygen, Diatomic (O₂)

(Reference State - Ideal Gas) Mol. Wt. = 31.9988

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹	H° - H° ₂₉₈	ΔH _f °	ΔF _f °	Log K _p
0	∞.000	∞.000	INFINITE	-	2.075	∞.000	∞.000	∞.000
100	6.958	41.395	55.205	-	1.381	∞.000	∞.000	∞.000
200	6.961	46.218	49.643	∞.685	∞.000	∞.000	∞.000	∞.000
298	7.020	49.004	49.004	∞.000	∞.000	∞.000	∞.000	∞.000
300	7.023	49.047	49.004	∞.013	∞.000	∞.000	∞.000	∞.000
400	7.196	51.091	49.282	∞.724	∞.000	∞.000	∞.000	∞.000
500	7.431	52.722	49.812	1.455	∞.000	∞.000	∞.000	∞.000
600	7.670	54.098	50.414	2.210	∞.000	∞.000	∞.000	∞.000
700	7.883	55.297	51.028	2.788	∞.000	∞.000	∞.000	∞.000
800	8.063	56.361	51.629	3.786	∞.000	∞.000	∞.000	∞.000
900	8.212	57.320	52.209	4.600	∞.000	∞.000	∞.000	∞.000
1000	8.336	58.192	52.765	5.427	∞.000	∞.000	∞.000	∞.000
1100	8.439	58.991	53.295	6.266	∞.000	∞.000	∞.000	∞.000
1200	8.527	59.729	53.801	7.114	∞.000	∞.000	∞.000	∞.000
1300	8.604	60.415	54.283	7.971	∞.000	∞.000	∞.000	∞.000
1400	8.674	61.055	54.744	8.835	∞.000	∞.000	∞.000	∞.000
1500	8.738	61.656	55.185	9.706	∞.000	∞.000	∞.000	∞.000
1600	8.800	62.222	55.608	10.583	∞.000	∞.000	∞.000	∞.000
1700	8.858	62.757	56.013	11.465	∞.000	∞.000	∞.000	∞.000
1800	8.916	63.265	56.401	12.354	∞.000	∞.000	∞.000	∞.000
1900	8.973	63.749	56.776	13.249	∞.000	∞.000	∞.000	∞.000
2000	9.029	64.210	57.136	14.149	∞.000	∞.000	∞.000	∞.000
2100	9.084	64.652	57.483	15.054	∞.000	∞.000	∞.000	∞.000
2200	9.139	65.076	57.819	15.966	∞.000	∞.000	∞.000	∞.000
2300	9.194	65.483	58.143	16.882	∞.000	∞.000	∞.000	∞.000
2400	9.248	65.876	58.457	17.804	∞.000	∞.000	∞.000	∞.000
2500	9.301	66.254	58.762	18.732	∞.000	∞.000	∞.000	∞.000
2600	9.354	66.620	59.057	19.664	∞.000	∞.000	∞.000	∞.000
2700	9.405	66.974	59.344	20.602	∞.000	∞.000	∞.000	∞.000
2800	9.455	67.317	59.622	21.545	∞.000	∞.000	∞.000	∞.000
2900	9.503	67.650	59.893	22.493	∞.000	∞.000	∞.000	∞.000
3000	9.551	67.973	60.157	23.446	∞.000	∞.000	∞.000	∞.000
3100	9.596	68.287	60.415	24.403	∞.000	∞.000	∞.000	∞.000
3200	9.640	68.592	60.665	25.365	∞.000	∞.000	∞.000	∞.000
3300	9.682	68.889	60.910	26.331	∞.000	∞.000	∞.000	∞.000
3400	9.723	69.179	61.149	27.302	∞.000	∞.000	∞.000	∞.000
3500	9.762	69.461	61.383	28.276	∞.000	∞.000	∞.000	∞.000
3600	9.799	69.737	61.611	29.254	∞.000	∞.000	∞.000	∞.000
3700	9.835	70.006	61.834	30.234	∞.000	∞.000	∞.000	∞.000
3800	9.869	70.269	62.053	31.221	∞.000	∞.000	∞.000	∞.000
3900	9.901	70.525	62.267	32.209	∞.000	∞.000	∞.000	∞.000
4000	9.932	70.776	62.476	33.201	∞.000	∞.000	∞.000	∞.000
4100	9.961	71.022	62.682	34.196	∞.000	∞.000	∞.000	∞.000
4200	9.988	71.262	62.883	35.193	∞.000	∞.000	∞.000	∞.000
4300	10.015	71.498	63.081	36.193	∞.000	∞.000	∞.000	∞.000
4400	10.039	71.728	63.275	37.196	∞.000	∞.000	∞.000	∞.000
4500	10.062	71.954	63.465	38.201	∞.000	∞.000	∞.000	∞.000
4600	10.084	72.176	63.652	39.208	∞.000	∞.000	∞.000	∞.000
4700	10.104	72.393	63.836	40.218	∞.000	∞.000	∞.000	∞.000
4800	10.123	72.606	64.016	41.229	∞.000	∞.000	∞.000	∞.000
4900	10.140	72.814	64.194	42.242	∞.000	∞.000	∞.000	∞.000
5000	10.156	73.019	64.368	43.257	∞.000	∞.000	∞.000	∞.000
5100	10.172	73.221	64.540	44.274	∞.000	∞.000	∞.000	∞.000
5200	10.187	73.418	64.708	45.292	∞.000	∞.000	∞.000	∞.000
5300	10.200	73.613	64.875	46.311	∞.000	∞.000	∞.000	∞.000
5400	10.213	73.803	65.038	47.332	∞.000	∞.000	∞.000	∞.000
5500	10.225	73.991	65.199	48.353	∞.000	∞.000	∞.000	∞.000
5600	10.237	74.175	65.358	49.377	∞.000	∞.000	∞.000	∞.000
5700	10.247	74.356	65.514	50.401	∞.000	∞.000	∞.000	∞.000
5800	10.256	74.535	65.668	51.426	∞.000	∞.000	∞.000	∞.000
5900	10.267	74.710	65.820	52.452	∞.000	∞.000	∞.000	∞.000
6000	10.276	74.883	65.970	53.479	∞.000	∞.000	∞.000	∞.000

Dec. 31, 1960; Mar. 31, 1961; Sept. 30, 1965

OXYGEN, DIATOMIC (O₂) (REFERENCE STATE - IDEAL GAS)

Ground State Configuration 3Σ_g⁻ ΔH_f° 0 = 0

S_{298.15}° = 49.00 ± 0.01 cal. deg⁻¹ mole⁻¹ ΔH_f° 298.15 = 0

ω_e = 1580.245 cm.⁻¹ ω_ex_e = 12.071 cm.⁻¹ σ⁻ = 2

B_e = 1.445 cm.⁻¹ ω_e = 0.0158 cm.⁻¹ r_e = 1.2074 Å

Heat of Formation.

The heat of formation (ΔH_f°) for O₂(g) is zero at all temperatures, by definition.

Heat Capacity and Entropy.

The functions adopted here are based on those of H. W. Woolley, J. Research, Nat. Bur. Standards 40, 183 (1948), who used a direct summation to 5000°K. The spectroscopic constants used were the same as those listed by G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Co., 1950. Raman measurements of rotation-vibration levels by A. Weber and E. A. McInnis, J. Molec. Spect., 4, 195 (1960), support the constants selected by Herzberg which were changed on this table to apply to the naturally occurring isotopic composition given by D. Strominger, J. M. Hollander, and T. Seaborg, Rev. Mod. Phys. 30, 585 (1958).

The entropies listed by Woolley were reduced by 0.0065 cal. deg⁻¹ mole⁻¹ which was added by Woolley to account for the contribution due to the presence of both odd and even rotational levels in O₂¹⁶O¹⁷ and O₂¹⁶O¹⁸ molecules. This correction is not necessary when isotope mixing entropy is neglected, cf. W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. 55, 1731 (1933).

Diatomic Oxygen Uninegative Ion (O_2^-)
(Ideal Gas) GFW = 31.99935

T, °K	Cp ^a	S ^b - (C _p ^a - H _{298.15})/T	H ^c - H _{298.15}	ΔH ^c	ΔG ^f	Log K _p
0						
100						
200						
298	7.202	49.913	49.913	0.000	-11.390	-10.174
300						7.458
400	7.207	49.937	49.937	0.13	-11.390	-10.166
500	7.209	50.074	50.074	0.13	-11.390	-10.166
600	7.213	50.768	50.751	1.518	-12.330	-9.084
700	7.218	51.218	51.218	2.314	-12.766	-8.392
800	7.224	51.584	51.584	3.139	-13.242	-7.623
900	7.230	51.864	51.864	4.000	-13.762	-6.800
1000	7.236	52.064	52.064	4.904	-14.322	-6.000
1100	7.242	52.184	52.184	5.844	-14.924	-5.224
1200	7.248	52.224	52.224	6.824	-15.568	-4.472
1300	7.254	52.284	52.284	7.844	-16.244	-3.744
1400	7.260	52.364	52.364	8.904	-16.952	-3.044
1500	7.266	52.464	52.464	10.004	-17.692	-2.364
1600	7.272	52.584	52.584	11.144	-18.464	-1.704
1700	7.278	52.724	52.724	12.324	-19.268	-1.064
1800	7.284	52.884	52.884	13.544	-20.104	-0.444
1900	7.290	53.064	53.064	14.804	-20.972	0.156
2000	7.296	53.264	53.264	16.104	-21.872	0.796
2100	7.302	53.484	53.484	17.444	-22.804	1.472
2200	7.308	53.724	53.724	18.824	-23.768	2.184
2300	7.314	53.984	53.984	20.244	-24.764	2.932
2400	7.320	54.264	54.264	21.704	-25.792	3.716
2500	7.326	54.564	54.564	23.204	-26.852	4.536
2600	7.332	54.884	54.884	24.744	-27.944	5.392
2700	7.338	55.224	55.224	26.324	-29.068	6.284
2800	7.344	55.584	55.584	27.944	-30.224	7.212
2900	7.350	55.964	55.964	29.604	-31.412	8.176
3000	7.356	56.364	56.364	31.304	-32.632	9.176
3100	7.362	56.784	56.784	33.044	-33.884	10.212
3200	7.368	57.224	57.224	34.824	-35.168	11.284
3300	7.374	57.684	57.684	36.644	-36.484	12.392
3400	7.380	58.164	58.164	38.504	-37.832	13.536
3500	7.386	58.664	58.664	40.404	-39.212	14.716
3600	7.392	59.184	59.184	42.344	-40.624	15.932
3700	7.398	59.724	59.724	44.324	-42.068	17.184
3800	7.404	60.284	60.284	46.344	-43.544	18.472
3900	7.410	60.864	60.864	48.404	-45.052	19.796
4000	7.416	61.464	61.464	50.504	-46.592	21.156
4100	7.422	62.084	62.084	52.644	-48.164	22.552
4200	7.428	62.724	62.724	54.824	-49.768	23.984
4300	7.434	63.384	63.384	57.044	-51.404	25.452
4400	7.440	64.064	64.064	59.304	-53.072	26.956
4500	7.446	64.764	64.764	61.604	-54.772	28.496
4600	7.452	65.484	65.484	63.944	-56.504	30.072
4700	7.458	66.224	66.224	66.324	-58.268	31.684
4800	7.464	66.984	66.984	68.744	-60.064	33.332
4900	7.470	67.764	67.764	71.204	-61.892	35.016
5000	7.476	68.564	68.564	73.704	-63.752	36.736
5100	7.482	69.384	69.384	76.244	-65.644	38.492
5200	7.488	70.224	70.224	78.824	-67.568	40.284
5300	7.494	71.084	71.084	81.444	-69.524	42.112
5400	7.500	71.964	71.964	84.104	-71.512	43.976
5500	7.506	72.864	72.864	86.804	-73.532	45.876
5600	7.512	73.784	73.784	89.544	-75.584	47.812
5700	7.518	74.724	74.724	92.324	-77.668	49.784
5800	7.524	75.684	75.684	95.144	-79.784	51.792
5900	7.530	76.664	76.664	98.004	-81.932	53.836
6000	7.536	77.664	77.664	100.904	-84.112	55.916

Sept. 30, 1965, Dec. 31, 1966

DIATOMIC OXYGEN UNINEGATIVE ION (O_2^-) (IDEAL GAS) OFW = 31.99935

Ground State Configuration [$^2\Pi_g^-$]
 $S_{298.15}^\circ = 49.91 \pm 0.1$ gibbs/mol
 $\Delta H_{298.15}^\circ = -11.39 \pm 0.5$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_{\lambda}, \text{cm}^{-1}$	g_{λ}
0	[4]
29400	[4]
$\omega_e = 1170 \text{ cm}^{-1}$	
$\omega_e x_e = 8.5 \text{ cm}^{-1}$	
$\sigma_e = 2$	
$\alpha_e = [0.013] \text{ cm}^{-1}$	
$r_e = 1.30 \text{ \AA}$	

Heat of Formation.

The electron affinity of $O_2(g)$ has been measured in the electron detachment experiments of J. L. Pack and A. V. Phelps, J. Chem. Phys. **44**, 1870 (1966). The value reported is 0.43 ± 0.02 eV (9.92 ± 0.46 kcal/mol) which is in good agreement with the value 0.46 ± 0.1 eV selected by C. W. Beckett and E. C. Casady, Natl. Bur. Std. Report 6628, Jan. 1, 1965.

Heat Capacity and Entropy.

J. Rolfe, J. Chem. Phys. **40**, 1864 (1964), has deduced from fluorescence emission spectra of O_2^- in alkali halides, the vibrational constants and an excited electronic level. The $^2\Pi_g$ ground state is that predicted by molecular orbital theory and the first excited state should also be $^2\Pi_u$. By analogy with Cl_2^+ , which is isoelectronic, the first excited level is estimated to lie in the 20000 - 30000 cm^{-1} region. Thus, the level observed by Rolfe is assumed to be the first excited $^2\Pi_u$ state. The bond length is taken from F. R. Gilmore, The Rand Corporation, Memorandum RM-4034-1-Ph, AD 630997. B_e was calculated from the bond length and a_e was estimated from the above quantities using the Morse potential function relation.

The enthalpy at 0°K is -2.086 kcal/mol.

Phosphorus Dioxide (PO₂)

INTERIM TABLE

(Ideal Gas) Mol. Wt. = 62.975

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0	8.000	INFINITE	INFINITE	-	2.548	-	70.611	-	INFINITE
100	8.016	51.132	68.657	-	1.752	-	71.431	-	156.105
200	8.802	56.890	71.476	-	0.917	-	70.782	-	78.882
298	9.897	60.607	72.834	-	0.000	-	71.000	-	53.387
300	9.917	60.668	72.834	-	0.018	-	71.004	-	53.065
400	10.913	63.663	81.009	-	1.062	-	71.204	-	40.118
500	11.659	66.183	81.798	-	2.192	-	71.376	-	32.328
600	12.189	68.358	82.714	-	3.386	-	71.538	-	27.123
700	12.559	70.122	83.710	-	4.634	-	71.682	-	23.442
800	12.837	71.464	84.796	-	5.936	-	71.810	-	20.046
900	13.038	72.488	85.949	-	7.190	-	71.925	-	16.244
1000	13.188	73.267	87.163	-	8.402	-	72.020	-	12.500
1100	13.306	73.832	88.430	-	9.577	-	72.100	-	8.455
1200	13.395	74.299	89.740	-	10.722	-	72.167	-	4.481
1300	13.467	74.669	91.090	-	11.842	-	72.223	-	0.945
1400	13.525	74.949	92.473	-	12.942	-	72.270	-	-3.168
1500	13.573	75.134	93.886	-	14.019	-	72.308	-	-5.406
1600	13.612	75.230	95.324	-	15.071	-	72.338	-	-7.659
1700	13.642	75.246	96.786	-	16.097	-	72.360	-	-9.827
1800	13.663	75.183	98.269	-	17.097	-	72.376	-	-11.919
1900	13.677	75.044	99.770	-	18.071	-	72.387	-	-13.940
2000	13.684	74.830	101.290	-	19.019	-	72.393	-	-15.907
2100	13.685	74.551	102.829	-	19.942	-	72.395	-	-17.827
2200	13.680	74.218	104.386	-	20.840	-	72.393	-	-19.697
2300	13.670	73.832	105.959	-	21.713	-	72.387	-	-21.514
2400	13.655	73.396	107.544	-	22.562	-	72.376	-	-23.276
2500	13.636	72.910	109.139	-	23.387	-	72.360	-	-24.982
2600	13.613	72.375	110.744	-	24.190	-	72.340	-	-26.632
2700	13.586	71.790	112.358	-	24.972	-	72.316	-	-28.226
2800	13.555	71.154	113.980	-	25.734	-	72.289	-	-29.764
2900	13.520	70.468	115.609	-	26.477	-	72.259	-	-31.246
3000	13.482	69.732	117.244	-	27.202	-	72.225	-	-32.672
3100	13.441	68.946	118.884	-	27.909	-	72.188	-	-34.044
3200	13.397	68.110	120.528	-	28.600	-	72.147	-	-35.362
3300	13.350	67.224	122.175	-	29.275	-	72.102	-	-36.626
3400	13.300	66.288	123.824	-	29.935	-	72.054	-	-37.846
3500	13.247	65.302	125.474	-	30.580	-	72.003	-	-39.012
3600	13.191	64.266	127.124	-	31.210	-	71.949	-	-40.124
3700	13.132	63.180	128.774	-	31.825	-	71.892	-	-41.182
3800	13.070	62.044	130.424	-	32.426	-	71.832	-	-42.186
3900	13.005	60.858	132.074	-	33.013	-	71.769	-	-43.136
4000	12.938	59.622	133.724	-	33.586	-	71.703	-	-44.032
4100	12.868	58.336	135.374	-	34.145	-	71.634	-	-44.874
4200	12.795	57.000	137.024	-	34.690	-	71.562	-	-45.662
4300	12.719	55.614	138.674	-	35.221	-	71.487	-	-46.396
4400	12.640	54.178	140.324	-	35.739	-	71.409	-	-47.076
4500	12.558	52.692	141.974	-	36.244	-	71.328	-	-47.702
4600	12.473	51.156	143.624	-	36.736	-	71.244	-	-48.276
4700	12.385	49.570	145.274	-	37.215	-	71.157	-	-48.798
4800	12.294	47.934	146.924	-	37.681	-	71.067	-	-49.268
4900	12.200	46.248	148.574	-	38.134	-	70.974	-	-49.686
5000	12.103	44.512	150.224	-	38.574	-	70.878	-	-50.052
5100	12.004	42.726	151.874	-	39.001	-	70.779	-	-50.366
5200	11.902	40.890	153.524	-	39.415	-	70.677	-	-50.628
5300	11.797	39.004	155.174	-	39.816	-	70.572	-	-50.838
5400	11.690	37.068	156.824	-	40.204	-	70.464	-	-50.998
5500	11.580	35.082	158.474	-	40.579	-	70.353	-	-51.108
5600	11.467	33.046	160.124	-	40.942	-	70.239	-	-51.168
5700	11.352	30.960	161.774	-	41.293	-	70.122	-	-51.178
5800	11.234	28.824	163.424	-	41.632	-	70.003	-	-51.138
5900	11.114	26.638	165.074	-	41.959	-	69.881	-	-51.048
6000	10.991	24.402	166.724	-	42.273	-	69.756	-	-50.908

Dec. 31, 1960; Sept. 30, 1962

Phosphorus Dioxide (PO₂)

(Ideal Gas)

Mol. Wt. = 62.975

 $\Delta H_f^\circ 298.15 = [-71] \text{ kcal. mole}^{-1}$ $S_{298.15}^\circ = [60.6] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Point Group = C_{2v}

Ground State Degeneracy = 2

Vibrational Frequencies and Degeneracies

 $\omega, \text{ cm.}^{-1}$
 [960] (1)
 [515] (1)
 [1044] (1)

Angle O-P-O = 134° 4'

P-O distance = 1.485 Å

 $I_A = [10.81 \times 10^{-39}] \text{ g. cm.}^2$ $I_B = [9.933 \times 10^{-39}] \text{ g. cm.}^2$ $I_C = [0.677 \times 10^{-39}] \text{ g. cm.}^2$ $\sigma = 2$ Heat of Formation. $\Delta H_f^\circ 298.15$ was calculated from an estimated heat of dissociation ($270 \pm 25 \text{ kcal. mole}^{-1}$) reported by L. Brewer and G. M. Rosenblatt, Chem. Reviews, **61**, 257 (1961).

Heat Capacity and Entropy. The molecular constants selected for this table were estimated by J. S. Gordon. The molecular constants for PO₂(g) have been estimated by (1) J. S. Gordon, "Thermodynamic Data for Combustion Products," January 1960, Thiokol Chemical Corp., Reaction Motor Division, Danville, N. J.; (2) R. L. Fetter, V. N. DiStefano and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus-I," American Cyanamid Company; and (3) C. B. Henderson and R. S. Scheffer, "Survey of Thermochemical Data," January 1960, Atlantic Research Corp., Alexandria, Virginia. The entropies at 3000° calculated from these three estimates differ by less than 0.8 cal. deg.⁻¹ mole⁻¹.

INTERIM TABLE

T, °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	0.000	INFINITE	2.762	63.590	63.590	INFINITE	
100	7.500	5.733	19.483	2.411	2.411	64.375	58.916	130.940	
200	12.720	12.723	19.593	1.307	1.307	64.547	57.769	37.213	
298	14.871	14.277	19.277	0.000	0.000	64.547	57.769	37.213	
300	14.890	16.369	19.277	0.028	0.028	64.544	50.684	36.921	
400	13.820	22.794	14.874	1.568	1.568	64.367	46.069	25.180	
500	16.600	26.408	20.030	3.189	3.189	64.150	41.544	16.156	
600	17.380	29.508	21.387	4.888	4.888	63.896	37.045	13.493	
700	17.860	32.242	22.720	6.665	6.665	64.767	32.402	10.116	
800	18.940	34.717	24.067	8.520	8.520	64.431	27.802	7.595	
900	19.720	36.993	25.379	10.453	10.453	64.026	23.246	5.685	
1000	20.500	39.111	26.647	12.464	12.464	63.548	18.739	4.095	
1100	21.280	41.102	27.872	14.553	14.553	62.997	14.285	2.838	
1200	21.960	42.987	29.052	16.720	16.720	62.369	9.883	1.800	
1300	22.480	44.743	30.195	18.965	18.965	61.667	5.537	0.931	
1400	23.420	46.505	31.299	21.288	21.288	60.893	1.249	0.195	
1500	24.400	48.161	32.368	23.689	23.689	60.047	2.983	0.435	
1600	25.180	49.740	33.405	26.168	26.168	59.132	7.155	0.977	
1700	25.960	51.110	34.413	28.725	28.725	58.146	11.270	1.448	
1800	26.740	52.416	35.394	31.360	31.360	57.094	15.321	1.860	
1900	27.520	54.283	36.350	34.073	34.073	55.974	19.314	2.221	

March 31, 1962

Lead Dioxide (PbO₂) (crystal)

Mol. Wt. = 239.21

ΔH_f° 298.15 = -64.55 ± 0.16 kcal. mole⁻¹S° 298.15 = 18.3 ± 0.5 cal. deg.⁻¹ mole⁻¹

Heat of Formation. Recalculated from ΔH_f° 298.15 = 12.14 kcal. mole⁻¹ for the reaction: PbO(c) + 1/2O₂(g) = PbO₂(c) reported by M. Tschelitzow, Compt. rend., 100, 1458 (1885).

Heat Capacity and Entropy. C_p (69.9° to 297.2°K.) reported by R. W. Millar, J. Am. Chem. Soc. 51, 207 (1929). Above 298.15°K., the heat capacity value estimated by K. K. Kelley, U. S. Bur. Mines Bull. 594 (1960) was used. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation.

Sulfur Dioxide (SO₂)
(Ideal Gas) Mol. Wt. = 64.066

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞
100	4.000	INFINITE	2.522	70.341	70.341	INFINITE
200	4.033	49.492	1.665	70.421	70.421	175.088
300	4.066	50.298	1.003	70.507	70.507	222.342
400	4.098	50.958	0.618	70.592	70.592	266.168
500	4.129	51.583	0.437	70.674	70.674	308.308
600	4.159	52.180	0.323	70.752	70.752	348.816
700	4.188	52.753	0.237	70.826	70.826	387.888
800	4.216	53.301	0.174	70.896	70.896	425.624
900	4.243	53.823	0.126	70.962	70.962	462.128
1000	4.269	54.320	0.090	71.024	71.024	497.504
1100	4.294	54.793	0.063	71.082	71.082	531.856
1200	4.318	55.243	0.044	71.136	71.136	565.288
1300	4.341	55.671	0.031	71.186	71.186	597.808
1400	4.363	56.078	0.022	71.232	71.232	629.424
1500	4.385	56.464	0.016	71.274	71.274	660.144
1600	4.406	56.830	0.011	71.312	71.312	690.000
1700	4.426	57.177	0.007	71.346	71.346	719.040
1800	4.445	57.505	0.004	71.376	71.376	747.312
1900	4.463	57.814	0.003	71.402	71.402	774.768
2000	4.480	58.104	0.002	71.424	71.424	801.456
2100	4.496	58.375	0.001	71.442	71.442	827.328
2200	4.511	58.628	0.001	71.456	71.456	852.432
2300	4.525	58.863	0.000	71.466	71.466	876.720
2400	4.538	59.080	0.000	71.472	71.472	899.248
2500	4.550	59.280	0.000	71.475	71.475	920.000
2600	4.561	59.464	0.000	71.475	71.475	939.040
2700	4.571	59.633	0.000	71.472	71.472	956.416
2800	4.580	59.787	0.000	71.466	71.466	972.192
2900	4.588	59.927	0.000	71.456	71.456	986.432
3000	4.595	60.054	0.000	71.442	71.442	999.104
3100	4.601	60.169	0.000	71.424	71.424	1010.288
3200	4.606	60.272	0.000	71.402	71.402	1020.000
3300	4.610	60.364	0.000	71.376	71.376	1028.320
3400	4.613	60.445	0.000	71.346	71.346	1035.312
3500	4.615	60.515	0.000	71.312	71.312	1041.040
3600	4.616	60.574	0.000	71.274	71.274	1045.488
3700	4.616	60.622	0.000	71.232	71.232	1048.624
3800	4.615	60.659	0.000	71.186	71.186	1050.432
3900	4.613	60.685	0.000	71.136	71.136	1050.912
4000	4.610	60.700	0.000	71.082	71.082	1050.080
4100	4.606	60.704	0.000	71.024	71.024	1047.904
4200	4.601	60.698	0.000	70.962	70.962	1044.336
4300	4.595	60.681	0.000	70.896	70.896	1039.440
4400	4.588	60.654	0.000	70.826	70.826	1033.184
4500	4.580	60.617	0.000	70.752	70.752	1025.616
4600	4.571	60.570	0.000	70.674	70.674	1016.800
4700	4.561	60.513	0.000	70.592	70.592	1006.800
4800	4.550	60.445	0.000	70.507	70.507	995.584
4900	4.538	60.364	0.000	70.421	70.421	983.104
5000	4.525	60.272	0.000	70.341	70.341	969.360
5100	4.511	60.169	0.000	70.274	70.274	954.336
5200	4.496	60.054	0.000	70.232	70.232	938.000
5300	4.480	59.927	0.000	70.200	70.200	920.384
5400	4.463	59.787	0.000	70.174	70.174	901.536
5500	4.445	59.628	0.000	70.156	70.156	881.488
5600	4.426	59.464	0.000	70.142	70.142	860.288
5700	4.406	59.280	0.000	70.132	70.132	838.000
5800	4.385	59.080	0.000	70.124	70.124	814.720
5900	4.363	58.863	0.000	70.116	70.116	790.496
6000	4.341	58.628	0.000	70.109	70.109	765.280

June 30, 1961

Sulfur Dioxide (SO₂) (Ideal Gas)

MOL. WT. = 64.066

ΔH°_f 298.15 = -70.341 ± 0.05 kcal. mole⁻¹
 ΔH°_f 298.15 = -70.947 ± 0.05 kcal. mole⁻¹
 S°_{298.15} = 59.30 ± 0.02 cal. deg.⁻¹ mole⁻¹

Vibrational Levels and Multiplicities

ω, cm. ⁻¹
1151.36 (1)
517.69 (1)
1361.76 (1)

Bond Lengths and Angles S-O = 1.432 ± 0.003 Å. OSO = 119.53 ± 0.4°

Moments of Inertia I_A = 1.39046 × 10⁻³⁹ g. cm.² I_B = 8.13067 × 10⁻³⁹ g. cm.² I_C = 9.53376 × 10⁻³⁹ g. cm.² σ⁰ = 2

Heat of Formation

J. R. Eohman and P. D. Rossini, J. Research Nat. Bur. Standards **53**, 597 (1959), measured the heat of combustion of rhombic sulfur to SO₂. Changes due to different atomic weights and electrical constants though negligible have been made.

Heat Capacities and Entropies

The functions were calculated by J. Gordon, private communication, Feb. 2, 1961, using the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954). Structural parameters are given by M. H. Sirvets, J. Chem. Phys. **19**, 938 (1951), obtained from microwave measurements. Frequencies were measured by R. D. Shelton, A. H. Nielsen, W. H. Fletcher, J. Chem. Phys. **23**, 2178 (1955) and **22**, 1791 (1954). A third law value of S°_{298.15} = 59.24 cal. deg.⁻¹ mole⁻¹ was obtained by W. F. Duanque and C. C. Stevenson, J. Am. Chem. Soc. **80**, 1389 (1958).

O₂S

O₂S

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	.0000	INFINITE	INFINITE	- 1.653	- 216.509	- 216.509	INFINITE
100	3.749	2.317	17.327	- 1.501	- 217.115	- 213.116	465.764
200	7.801	6.235	10.800	- .913	- 217.504	- 208.950	228.330
298	10.557	9.910	9.910	.000	- 217.700	- 204.703	150.051
300	10.700	9.976	9.910	.020	- 217.702	- 204.423	149.067
400	12.770	13.354	10.357	1.199	- 217.741	- 200.253	109.413
500	14.255	16.372	11.264	2.554	- 217.661	- 195.988	95.622
600	15.396	19.075	12.344	4.038	- 217.500	- 191.687	80.771
700	16.115	21.798	13.432	5.730	- 217.270	- 187.359	68.469
800	16.480	24.008	14.632	7.330	- 216.969	- 182.969	58.085
900	16.480	26.008	16.095	10.840	- 216.336	- 174.561	38.150
1000	16.720	29.311	17.947	12.900	- 216.350	- 170.393	33.678
1100	17.000	32.146	19.916	15.492	- 215.763	- 162.104	27.253
1200	17.200	34.638	21.718	17.624	- 215.560	- 157.987	24.663
1300	17.440	36.638	23.438	19.380	- 215.350	- 153.981	22.420
1400	17.640	38.287	25.012	21.160	- 215.132	- 149.791	20.460
1500	17.800	39.689	26.472	24.792	- 226.409	- 140.833	17.099
1600	18.000	40.926	27.826	26.644	- 226.302	- 136.076	15.652
1700	18.200	42.033	29.000	28.520	- 225.976	- 131.339	14.352

ΔH°₂₉₈ = -216.5 ± 0.4 kcal/mol
 ΔH°_{298.15} = -217.7 ± 0.4 kcal/mol
 ΔH°₁ = 847 ± 1.5°K (low quartz + high quartz)
 ΔH°₂ = 1079 ± 250°K (high quartz + high cristobalite)
 ΔH°_m = 1.84 ± 0.2 kcal/mol

Heat of Formation

The heat of formation is based on data of Wise (1) for combustion of SiO₂ (low quartz) and Si(c) in F₂ to form SiF₄(g). Good (2) burned a mixture of Si(c) and vinylidene fluoride polymer in oxygen in the presence of HF(aq) to form H₂SiF₆(aq HF). Combining this result with a previous heat of solution of quartz (3), the authors derived ΔH°₂₉₈ = -217.5 ± 0.5 kcal/mol. Agreement with the adopted value is excellent, considering the complexity of the latter scheme. Both schemes are independent of ΔH°_f (HF), although the polymer-Si scheme depends on the heat of dilution of HF(aq). Wise (1) has reviewed other data which confirm the adopted value rather than the oxygen combustion value (4) of -209.9 kcal/mol. Pertinent equilibrium data are analyzed on the table for SiO₂ (low cristobalite), while the calorimetric results are summarized below.

Source	Reaction	ΔH° ₂₉₈ , kcal/mol	ΔH° ₁ , kcal/mol
1. Wise (1963)	SiO ₂ (low quartz) + 2F ₂ (g) → SiF ₄ (g) + O ₂ (g)	-188.26 ± 0.78	-217.72 ± 0.34
2. Good (1964)	See text.	-	-217.5
3. Humphrey (1962)	Si(c) + 2O ₂ (g) → SiO ₂ (low quartz)	-209.9	-209.9

Heat Capacity and Entropy

Heat capacities below 300°K are based on data of Jones (5) and Westrum (6). Earlier data of Anderson (7) are in good agreement. The entropy is obtained from Cp° using S°₂ = 0.00001 eu. Cp° from 300° to 847°K is derived from adiabatic calorimetric data of Moser (8) and Sineil'nikov (9). The adopted Cp° is discontinuous at 847°K and ΔCp° = -2.17 gibbs/mol. Values above the transition temperature are based on data of Moser and on data up to 1473°K obtained with a thermal analysis method by Leonidov (10). Cp° is extrapolated linearly to higher temperatures.

From a review of data available before 1953, Kelley (11) selected almost identical enthalpies below 847°K but a value higher by 96 cal/mol at 900°K. The higher value, due to use of a larger ΔH°_f, was presumably based on Roth (12), Wietzel (13) and White (14) whose enthalpy data were given the most weight by Kelley. Near 900°K these three sets of data deviate from the adopted function by -150±30, +130±40 and +15±35 cal/mol, respectively; however, a recent enthalpy datum (15) obtained by transposed temperature drop calorimetry deviates by +75 cal/mol at 968°K.

Transition Data

T₁ is taken as 847 ± 1.5°K based on thermal analysis of many specimens by Kieth and Tuttle (16). Wide variations in T₁ for some specimens were attributed by the authors to small amounts of impurities. The discontinuity in the volume curve (17) during inversion from trigonal low quartz to hexagonal high quartz suggests that the transition should be treated as first order. Thus, the heat of transition is derived as (1011-854)/17 = 174 cal/mol, where 1011 ± 6 is (H°_{298.15} - H°_{847.15}) measured by Moser (8), 854 is the corresponding increment calculated from the JANAF Cp°, and 17 is an endpoint correction for the difference between the observed and adopted curves below 823.15°K. Some of the more recent data which confirm the adopted ΔH°₁ are summarized below.

Source	Method	ΔH° ₁ , kcal/mol
8. Moser (1936)	H and Cp from adiabatic calorimetry	0.174
9. Sineil'nikov (1953)	Integration of Cp from adiabatic calorimetry	0.143
10. Leonidov (1964)	Thermal analysis	0.198
17. Berger (1964)	ΔV with dT/dP = 0.076°K/atm	0.12
18. Berger (1965)	Microcalorimetric thermal analysis	0.156, 0.165, 0.178 ± 0.010
	Single crystal	0.124 to 0.193
	Various crushed samples	

Additional polymorphism of SiO₂ is discussed on the table for high cristobalite. Quartz has been superheated through the cristobalite region to some 300° above its metastable melting point. This melting point is calculated from the adopted tables as 1896 ± 50°K, which agrees well with the range 1673 - 1773°K indicated by the data of Mackenzie (18). The adopted tables predict the inversion of high quartz to high cristobalite at 1079 ± 250°K. Holmquist (20) tentatively placed this inversion at 1298 ± 25°K. ΔH°₂ and ΔH°_m are calculated from the differences in heats of formation of the appropriate phases at T₂ and T_m.

References

1. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.* **67**, 815 (1963). ΔH°_f.
2. W. D. Good, J. L. Lacina, B. L. DePrater and J. P. McCullough, *J. Phys. Chem.* **68**, 579 (1964); **68**, 380 (1962). ΔH°_f.
3. E. C. King, *J. Am. Chem. Soc.* **73**, 656 (1951). ΔH°_f.
4. L. Humphrey and R. C. H. Allister, *Can. J. Phys.* **38**, 696 (1960). CP, 2-4°K. ΔH°_f.
5. G. N. Sineil'nikov, *Dokl. Akad. Nauk SSSR* **211**, 135 (1973).
6. E. F. Westrum, Jr., et al., private comm. Univ. Michigan, May 19, 1960; see also A. J. Leadbetter and J. A. Morrison, *Phys. Chem. Glasses* **4**, 188 (1963). CP, 5-300°K.
7. C. T. Anderson, *J. Am. Chem. Soc.* **58**, 568 (1936). CP, 5-300°K.
8. H. Moser, *Physik. Z.* **37**, 737 (1936). CP, 317-349°K.
9. V. Sineil'nikov, *Dokl. Akad. Nauk SSSR* **211**, 135 (1973). CP, 300-900°K, given graphically.
10. V. Sineil'nikov, Yu. P. Barakki and N. I. Khitarov, *Goschimistry (English Transl.)* **1964**, 409 (1964).
11. K. K. Kelley, U. S. Bur. Mines Bull. **584**, 1960.
12. W. A. Roth and W. W. Bertram, *Z. Elektrochem.* **35**, 297 (1929). H, 369-1171°K.
13. R. Wietzel, *Z. Anorg. Allgem. Chem.* **115**, 71 (1921). H, 373-1673°K.
14. J. F. Holmquist, *Am. J. Sci.* **25**, 135 (1926).
15. J. L. Holmquist, O. J. Kleppa and E. F. Westrum, *J. Res. Natl. Bur. Stand.* **72A**, 135 (1968).
16. M. L. Keith and O. F. Tuttle, *Am. J. Sci.* **252**, 203 (1952). T₁.
17. C. Berger, L. Eyraud, M. Richard and R. Riviere, *Bull. Soc. Chim. France* **1956**, 628 (1956). Transition data.
18. C. Berger, M. Richard and L. Eyraud, *Bull. Soc. Chim. France* **1955**, 1491 (1955). ΔH°_f.
19. J. D. Mackenzie, *J. Am. Ceram. Soc.* **43**, 615 (1960). T_m.
20. S. B. Holmquist, *J. Am. Ceram. Soc.* **43**, 82 (1961). T₂.

Cristobalite, Low (SiO₂)

(Crystal) GFW = 60.0848

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	-215.938	-	INFINITE
100	3.424	2.688	17.866	-1.518	-216.532	-212.570	464.571
200	7.886	6.663	11.268	-0.921	-216.912	-208.443	227.776
298	10.744	10.372	10.372	0.000	-217.100	-204.241	149.712
300	10.790	10.439	10.372	0.020	-217.102	-204.141	148.731
400	12.702	13.426	10.421	1.202	-217.138	-199.839	109.187
500	14.023	16.608	11.726	2.541	-217.074	-195.519	85.461
600	15.050	19.461	12.799	3.998	-216.940	-191.220	69.652
700	15.700	21.933	13.663	5.530	-216.763	-186.942	56.397
800	16.100	24.063	14.367	7.300	-216.569	-182.742	45.342
900	16.300	25.882	14.946	8.763	-216.362	-178.478	35.340
1000	16.400	27.637	17.208	10.428	-216.148	-174.281	38.099

CRISTOBALITE, LOW (SiO₂)

(CRYSTAL)

GFW = 60.0848

O₂Si

ΔHf° = -215.9 ± 0.5 kcal/mol

ΔHf°_{298.15} = -217.1 ± 0.5 kcal/mol

ΔHt° = 0.321 ± 0.06 kcal/mol

S°_{298.15} = 10.372 ± 0.03 gibbs/mol

Tt = 543 ± 3°K (Low cristobalite + high cristobalite)

Heat of Formation

The heat of formation is calculated from that of quartz using ΔHr°₂₉₈ = 0.45 ± 0.15 kcal/mol for high quartz + high cristobalite, as determined by Holm(1) from ΔHsoln in an oxide melt. This value reduces to ΔHr°₂₉₈ = 0.60 kcal/mol for low quartz + low cristobalite. Kracek(2) obtained essentially the same value, ΔHr°₂₉₈ = 0.63 kcal/mol, from ΔHsoln in HF(aq, 74.7°C), while Hummel(3) found ΔHr°₂₉₈ = 1.80 kcal/mol from ΔHsoln in HF(aq, 26.5°C). The larger ΔHr° corresponds to a less negative ΔHf° (i.e., less stable) and suggests that the sample of Hummel has disorder approaching that of vitreous silica. Presumably, this disagreement arises from different methods of preparation of cristobalite from quartz. Holm heated for 24 hours at 1743°K, while Hummel heated for 4 hours at 1737°K. Hummel's sample was then ground and treated with dilute HF to remove amorphous surface layers created by grinding; particles smaller than 2.5 microns were used in order to obtain adequate rates of dissolution. Neither author gave X-ray or DTA evidence to confirm that the samples were the more stable, ordered form of cristobalite(13).

The calorimetric data are summarized below along with equilibrium data which confirm the adopted values of ΔHf° for cristobalite and quartz. Data from Matoba(5) and Rein(6) were reduced to the standard state of Si(l) using activity coefficients from the curves of (10).

Source	Method	Reaction	Range, T, °K	No. of Points	ΔHr° ₂₉₈ , kcal/mol	Drift, au	ΔHf° ₂₉₈ , kcal/mol
1. Holm (1967)	ΔHsoln in oxide melt	A	279-65	3	0.45±0.15	-	-217.10
2. Hummel (1959)	ΔHsoln in HF(aq, 26.5°C)	A	299-65	8	1.80±0.2	-	-215.90
3. Kracek (1953)	ΔHsoln in HF(aq, 74.7°C)	A	298-348	6	0.63±0.05	-	-217.07
4. Humphrey (1952)	ΔHsoln in HF(aq, 73.7°C)	B	298-347	6	1.04±0.6*	-	-216.77
5. Matoba (1959)	Keq + Y(Si)	C	1843-1953	3	-	0.8	-217.17
6. Rein (1963)	Keq + Y(Si)	D	1773-1798	6	-	175.42*	-217.38
7. Kay (1960)	Keq + Y(Si)	E	1703-1823	6	-	146.92*	-217.94
8. Baird (1958)	Kp	E	1673-1853	15	145.92±1.3*	-2.9±7	-217.94
					147.43*	-1.8±1.9	-218.45

*Values at T are from second law analysis while those at 298.15°K are from third law.

A. SiO₂ (quartz, low or high) = SiO₂ (cristobalite, low or high)

B. SiO₂ (high cristobalite) + 2H₂(g) = Si(l) + 2H₂O(g)

C. SiO₂ (high cristobalite) + 2C(graph) = Si(l) + 2CO(g)

D. SiO₂ (high cristobalite) + 2SiC(β) = 3Si(l) + 2CO(g)

E. SiO₂ (high cristobalite) + 3C(graph) = SiC(β) + 2CO(g)

Heat Capacity and Entropy

Cp° below 300°K is based on data of Westrum(11). Earlier data of Anderson(12) are in satisfactory agreement. The entropy is obtained from Cp° using S° = 0.0007 eu. Cp° above 300°K is derived from enthalpy data of Moesman(13) and White(14). The former deviate from the adopted functions by -0.7 to 0.51 and the latter by +0.44. Although the functions above 300°K appear to be reliable, it would be desirable to have new data for a well-characterized sample (see Transition Data).

Transition Data

Low cristobalite is metastable with respect to quartz but persists up to Tt. Tt is taken as the temperature at the peak in the heating curve for well-ordered cristobalite; however, see (15, 16) for detailed discussions of temperatures about 25° lower which were found from cooling curves. ΔHt° is derived from enthalpy data(13, 14) for high cristobalite using the adopted enthalpy for the low form. The enthalpy data of Moesman(13) gave a lower Tt which suggests that the sample was less well-ordered than desirable. ΔHt° is confirmed, however, by other data which are summarized below. Additional polymorphism is discussed on the table for high cristobalite.

Source	Method	ΔHt°, kcal/mol
13. Moesman (1941)	Enthalpy data	0.321
17. Berger (1965)	Microcalorimetric thermal analysis	0.318±0.018
18. Majumdar (1964)	ΔV and dT/DP	0.27
19. Sabatier (1957)	Differential thermal analysis	0.76±0.01

References

1. J. L. Holm, O. J. Kleppa and E. F. Westrum, Jr., *Geochim. Cosmochim. Acta*, to be published. ΔHsoln.
2. J. L. Holm and H. E. Schwiete, *Glaetche. Ber.*, 32, 327 (1959); *ΔHsoln*, 1215. 69 (1953). ΔHsoln.
3. F. C. Kracek, *Repts. Director, U.S. Geol. Surv.*, 1953, 100, 101 (1953). ΔHsoln.
4. L. Humphrey and E. G. King, *Am. Chem. Soc.*, 74, 2091 (1952); 73, 656 (1951). ΔHsoln.
5. S. Matoba, K. Gunji and T. Kuwana, *Tetsu to Hagane*, 45, 229 (1953); *Stahl Eisen*, 80, 299 (1960). Keq.
6. R. H. Rein and J. Chipman, *J. Phys. Chem.*, 67, 839 (1963). Keq.
7. D. A. R. Kay and J. Taylor, *Trans. Faraday Soc.*, 56, 1372 (1960). Kp.
8. M. Baird and J. Taylor, *Trans. Faraday Soc.*, 56, 826 (1959). Kp.
9. J. Chipman and R. Baerchitz, *Trans. AIME*, 227, 473 (1963); 233, 415 (1965). Si act. coeff.
10. J. Chipman and R. Baerchitz, *Trans. AIME*, 227, 473 (1963); 233, 415 (1965). Si act. coeff.
11. E. F. Westrum, Jr., et al., private comm., Univ. Michigan, May 19, 1960; see also *Phys. Chem. Glasses*, 4, 188 (1963).
12. C. T. Anderson, *J. Am. Chem. Soc.*, 58, 568 (1936). Cp, 55-297°K.
13. H. P. Moesman and K. S. Pitzer, *J. Am. Chem. Soc.*, 63, 2348 (1941). H, 367-498°K.
14. H. P. Moesman, *J. Am. Chem. Soc.*, 63, 2348 (1941). H, 367-498°K.
15. W. G. Hill and R. Roy, *J. Am. Ceram. Soc.*, 41, 532-7 (1958). Transition data.
16. R. F. Walker, S. Zarfoss, S. F. Holley and T. J. Gross, *J. Res. Natl. Bur. Std.*, 61, 251 (1958). Tt.
17. C. Berger, M. Richard and L. Eyraud, *Bull. Soc. Chim. France*, 1965, 1491 (1965). ΔHt.
18. A. J. Majumdar, H. A. McKinstry and R. Roy, *J. Phys. Chem. Solids*, 25, 1487 (1964). ΔHt.
19. G. Sabatier, *Bull. Soc. Franc. Mineral. Crist.*, 80, 444 (1957). ΔHt.

June 30, 1967

O₂Si

T, °K	Cp°	S°	(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
100							
200							
298	6.353	11.963		.000	-216.417	-204.032	149.560
300	6.490	12.003		.012	-216.327	-203.956	148.581
400	11.590	17.428		2.195	-216.737	-199.492	85.449
500	14.830	20.026	13.991	3.621	-216.634	-191.252	69.663
600	15.500	22.373	15.023	5.145	-216.473	-187.033	56.394
800	16.094	24.490	16.077	6.731	-216.285	-182.842	49.950
1000	16.712	26.156	16.137	8.387	-216.073	-178.672	43.367
1100	16.915	26.757	19.122	11.699	-215.668	-170.402	33.656
1200	17.076	31.236	20.070	13.399	-215.461	-166.296	30.287
1300	17.208	32.608	20.983	15.113	-215.259	-162.207	27.269
1400	17.320	33.686	21.959	16.840	-215.061	-158.134	24.666
1500	17.416	35.086	22.901	18.577	-214.870	-154.074	22.449
1600	17.500	36.213	23.511	20.323	-214.686	-150.027	20.493
1700	17.575	37.276	24.290	22.076	-214.503	-145.985	18.755
1800	17.642	38.282	25.039	23.837	-214.321	-141.948	17.138
1900	17.702	39.239	25.762	25.605	-214.140	-137.926	15.693
2000	17.752	40.147	26.458	27.374	-213.959	-133.913	14.393
2100	17.816	41.015	27.131	29.157	-213.778	-129.902	13.218
2200	17.866	41.845	27.781	30.941	-213.599	-125.899	12.152
2300	17.914	42.641	28.410	32.730	-213.422	-121.896	11.179
2400	17.960	43.404	29.024	34.524	-213.246	-117.892	10.286
2500	18.005	44.138	29.609	36.322	-213.074	-113.874	9.469
2600	18.047	44.845	30.182	38.125	-212.903	-109.814	8.713
2700	18.089	45.527	30.734	39.931	-212.735	-105.761	8.015
2800	18.129	46.186	31.278	41.742	-212.567	-101.722	7.367
2900	18.168	46.822	31.803	43.557	-212.400	-97.695	6.764
3000	18.207	47.432	32.314	45.376	-212.234	-93.683	6.202

June 30, 1967

CRISTOBALITE, HIGH (SiO₂)

(CRYSTAL)

GFW = 60.0848

$\Delta H_f^{298.15} = -216.417$ kcal/mol
 $\Delta H_f^{\circ} = 0.321 \pm 0.06$ kcal/mol
 $\Delta H_f^{\circ} = 0.48 \pm 0.15$ kcal/mol
 $\Delta H_m^{\circ} = 2.29 \pm 0.5$ kcal/mol

Heat of Formation

The heat of formation is calculated from that of low cristobalite by addition of $\Delta H_f^{\circ} = 0.321$ kcal/mol and the difference between $H_{SiO_2}^{\circ} - H_{SiO_2}^{\circ}$ for low and high forms.

Heat Capacity and Entropy

C_p° is derived from enthalpies of Nosenman (1) and White (2), whose data deviate from the adopted functions by -0.6 to +0.5% and +0.9 to 0.0%, respectively. White's deviations for cristobalite have a magnitude and trend similar to his deviations for quartz and vitreous silica. Data of Wietzel (3) for his sample prepared at 1600°C deviate by +3% at 673°K and +1.6% at 1973°K. C_p° below 543°K is smoothly extrapolated to give the proper trend in the Gibbs energy, but the heat capacity at 298°K is not realistic. The entropy is calculated in a manner analogous to that of the heat of formation.

Transition Data

Literature on the polymorphism of SiO₂ is voluminous but is summarized in detail in recent books by Sosman (4) and Eitel (5). The known phases of SiO₂ include quartz, tridymite(?), cristobalite, vitreous silica and the more recently discovered high pressure phases. Muan (6) concisely reviewed the still controversial question of whether tridymite is stabilized only by the presence of foreign ions or whether it is a stable phase of SiO₂ intermediate between quartz and cristobalite. Transitions among the different phases are generally sluggish because of large energy barriers to the structural change and small differences in Gibbs free energies. As a result, the phases often persist far into metastable regions. In contrast, transitions within a particular phase are rapid and reversible (i.e., the low + high inversions of quartz or cristobalite).

High cristobalite is the stable phase near T_m . It becomes metastable with respect to quartz at lower temperatures but persists down to the high + low inversion at 543°K (see table for low cristobalite). The high form is cubic and the low form tetragonal (12, 13).

The adopted tables give 1079+250°K as the temperatures at which $\Delta G^{\circ} = 0$ for high quartz + high cristobalite; which, in turn, is taken from $\Delta H_f^{298} = 0.45 \pm 0.15$ kcal/mol obtained by Holm (7) from ΔH_{soln} measurements in an oxide melt. It is apparent that T_t is extremely sensitive to small changes in G or H . Holmquist (8) tentatively placed this inversion at 1298+25°K but did observe cristobalite formation at temperatures as low as 1171°K.

Melting Data

Melting point data were reviewed by Schneider (9) and adjusted to the 1948 International Temperature Scale. The adopted melting point for cristobalite is based on Greig (10). ΔH_m° is calculated as the difference in ΔH_f° for liquid and crystal at T_m . Mackenzie et al. (11) showed that cristobalite may be superheated by as much as 40° above T_m due to its slow rate of fusion.

References

1. M. A. Nosenman and K. S. Pitzer, *J. Am. Chem. Soc.* **63**, 2348 (1941). H, 542 - 622°K.
2. W. P. White, *Am. J. Sci.* **47**, 1 (1919). H, 573-1673°K.
3. R. Wietzel, *Z. Anorg. Allgem. Chem.* **116**, 71 (1921). H, 673 - 1973°K.
4. R. B. Sosman, "Phases of Silica," 388 pp., Rutgers Univ. Press, New Brunswick, N. J., 1965.
5. W. Eitel, "Silicate Science," Vol. III, pp. 44-157, Academic Press, New York, 1965.
6. A. Muan and E. F. Osborn, "Phase Equilibria among Oxides in Steelmaking," pp. 17-20, Addison-Wesley Publishing Co., Reading, Mass., 1965.
7. J. L. Holm, O. J. Kleppa and E. F. Westrum, Jr., *Geochim. Cosmochim. Acta*, to be published. ΔH_{soln} .
8. S. B. Holmquist, *J. Am. Ceram. Soc.* **44**, 82 (1961). T_t .
9. S. J. Schneider, *U. S. Natl. Bur. Std. Monograph* **68**, 1963.
10. J. W. Greig, *Am. J. Sci.* **13**, 1 (1927). T_m .
11. N. G. Ainslie, J. D. Mackenzie and D. Turnbull, *J. Phys. Chem.* **65**, 1718 (1961); *J. Am. Ceram. Soc.* **43**, 615 (1960).
12. C. Berger, L. Eyraud, M. Richard and R. Riviere, *Bull. Soc. Chim. France* **1966**, 628 (1966). Crystal structure.
13. W. A. Dollase, *Z. Krist.* **121**, 369 (1965). Crystal structure.

Silicon Dioxide (SiO₂)

(Liquid) GFW = 60.0848

SILICON DIOXIDE (SiO₂)

(LIQUID)

GFW = 60.0848

$$\Delta H_{298.15}^{\circ} = 11.455 \pm 0.3 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = -215.74 \text{ kcal/mol}$$



$$T_m = 1996 \pm 5^{\circ}\text{K (high cristobalite} \rightarrow \text{liquid)}$$

$$\Delta H_m^{\circ} = 2.29 \pm 0.5 \text{ kcal/mol}$$

Heat of Formation

The heat of formation is calculated from that of quartz using $\Delta H_{970}^{\circ} = 1.45 \pm 0.15 \text{ kcal/mol}$ for high quartz $\rightarrow \text{SiO}_2(l)$, as determined by Holm (1) from ΔH_{soln} in an oxide melt. This value reduces to $\Delta H_{298}^{\circ} = 1.96 \text{ kcal/mol}$ for low quartz $\rightarrow \text{SiO}_2(l)$ and is consistent within $\pm 0.3 \text{ kcal/mol}$ with other calorimetric data summarized below. Earlier results were reviewed by Hummel (4).

Source	Method	Reaction	T, °K	ΔH_{298}° kcal/mol	ΔH_{970}° kcal/mol	ΔH_{298}° kcal/mol
1. Holm (1967)	ΔH_{soln} in oxide melt	A	970	1.45 \pm 0.15	1.96	-215.74
2. Wise (1963)	ΔH_c in fluorine	B	298	1.78 \pm 0.46	1.78	-215.92
3. Kracek (1963)	ΔH_{soln} in HF(aq, 74.7°C)	A	298-348	2.18 \pm 0.05		-215.52
4. Hummel (1959)	ΔH_{soln} in HF(aq, 26.5°C)	A	300	2.27 \pm 0.2	2.27	-215.43
A. $\text{SiO}_2(\text{quartz, low or high}) + \text{SiO}_2(l)$						
B. $\text{SiO}_2(l) + 2\text{F}_2(g) + \text{SiF}_4(g) + \text{O}_2(g)$						

Heat Capacity and Entropy

C_p° below 300°K is based on data of Flubacher (5) and Westrum (6) for samples annealed at 1100 and 1070°C, respectively. Data of Turdakin (7) are higher by about 1 percent in the range 60-160°K and at 300°K but are in agreement elsewhere. The entropy is calculated from C_p° using $S_{2.34}^{\circ} - S_0^{\circ} = 0.0001 \text{ eu}$ and $S_0^{\circ} = 1.098 \text{ eu}$. C_p° data (8) for a different sample annealed at 1300°C yield an entropy larger by $<0.04 \text{ eu}$. Earlier data were reviewed by Kelley (9). The residual entropy is calculated from $S_0^{\circ} = S_{996}^{\circ} - (S_{996}^{\circ} - S_0^{\circ}) = 41.258 - 40.160 = 1.098 \text{ eu}$, where 40.160 is obtained from the adopted functions, while 41.258 is the sum of $\Delta S_m^{\circ} = 1.447 \text{ eu}$ and $S_0^{\circ} = 40.111 \text{ eu}$ for high cristobalite. We estimate the uncertainty as $\pm 0.3 \text{ eu}$, primarily from the uncertainty in ΔH_m° .

C_p° above 300°K is based on adiabatic calorimetric data of Moser (5) up to 900°K. Enthalpy data of White (10) and Fischer (11) are in excellent agreement. C_p° from 900 to 1500°K is derived from enthalpy data of Southard (12) and White (10). Maximum deviation of the data from the adopted values in this range is 0.5 percent. Enthalpy data of Egan (13) and Kelley (14) deviate from the adopted values by less than 1 percent in the range 1000-1500°K, although large positive deviations appear at lower temperatures.

In the region 1500-1700°K, the adopted C_p° shows a rapid, sigmoidal rise which is suggested by the enthalpy data of Wiestel (15). This is presumed to be the glass transition region in which C_p° rises to that of the stable liquid. C_p° above 1700°K is estimated as 20.5 gibbs/mol or 6.83 gibbs/g-atom. This value is consistent with the enthalpy data (15) and with liquid heat capacities of Al_2O_3 , $\text{Na}_2\text{Si}_2\text{O}_5$ and Na_2SiO_3 .

Melting Data

The melting point of high cristobalite is $1996 \pm 5^{\circ}\text{K}$, while the metastable melting point of high quartz is $1696 \pm 50^{\circ}\text{K}$. ΔH_m° is the difference between ΔH° for liquid and high cristobalite at T_m . Values ranging from 1.8 to 3.6 kcal/mol have been derived from various interpretations of phase diagrams (1).

References

1. J. L. Holm, O. J. Kleppa and E. F. Westrum, Jr., *Geochim. Cosmochim. Acta*, to be published. ΔH_{soln} .
2. S. S. Wise, J. L. Margrave, H. M. Feder and W. N. Hubbard, *J. Phys. Chem.* **67**, 815 (1963). ΔH_r .
3. F. C. Kracek, *Ann. Rept. Director of the Geophysical Laboratory*, No. 1215, 69 (1953). ΔH_{soln} .
4. C. Hummel and H. E. Schwiete, *Glastech. Ber.* **32**, 327 (1959). ΔH_{soln} .
5. P. Flubacher, A. J. Leadbetter, J. A. Morrison and B. P. Stoicheff, *Phys. Chem. Solids* **12**, 53 (1959). C_p , 2.3-19°K.
6. E. F. Westrum, Jr., et al., private comm., Univ. Michigan, May 19, 1960. C_p , 5-300°K.
7. V. F. Tarasov, *Phys. Status Solidi* **20**, 37 (1967). C_p , 50-300°K measured by Turdakin.
8. K. K. Kelley and E. G. King, U. S. Bur. Mines Bulletin 592, 1961.
9. H. Moser, *Physik. Z.* **37**, 737 (1936). C_p , 324-936°K.
10. W. P. White, *J. Am. Chem. Soc.* **55**, 1047 (1933). H , 573-1173°K.
11. W. Fischer, *Z. Anorg. Allgem. Chem.* **200**, 335 (1931). H , 321-577°K.
12. J. C. Southard, *J. Am. Chem. Soc.* **63**, 3142 (1941). H , 506-1522°K.
13. E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, *J. Am. Chem. Soc.* **72**, 2418 (1950). H , 763-1470°K.
14. K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686, 1946. H , 400-1500°K.
15. R. Wiestel, *Z. Anorg. Allgem. Chem.* **116**, 71 (1921). H , 373-1973°K.

SILICON DIOXIDE (SiO₂)

(IDEAL GAS)

GFW = 60.0848

Point Group [D_{2h}]S_{298.15}° = [84.7] gibbs/mol $\Delta H_f^\circ = -72.7 \pm 8$ kcal/mol $\Delta H_f^\circ_{298.15} = -73 \pm 8$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

 ω, cm^{-1}

[980] (1)

[370] (2)

[1430] (1)

Bond Distance: Si-O = [1.55] Å

Bond Angle: O-Si-O = [180°]

Rotational Constant: B₀ = [0.2193] cm⁻¹

Heat of Formation

The adopted value is based on the data summarized below. Margrave (1) has reported a value of $\Delta H_f^\circ_{298} = 140.9 \pm 1$ kcal/mol but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta H_f^\circ_{298} = -75.5$ kcal/mol. Firsova (2) reported two values of the sublimation pressure which were derived from Knudsen effusion data using auxiliary data for SiO(g). Porter (3) derived two pressures from a mass spectrometric study and also obtained a 2nd Law value for ΔH_f° from ion intensities. The resulting range for $\Delta H_f^\circ_{298}$, 136 to 141 kcal/mol, is consistent with the lower limit of 130 kcal/mol obtained by Bergman (3) from a method involving explosion in a spherical bomb. An alternative analysis of the mass spectrometric data (4) using the gas phase reaction B suggests an even higher ΔH_f° of 148 kcal/mol. The adopted ΔH_f° corresponds to $\Delta H_f^\circ_{298} = 143.4 \pm 4$ kcal/mol and to $\Delta H_{\text{atom}}^\circ = 297.3 \pm 8$ kcal/mol.

Source	Reaction	Method	Range, °K	$\Delta H_f^\circ_{298}$, kcal/mol	Drift
Margrave (1967)	A	-	-	140.9 ± 1	-
Firsova (1960)	A	Knudsen, calculation	1600-1800	-	-75.4
Bergman (1959)	A	Explosion	-	>130	-
Porter (1955)	A	Knudsen mass spec.	1800-1900	128	>86
	A	Ion intensities	1750-1980	136 ± 8	-76.8
	B	Knudsen mass spec.	1800-1900	-2	-80
	A. SiO ₂ (high cristobalite) = SiO ₂ (g)	-	-	-44.8 ± 1.2	-23
	B. SiO(g) + 1/2 O ₂ (g) = SiO ₂ (g)	-	-	-68.8	-

Heat Capacity and Entropy

Point group, ground state quantum weight and the linear symmetrical configuration are estimated by analogy with the properties of CO₂. From the bond lengths in SiO, CO₂ and CO, the length in SiO₂ is estimated as 1.509 × 1.180/1.128. Bond lengths and atomization energies for these molecules are reasonably consistent with the existence of six-electron bonds in the monoxides and four-electron bonds in the dioxides (5). Vibrational frequencies are estimated from a valence bond calculation using force constants, $k = 9 \times 10^5$ and $k_6/k_2 = 0.3 \times 10^5$ dyne/cm, which are obtained from those of SiO, CO₂ and CO. The moment of inertia is 12.76 × 10⁻³⁹ g cm².

References

1. J. L. Margrave, 5th Meeting ICRP Thermochemistry Working Group, Linden, New Jersey, March 1967.
2. L. P. Firsova and An. N. Neameyanov, Russ. J. Phys. Chem. (English Transl.) 34, 1279, 1232, 906 (1960).
3. G. A. Bergman and V. A. Medvedev, Sbornik Trudov Gosudarst. Inst. Priklad. Khim. 1959, 158 (1959).
4. R. F. Porter, W. A. Chupka and M. G. Inghram, J. Chem. Phys. 23, 216 (1955).
5. J. W. Linnett, "The Electronic Structure of Molecules," pp. 43-55, Methuen and Co. Ltd., London, 1964.

Dec. 31, 1960; Dec. 31, 1962; Sept. 30, 1967

Titanium Dioxide, Anatase (TiO₂)

(Crystal)

QFW = 79.8988

T, °K	Cp°	gibbs/mol -S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-	-	-	INFINITE
100	4.585	2.302	21.322	-	-221.835	-221.835	477.306
200	10.009	7.293	13.048	-	-222.503	-218.397	233.965
298	13.257	11.931	11.931	0.000	-222.906	-214.107	153.760
300	13.312	12.013	11.931	-0.025	-222.999	-209.481	152.752
400	15.244	14.144	12.491	1.465	-222.888	-205.253	112.145
500	16.153	15.454	13.575	3.040	-222.690	-200.867	87.799
600	16.458	16.447	14.843	4.682	-222.469	-196.524	71.584
700	16.973	17.230	15.188	6.364	-222.251	-192.217	60.013
800	17.346	17.846	15.666	8.799	-221.874	-183.658	44.603
900	17.459	18.187	16.048	11.540	-221.724	-179.452	39.219
1000	17.553	18.356	16.274	13.290	-221.602	-175.231	34.815
1200	17.830	18.866	17.045	15.050	-222.442	-170.982	31.140
1400	18.296	19.535	18.035	16.546	-222.251	-162.437	25.358
1600	18.756	20.314	19.263	18.588	-222.068	-152.437	23.047
1800	19.206	21.141	20.366	20.366	-221.906	-145.184	21.027
2000	19.611	21.993	21.499	22.149	-221.763	-135.939	17.246
2100	19.646	22.072	21.526	22.149	-221.640	-127.983	16.248
2200	19.679	22.142	21.552	22.149	-221.524	-120.955	14.958
2300	19.704	22.203	21.577	22.149	-221.409	-114.658	
2400	19.724	22.258	21.601	22.149	-221.294	-108.371	
2500	19.740	22.308	21.625	22.149	-221.179	-102.083	
2600	19.753	22.354	21.648	22.149	-221.064	-95.795	
2700	19.764	22.396	21.670	22.149	-220.949	-89.507	
2800	19.773	22.435	21.691	22.149	-220.834	-83.219	
2900	19.780	22.471	21.711	22.149	-220.719	-76.931	
3000	19.785	22.504	21.730	22.149	-220.604	-70.643	

TITANIUM DIOXIDE, ANATASE (TiO₂)

(CRYSTAL)

QFW = 79.8988

O₂Ti

$\Delta H_f^\circ = -221.8 \pm 1 \text{ kcal/mol}$
 $\Delta H_{298}^\circ = -223.0 \pm 1 \text{ kcal/mol}$
 $\Delta H^\circ = [0.0] \text{ kcal/mol}$
 $\Delta H_m^\circ = \text{Unknown}$
 $\Delta H_{298}^\circ = 161 \text{ kcal/mol}$

$S_{298}^\circ = 11.93 \text{ gibbs/mol}$
 $T_f = 918^\circ \text{K}$
 $T_m = \text{Unknown}$

Heat of Formation.

The value of ΔH_f° (anatase) is obtained from J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. AFML-TR-65-123, August 1965, Rice University, Houston, Texas. The authors measured the heat of fluorination of anatase, according to the reaction $\text{TiO}_2 (\text{anatase}) + 2\text{P}_2(\text{g}) = \text{TiF}_4(\text{c}) + \text{O}_2(\text{g})$, but no experimental data were given.

F. W. Vahldiek, J. Less-Common Metals 11, 99 (1966), studied the irreversible anatase-rutile phase transition at pressures of 3.8 to 24 kbars and temperatures 20 to 1000°C. Isothermal phase-transition studies were also carried out at 1 bar pressure and 880-950°C. From the slope, dT/dP , the enthalpy differences between rutile and anatase were calculated to be -2.79 and -2.89 kcal/mol at 1183 and 1223°K, respectively. Using these data and $\Delta H_f^\circ(\text{rutile}) = -255.8 \text{ kcal/mol}$, the value of $\Delta H_f^\circ(\text{anatase})$ is derived as -223.23 kcal/mol, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy.

Low temperature heat capacities, 52-296°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 59, 218 (1947).

Enthalpy data were determined in the range 416-1305°K by B. F. Naylor, J. Am. Chem. Soc. 58, 1077 (1946), and in the range 580 - 1000°K by J. Lietz, Hamburger Beitr. Angew. Mineral. Kristallphysik 1, 229 (1956). High temperature heat capacities are derived from the enthalpy data, subject to the constraint that there be a smooth joint at 298°K. The resulting enthalpies are higher by 1 to 3% than those measured by Lietz and lower by 1 to 4% than those measured by Naylor. Values above 1300°K are smoothly extrapolated. S_{298}° is calculated from the low temperature C_p° using $S_{50}^\circ = 0.45 \text{ eu}$.

In view of the discrepancies in the enthalpy data, a review of the anatase samples is pertinent. Those of Shomate and Lietz were prepared by precipitation of the hydrated oxide and conversion to the oxide at 550 - 565°C. Shomate's starting material was high purity Ti and the product analyzed as 99.3% TiO₂. Lietz' starting material was high purity TiCl₄. Naylor's sample, obtained from J. T. Baker Co., was dried at 1050°C; spectrographic analysis indicated 0.3% SiO₂ and 0.15% CaO. All three samples gave only the X-ray lines of anatase.

Transition Data.

$T_m = 918^\circ \text{K}$ and $\Delta H^\circ = 0.040 \text{ kcal/mol}$ have been reported by J. Lietz, loc. cit. A. Schröder, Z. Kryst. 65, 493 (1928), suggested a transition temperature at 915°K on the basis of a peak in the thermal expansion curve. Lietz reported $\Delta H^\circ = 0.04 \text{ kcal/mol}$, but this value is not adopted since its magnitude is much less than the uncertainty in the selected enthalpies. Further study is desirable to confirm this transition.

Heat of Sublimation.

ΔH_{298}° is calculated as the difference between ΔH_f° for TiO₂(g) and TiO₂(anatase).

O₂Ti

T, °K	C _p ^a	μbbs/mol S ^b	-(C _p ^a - H ₂₉₈)/T	H ^c - H ₂₉₈	kcal/mol ΔH ^c	ΔG ^d	Log K ^p
0	0.000	INFINITE		2.065	-224.636	-224.636	INFINITE
100	4.430	21.438		1.900	-225.101	-225.101	483.450
200	10.115	7.725		1.605	-225.517	-225.517	155.834
298	13.153	12.031	12.031	0.000	-225.600	-212.591	
300	13.191	12.112	12.031	-0.024	-225.600	-212.511	154.814
400	14.421	16.126	12.569	1.423	-225.730	-206.089	113.694
500	15.429	19.481	13.625	2.928	-225.602	-203.692	89.034
600	15.991	22.346	14.846	4.500	-225.451	-199.325	72.404
700	16.438	24.845	16.090	6.122	-225.293	-194.983	60.876
800	16.824	27.046	17.334	7.785	-225.136	-190.665	52.087
900	17.173	29.068	18.528	9.485	-224.988	-186.364	45.255
1000	17.500	30.494	19.675	11.219	-224.845	-182.080	39.794
1100	17.813	32.577	20.772	12.985	-224.707	-177.810	35.328
1200	18.116	34.160	21.822	14.781	-225.511	-173.515	31.401
1300	18.412	35.601	22.826	16.604	-225.255	-169.191	28.444
1400	18.703	36.977	23.788	18.464	-224.992	-164.990	25.741
1500	18.990	38.277	24.711	20.348	-224.724	-160.806	23.400
1600	19.274	39.511	25.598	22.262	-224.450	-156.639	21.355
1700	19.556	40.688	26.451	24.203	-224.174	-152.091	19.553
1800	19.836	41.814	27.276	26.173	-223.894	-147.659	17.953
1900	20.115	42.884	28.068	28.170	-223.623	-143.642	16.523
2000	20.393	43.933	28.835	30.194	-223.795	-139.587	15.221
2100	20.670	44.934	29.578	32.249	-227.497	-134.866	14.036
2200	20.946	45.902	30.298	34.330	-227.178	-130.464	12.960
2300	21.221	46.840	30.997	36.434	-226.836	-126.078	11.940
2400	21.496	47.749	31.676	38.578	-226.472	-121.703	11.043
2500	21.771	48.632	32.337	40.737	-226.087	-117.347	10.256

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE, RUTILE (TiO₂)

OPW = 79.8988

(CRYSTAL)

$\Delta H_f^\circ = -224.6 \pm 1 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = -225.8 \pm 1 \text{ kcal/mol}$
 $\Delta H_m^\circ = [16] \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = 163.8 \text{ kcal/mol}$

$S_{298.15}^\circ = 12.03 \text{ gibbs/mol}$

$T_m = 2143^\circ\text{K}$

Heat of Formation.

The heat of formation for rutile has been determined from combustion calorimetry by many investigators. Several of the more consistent ΔH_f° values are listed in the table below. Ariya et al.³ reported that the composition of the rutile obtained from combustion of Ti(c) was between TiO_{1.94} and TiO_{1.95}. Emf studies by R. N. Blumenthal and D. H. Whitmore, J. Electrochem. Soc. 110, 92 (1963), indicate that at 1200°K there is a two-phase region beginning at about TiO_{1.98}. If this region extends to 298°K, then the non-atmospheric combustion products probably involve a mixture of two phases. Meh et al.⁴ applied an approximate energy correction for incomplete combustion which corresponds to 0.7 - 1.5 kcal/mol in ΔH_f° . Analogous corrections were applied by Ariya et al.³ but were not mentioned by Neumann et al.^{1,2} and Humphrey.⁵

The ΔH_f° value reported by Margrave and Kybett⁵ was obtained by fluorine bomb calorimetry, according to the reaction $\text{TiO}_2(\text{rutile}) + 2\text{F}_2(\text{g}) = \text{TiF}_4(\text{c}) + \text{O}_2(\text{g})$. No experimental data were given.

Comparison of the fluorine result with the oxygen results indicates that the magnitude of the corrections for the oxygen data is reasonable, probably within $\pm 1 \text{ kcal/mol}$, provided that the fluorine data refer to stoichiometric TiO₂. Corresponding ΔG_f° corrections for TiO_{2-x} are of the same order of magnitude when estimated from the partial molar free energy values given by P. Korstad, J. Phys. Chem. Solids 23, 1579 (1962), and J. B. Moser, R. N. Blumenthal and D. H. Whitmore, J. Am. Ceram. Soc. 49, 384 (1965).

The ΔH_f° value determined by Meh et al.⁴ is adopted.

ΔH_f° , kcal/mol	Source
-225.5 \pm 0.3	1. B. Neumann, C. Kröger and H. Kunz, Z. Anorg. Allgem. Chem. 218, 379 (1934).
-225.3 \pm 0.2	2. G. L. Humphrey, J. Am. Chem. Soc. 73, 1567 (1951).
-224.9 \pm 0.4	3. S. Ariya, M. Morozova, and E. Volf, Z. Neorg. Khim 13, 13 (1957).
-225.8 \pm 0.1	4. A. Meh, K. K. Kelley, E. G. King, and C. O'Brien, U. S. Bur Mines R15316 (1957).
-225 \pm 1	5. J. L. Margrave and B. D. Kybett, "Thermodynamic and Kinetic Studies of Borides and Other Refractory Materials at High Temperatures," Tech. Rept. APWL-TP-65-123, Aug. 1965, Rice University, Houston, Texas.

Heat Capacity and Entropy.

The low temperature heat capacities, 10 - 297.7°K, have been measured by the following investigators: P. H. Keesom and N. Pearlman, Phys. Rev. 112, 800 (1936), 10 - 20°K; J. S. Dugdale, J. A. Morrison and D. Patterson, Proc. Roy. Soc. (London) A224, 228 (1954), 20 - 50°K; H. Shomate, J. Am. Chem. Soc. 69, 218 (1947), 52.5 - 297.7°K; and H. J. McDonald and H. Seltz, J. Am. Chem. Soc. 61, 2405 (1939), 68.78 - 295.0°K. The first three sets of Cp data are joined smoothly and extrapolated to 298°K, yielding $S_{298}^\circ = 12.03 \text{ eu}$, based on $S_{10}^\circ = 0.0014 \text{ eu}$. The Cp values reported by McDonald and Seltz seem too high and are not used.

The high temperature enthalpies have been determined by B. P. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), 393.5 - 1746°K; J. S. Arthur, J. Appl. Phys. 21, 732 (1950), 293.2 - 1073.2°K; and J. Lietz, Hamburger Beiträge Angew. Mineral u. Kristall Phys. 1, 229 (1956), 577.7 - 1293.0°K. The Cp values are derived from the data of Lietz and join smoothly at 298°K with the low temperature data. Deviations from the selected values are -1.6 to +1.0% for Lietz, -5.1 to +4.0% for Arthur, and +6.6 to -0.8% for Naylor. The data point of Lietz at 947.95°K is omitted as a probable typographical error. The largest deviations in the case of Naylor and Arthur are near 400 and 500°K, respectively.

The mean specific enthalpies have also been measured by L. P. Nilsen and O. Pettersson, Z. Physik, Chem. 1, 27 (1987), 373.2 - 717.2°K.

The samples used by Keesom and Pearlman, Dugdale et al., Shomate, Arthur and Lietz were of high purity, according to chemical and spectroscopic analysis. However, the sample employed by Naylor was black-colored and chemical analysis gave 97.9% TiO₂. The main impurities were: 0.55% ZrO₂, 0.50% SiO₂, 0.27% V₂O₅, 0.15% CaO, 0.15% Fe₂O₃ and 0.1% Al₂O₃. The sample of McDonald and Seltz was obtained commercially. Therefore the results reported by Naylor and McDonald et al. are given the least weight.

Melting Data.

See TiO₂(1) table for details.

Heat of Sublimation.

The difference between ΔH_{298}° for TiO₂(g) and TiO₂(rutile) is ΔH_{298}° .

Titanium Dioxide (TiO₂)
(Liquid)

GFW = 79.8988

O₂Ti

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	13.153	16.934	18.934	.000	-210.726	-199.377	146.294
300	13.151	16.935	18.934	.024	-210.726	-199.407	145.301
350	13.149	16.937	18.932	1.924	-210.556	-198.774	144.967
400	13.146	16.939	18.929	2.228	-210.328	-197.070	83.954
500	15.459	26.384	20.526				
600	15.991	29.249	21.749	4.500	-210.377	-188.393	68.622
700	16.438	31.748	23.002	7.122	-210.219	-184.741	57.679
800	16.824	33.891	24.281	9.685	-210.084	-181.503	48.828
900	17.158	35.707	25.491	11.219	-209.914	-177.503	43.104
1000	17.500	37.747	26.578	11.219	-209.771	-173.909	38.008
1100	17.813	39.480	27.675	12.995	-209.633	-170.329	33.641
1200	18.116	41.043	28.755	14.781	-210.437	-166.724	30.365
1300	18.412	42.504	29.759	16.508	-210.913	-163.081	27.486
1400	18.699	43.861	30.691	18.184	-211.104	-159.406	24.896
1500	18.980	45.138	31.619	20.564	-210.434	-155.493	22.714
1600	21.000	46.684	32.519	22.664	-208.974	-152.339	20.609
1700	21.000	47.937	33.390	24.764	-208.539	-148.813	19.131
1800	21.000	49.137	34.233	26.864	-208.123	-145.312	17.415
1900	21.000	50.281	35.043	28.964	-207.723	-141.832	15.515
2000	21.000	51.370	35.836	31.064	-211.853	-138.219	15.104
2100	21.000	52.394	36.602	33.164	-211.508	-134.543	14.002
2200	21.000	53.371	37.342	35.264	-211.170	-130.886	13.003
2300	21.000	54.305	38.080	37.364	-210.806	-127.247	12.127
2400	21.000	55.198	38.812	39.464	-210.426	-123.647	11.297
2500	21.000	56.056	39.430	41.564	-210.186	-120.006	10.491
2600	21.000	56.879	40.086	43.664	-209.968	-116.404	9.785
2700	21.000	57.672	40.722	45.764	-209.556	-112.815	9.132
2800	21.000	58.443	41.341	47.864	-209.164	-109.247	8.528
2900	21.000	59.191	41.944	49.964	-208.947	-105.670	7.963
3000	21.000	59.884	42.530	52.064	-208.650	-102.111	7.439
3100	21.000	60.573	43.101	54.164	-208.357	-98.565	6.949
3200	21.000	61.240	43.657	56.264	-208.069	-95.033	6.490
3300	21.000	61.896	44.200	58.364	-207.605	-91.503	6.069
3400	21.000	62.542	44.734	60.464	-207.164	-88.000	5.684
3500	21.000	63.122	45.246	62.564	-207.230	-84.475	5.275
3600	21.000	63.713	45.751	64.664	-308.584	-80.704	4.899
3700	21.000	64.289	46.244	66.764	-308.288	-74.382	4.394
3800	21.000	64.994	46.714	68.864	-307.984	-68.000	3.844
3900	21.000	65.694	47.164	70.964	-307.684	-61.552	3.240
4000	21.000	65.926	47.660	73.064	-307.497	-55.449	3.030
4100	21.000	66.444	48.112	75.164	-307.266	-49.147	2.620
4200	21.000	66.950	48.554	77.264	-307.049	-42.837	2.230
4300	21.000	67.597	48.988	79.364	-306.849	-36.571	1.859
4400	21.000	68.284	49.414	81.464	-306.664	-30.300	1.509
4500	21.000	68.959	49.830	83.564	-306.484	-24.006	1.166
4600	21.000	69.661	50.238	85.664	-306.321	-17.727	.842
4700	21.000	69.312	50.639	87.764	-306.171	-11.453	.533
4800	21.000	69.178	51.034	89.864	-306.002	-5.196	.268
4900	21.000	70.128	51.428	91.964	-305.802	1.196	.068
5000	21.000	70.612	51.799	94.064	-305.786	7.339	.321

TITANIUM DIOXIDE (TiO₂)

(LIQUID)

GFW = 79.8988

S_{298.15} = [18.934] gibbs/mol
ΔH_{298.15} = [-210.726] kcal/mol
ΔHm° = [16] kcal/mol

Tm = 2143°K

Heat of Formation.

The ΔH_f²⁹⁸(l) is calculated from ΔH_f²⁹⁸(rutile, c) by adding ΔHm° and the difference between S₂₁₄₃° - S_{298.15}° for TiO₂(rutile, c) and TiO₂(l).

Heat Capacity and Entropy.

The heat capacity of TiO₂(l) is estimated on the basis of 7.0 gibbs/g-atom. The value of S₂₉₈° is obtained in a manner analogous to that of the heat of formation.

Melting Data.

The melting point of TiO₂(rutile) has been measured by many investigators. Eleven pertinent Tm values were reviewed and corrected, according to the International Temperature Scale of 1948, by S. J. Schneider, Natl. Bur. Std. Monograph 68, October 10, 1963. The adopted melting point is obtained from G. Brauer and W. Litke, J. Inorg. Nucl. Chem. 16, 67 (1960). These authors found that TiO₂ loses oxygen on heating and the solid residue consists of a non-stoichiometric compound of the composition TiO_{2-x}. The value of the coefficient x depends on the temperature and on the oxygen pressure of the gaseous phase. Under oxygen pressures greater than or equal to 300 torr, the solid residue was TiO_{2.000} within the sensitivity of chemical analysis; however, color of the residue was a more sensitive indicator of composition. At pressures of 600 torr or greater, the residue was bright yellow rather than blue-gray and the melting point was constant at the maximum value of 2143 ± 15°K. This value is adopted.

The heat of melting is calculated using an estimated entropy of melting, ΔSm° = 2.5 eu/g-atom.

O₂Ti

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	-0.000	0.000	INFINITE	2.597	61.370	61.370	INFINITE
100	7.760	46.055	46.906	1.885	61.755	61.755	134.966
200	9.634	52.055	57.100	1.007	61.762	61.762	67.661
298	10.636	56.146	56.146	0.000	62.004	62.004	45.407
300	10.658	56.213	56.146	.020	62.004	61.945	45.127
400	11.820	59.474	56.584	1.154	62.197	63.818	33.818
500	12.588	62.194	57.442	2.374	62.354	61.801	27.013
600	13.070	64.531	58.433	3.459	62.492	61.677	22.466
700	13.268	66.578	59.422	4.422	62.615	61.535	18.764
800	13.766	68.395	60.460	5.344	62.775	61.365	16.744
900	13.957	70.027	61.434	6.734	62.939	61.179	14.856
1000	14.117	71.506	62.368	8.136	63.126	60.973	13.326
1100	14.241	72.856	63.251	10.556	63.336	60.744	12.069
1200	14.341	74.094	64.086	12.924	63.562	60.482	11.017
1300	14.417	75.222	64.823	15.246	63.806	60.193	10.107
1400	14.460	76.323	65.703	17.668	64.068	59.770	9.331
1500	14.532	77.324	66.744	20.139	64.353	59.406	8.655
1600	14.575	78.263	67.834	22.664	64.658	59.029	8.063
1700	14.601	79.146	68.964	25.244	64.982	58.642	7.542
1800	14.618	80.000	70.132	27.876	65.325	58.247	7.071
1900	14.627	80.776	71.342	30.559	65.685	57.842	6.652
2000	14.630	81.529	72.594	33.291	66.060	57.425	6.255
2100	14.700	82.246	73.884	36.069	66.450	56.997	5.887
2200	14.754	82.924	75.212	38.899	66.854	56.557	5.547
2300	14.781	83.566	76.576	41.775	67.272	56.103	5.226
2400	14.794	84.173	77.971	44.700	67.704	55.636	4.924
2500	14.795	84.754	79.400	47.671	68.150	55.157	4.639
2600	14.774	85.305	80.862	50.688	68.610	54.665	4.368
2700	14.745	85.823	82.356	53.750	69.084	54.158	4.109
2800	14.703	86.307	83.882	56.857	69.572	53.636	3.862
2900	14.650	86.754	85.442	59.999	70.074	53.091	3.626
3000	14.597	87.157	87.024	63.176	70.590	52.526	3.398
3100	14.534	87.521	88.624	66.389	71.120	51.943	3.176
3200	14.460	87.846	90.256	69.642	71.664	51.336	2.959
3300	14.376	88.134	91.924	72.936	72.222	50.709	2.746
3400	14.284	88.386	93.624	76.262	72.794	50.063	2.536
3500	14.184	88.600	95.356	79.632	73.379	49.397	2.330
3600	14.076	88.778	97.116	83.044	73.976	48.722	2.128
3700	13.960	88.921	98.904	86.490	74.584	48.036	1.929
3800	13.836	89.030	100.716	89.970	75.202	47.340	1.734
3900	13.704	89.104	102.556	93.484	75.830	46.634	1.542
4000	13.564	89.144	104.424	97.032	76.468	45.918	1.352
4100	13.416	89.150	106.320	100.612	77.116	45.192	1.164
4200	13.260	89.124	108.244	104.224	77.774	44.456	0.978
4300	13.096	89.066	110.196	107.872	78.442	43.710	0.794
4400	12.924	88.976	112.176	111.556	79.116	42.954	0.612
4500	12.744	88.854	114.184	115.276	79.794	42.188	0.432
4600	12.556	88.694	116.216	119.032	80.476	41.412	0.254
4700	12.360	88.496	118.272	122.824	81.156	40.626	0.078
4800	12.156	88.260	120.356	126.648	81.836	39.830	-0.100
4900	11.944	87.984	122.464	130.504	82.516	39.024	-0.280
5000	11.724	87.676	124.596	134.392	83.196	38.208	-0.460
5100	11.496	87.336	126.756	138.312	83.876	37.382	-0.640
5200	11.260	86.964	128.944	142.264	84.556	36.546	-0.820
5300	11.016	86.560	131.160	146.248	85.236	35.700	-1.000
5400	10.764	86.124	133.404	150.264	85.916	34.844	-1.180
5500	10.504	85.656	135.676	154.312	86.596	33.978	-1.360
5600	10.236	85.160	137.976	158.392	87.276	33.102	-1.540
5700	9.960	84.636	140.304	162.504	87.956	32.216	-1.720
5800	9.676	84.076	142.664	166.648	88.636	31.320	-1.900
5900	9.384	83.484	145.056	170.824	89.316	30.414	-2.080
6000	9.084	82.860	147.480	175.032	89.996	29.500	-2.260

Dec. 31, 1960; Mar. 31, 1967

TITANIUM DIOXIDE (TiO₂)

(IDEAL GAS)

GFW = 79.8988

Point Group [D_{2h}]ΔH_f⁰ = 61.4 ± 10 kcal/molΔH_f⁰₂₉₈ = -62.0 ± 10 kcal/molS⁰_{298.15} = [56] gibbs/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
940 (1)	
[328] (2)	
[1214] (1)	

Bond Distances: Ti-O = [1.62] Å

Bond Angles: O-Ti-O = [180]°

σ = 2

Rotational Constant: B₀ = [0.2007] cm⁻¹

Heat of Formation.

P. W. Gilles, K. D. Carlson, H. F. Frenzen, and P. G. Wahlbeck, *J. Chem. Phys.* **45**, 2461 (1967), studied the vaporization behavior of the titanium-oxygen system and found that Ti₃O₅ is the final residue of both higher and lower titanium oxides; hence Ti₃O₅ is the congruently vaporizing phase. This conclusion was obtained by measurement of the change in composition of the solid residue accompanying vaporization as determined by x-ray diffraction, chemical analysis, and color of sample.

From mass spectrometric studies over Ti₃O₅(s) near 2000°K, P. G. Wahlbeck and P. W. Gilles, *J. Chem. Phys.* **45**, 2465 (1967), concluded that the partial pressure of TiO₂ is probably less than 1% of the pressure of TiO produced by the main vaporization, Ti₃O₅(s) = 3 TiO(g) + 2 O(g). This yields ΔH⁰₂₀₀₀ ≥ 228 kcal for the reaction Ti₃O₅(s) = 2 TiO₂(g) + TiO(g) and ΔH⁰₂₉₈ TiO₂(g) ≥ -62 kcal/mol, which is the value adopted. The corresponding atomization energy is D₀⁰ ≤ 292 kcal/mol.

Earlier vaporization studies over TiO₂-x gave apparent heats of formation which are more negative by 20-35 kcal; however, the results appear to be uncertain due to lack of sufficient auxiliary data for the oxygen-deficient condensed phase. Knudsen effusion-mass spectrometric studies of J. Berkowitz, W. A. Chupka and M. G. Inghram, *J. Phys. Chem.* **61**, 1559 (1957), revealed the initial evolution of large amounts of MoO₃(g), suggesting that the reduction of TiO₂ is enhanced by the Mo cell. In order to reduce the effect of the initial high rate of evaporation, W. O. Groves, M. Hoch and H. L. Johnston, *J. Phys. Chem.* **59**, 127 (1955), conducted their Knudsen effusion-weight loss studies on TiO₂. Preferential loss of oxygen during the experiment, as indicated by a residue of TiO_{1.85}, was apparently ignored. Groves et al. estimated the activity of TiO₂(rutile) as 0.53; Berkowitz et al. assumed unit activity but did not indicate the composition of their condensed phase. These activities may be in serious error due to the presence of a series of distinct phases between TiO_{1.8} and TiO_{1.9} [cf. S. Andersson, *Acta Chem. Scand.* **14**, 1161 (1960)] and to the possible existence of a two phase region near TiO_{1.99} [cf. R. N. Blumenthal and D. H. Whitmore, *J. Electrochem. Soc.* **110**, 92 (1963)]. Second and third law analyses of the data, using the authors' original assumptions, are summarized below. No weight is given to these results.

Investigator	Temperature, °K	No. of Points	ΔH ⁰ ₂₉₈ kcal/mol	Drift, eu
Groves et al.	1849 - 2010	14	128.7 ± 7.5	130.1
Berkowitz et al.	1891	3	142.7 ± 5**	142.8

*Calculation based on the third law ΔH⁰₂₉₈.

**Obtained from the temperature variation experiments, reported in the original paper.

Heat Capacity and Entropy.

The molecular structure is assumed to be linear. The Ti-O bond distance is estimated as the same as that in TiO(g). The vibrational frequency 940 cm⁻¹ was observed in matrix isolation by W. Waltner, Jr., and D. McLeod, Jr., *J. Phys. Chem.* **69**, 3488 (1965). The other two frequencies are calculated, based on the valence bond method as suggested by Berkowitz, Chupka and Inghram, loc. cit. The moment of inertia is 1.3944 x 10⁻³⁶ g cm².

Tungsten Dioxide (WO₂)

(Crystal) GFW = 215.8488

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	0.000	0.000	INFINITE	-2.081	-139.757	-139.757	INFINITE
100	4.566	2.388	21.558	-1.917	-140.462	-136.310	297.925
200	10.089	7.384	13.204	-1.164	-140.869	-131.987	146.229
298	13.322	12.077	12.077	0.000	-140.940	-127.603	93.535
300	13.340	12.159	12.077	0.028	-140.939	-127.520	92.698
400	15.160	13.267	12.925	1.057	-140.807	-124.053	65.239
500	16.290	14.781	13.713	3.034	-140.562	-118.654	51.864
600	17.042	22.821	14.984	4.702	-140.260	-114.300	41.634
700	17.596	25.492	15.298	6.453	-139.926	-109.999	34.343
800	18.000	27.841	15.561	8.204	-139.561	-105.748	28.648
900	18.398	30.017	15.861	10.040	-139.208	-101.542	24.598
1000	18.684	31.971	20.076	11.895	-138.834	-97.376	21.281
1100	18.911	33.763	21.240	13.775	-138.457	-93.250	18.227
1200	19.115	35.517	22.353	15.676	-138.079	-89.156	15.237
1300	19.298	37.140	23.420	17.596	-137.698	-85.092	12.308
1400	19.430	38.606	24.437	19.536	-137.303	-81.063	9.435
1500	20.340	39.792	25.415	21.559	-136.872	-77.059	6.628
1600	21.040	41.128	26.356	23.636	-136.398	-73.088	3.883
1700	21.760	42.625	27.263	25.766	-135.871	-69.146	1.200
1800	22.485	44.316	28.140	27.946	-135.292	-65.232	-1.414
1900	23.185	46.168	28.990	30.267	-134.669	-61.353	-4.054
2000	23.870	48.108	29.817	32.730	-134.011	-57.523	-6.786
2100	24.500	49.263	30.621	34.949	-133.324	-53.713	-9.590
2200	25.080	50.575	31.403	36.854	-132.617	-49.936	-12.462
2300	25.610	52.037	32.163	38.497	-131.897	-46.202	-15.394
2400	26.100	53.637	32.909	42.307	-131.117	-42.489	-18.393
2500	26.560	55.372	33.634	44.843	-130.333	-38.816	-21.449
2600	26.990	57.242	34.344	47.419	-129.526	-35.169	-24.566
2700	27.390	59.247	35.036	50.036	-128.694	-31.553	-27.744
2800	27.760	61.387	35.712	52.697	-127.842	-27.972	-30.982
2900	28.120	63.661	36.382	55.396	-127.022	-24.420	-34.280
3000	27.810	66.006	37.034	58.117	-126.200	-20.894	-37.628

- Reference 1. G. R. St. Pierre, W. T. Ebbel, M. J. Pool and R. Speiser, *Trans. AIME* 224, 259 (1962).
 2. Ya. I. Gerasimov, I. A. Vasil'eva, T. P. Chusova, V. W. Geiderikh, and M. A. Timofeeva, *Zh. Fiz. Khim.* 36, 358 (1962).
 3. I. A. Vasil'eva, Ya. I. Gerasimov and Yu. P. Smanov, *Zh. Fiz. Khim.* 34, 1811 (1960).
 4. R. C. Griffiths, *J. Electrochem. Soc.* 106, 418 (1959).

Heat Capacity and Entropy.

E. G. King, W. W. Weiler, and A. U. Christensen, U. S. Bur. Mines RI 5664, (1960), have measured the low temperature heat capacities from 53° to 297°K and high temperature enthalpy changes from 398° to 1800°K by drop calorimetry. The low temperature and high temperature heat capacities were joined smoothly at 298.15°K. The entropy was obtained from the heat capacities based on S°₂₉₈ = 0.52 eu. It is possible that at temperatures below 50°K the entropy due to the uncoupling of the d² electrons will appear, contributing an additional 2.2 eu.

Temperature of Decomposition.

Tungsten dioxide (c) has no melting point, since disproportionation occurs to yield W(c) and WO₃(l) before melting starts. The Td is calculated as the temperature at which ΔG equals zero for 3 WO₂(c) = 2 WO₃(l) + W(c).

Heat of Sublimation.

June 30, 1962; Sept. 30, 1963

The heat of sublimation was calculated from the difference between the heats of formation of WO₂(g) and WO₂(c).

O₂W

TUNGSTEN DIOXIDE (WO₂)

(CRYSTAL) GFW = 215.8488

S°₂₉₈.15 = 12.08 ± 0.07 gibbs/mol
 Td = 1997°K
 ΔH°_f = -139.75 ± 0.21 kcal/mol
 ΔH°_f_{298.15} = -140.94 ± 0.21 kcal/mol
 ΔH°_f_{298.15} = 159.24 kcal/mol

Heat of Formation.

The adopted heat of formation, -140.94 ± 0.21 kcal/mol, was determined by combustion calorimetry by A. D. Mah, *J. Am. Chem. Soc.* 81, 1582 (1959). R. C. Griffiths, *J. Electrochem. Soc.* 105, 398 (1958), has measured the heat of combustion to WO₃(c) which yields ΔH°_f₂₉₈ (WO₂, c) = -139.8 ± 1.5 kcal/mol when recalculated with ΔH°_f₂₉₈ (WO₃, c) = -201.46 kcal/mol. This result is less certain because of the incomplete characterization of the final products.

Recent equilibrium data yield essentially the same average of the heat of formation by the third law method. The results are presented as follows.

Author	Reaction*	Temp. (°K)	No. of Points	ΔH° _f ₂₉₈ (kcal/mol)	Drift (eu)	ΔH° _f ₂₉₈ (kcal/mol)
1. St. Pierre (1962) et al.	A	1275 - 1497	10	2.672	0.036	-140.62
2. Gerasimov (1962) et al.	B	973 - 1467	6	11.994	12.076	-139.58
3. Vasil'eva (1960) et al.	C	923 - 1223	7	-70.281	-67.943	-140.56
4. Griffiths (1959)	B	1075 - 1210	5	12.949	13.051	-141.49
	B	873 - 1273	30	12.550	10.295	-140.70
*Reaction						
A: 1/2 WO ₂ (c) + CO(g) = 1/2 W(c) + CO ₂ (g)						
B: 1/2 WO ₂ (c) + H ₂ (g) = 1/2 W(c) + H ₂ O(g)						
C: 1/2 W(c) + 1/2 O ₂ (g) = 1/2 WO ₂ (c)						

O₂W

Tungsten Dioxide (WO₂)

(Ideal Gas)

GFW = 215.8488

TUNGSTEN DIOXIDE (WO₂)

(IDEAL GAS)

OPW = 215.8488

O₂W

T, °K	C _p ^o	S ^o	gibbs/mol -(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	Kcal/mol ΔH°	ΔG°	Log K _p
0	0.000	INFINITE	-	2.688	18.876	18.876	INFINITE
100	8.400	58.000	70.844	1.981	17.399	17.399	-38.025
200	9.508	60.233	68.209	0.000	16.853	16.853	-40.923
298	10.471	68.209	68.209	0.000	16.300	14.901	-10.923
300	10.489	68.274	68.209	0.019	18.295	14.880	-
400	11.355	71.415	68.631	1.113	18.089	13.774	-7.557
500	11.999	74.022	69.456	2.483	17.927	12.714	-
600	12.454	76.252	70.407	3.507	17.785	11.686	-4.257
700	12.776	78.197	71.384	4.769	17.648	10.681	-3.335
800	13.006	79.919	72.345	6.059	17.507	9.693	-2.648
900	13.176	81.461	73.274	7.368	17.360	8.727	-2.119
1000	13.303	82.856	74.164	8.693	17.204	7.777	-1.700
1100	13.401	84.129	75.013	10.028	17.036	6.840	-1.359
1200	13.477	85.299	75.822	11.372	16.857	5.922	-1.078
1300	13.538	86.380	76.593	12.723	16.665	5.018	-0.844
1400	13.587	87.385	77.328	14.079	16.460	4.129	-0.645
1500	13.627	88.324	78.030	15.440	16.242	3.257	-0.474
1600	13.660	89.204	78.701	16.805	16.011	2.399	-0.328
1700	13.688	90.033	79.344	18.172	15.765	1.556	-0.200
1800	13.711	90.816	79.960	19.542	15.504	0.728	-0.088
1900	13.731	91.558	80.551	20.914	15.228	0.010	-0.006
2000	13.748	92.263	81.119	22.288	14.937	-0.885	-0.097
2100	13.763	92.934	81.666	23.664	14.631	-1.667	-0.174
2200	13.776	93.575	82.193	25.041	14.307	-2.440	-0.242
2300	13.787	94.187	82.701	26.419	13.969	-3.192	-0.303
2400	13.796	94.774	83.192	27.798	13.614	-3.928	-0.358
2500	13.806	95.338	83.666	29.178	13.242	-4.655	-0.407
2600	13.815	95.879	84.126	30.559	12.855	-5.360	-0.451
2700	13.822	96.401	84.571	31.941	12.446	-6.054	-0.490
2800	13.829	96.904	85.002	33.324	12.007	-6.731	-0.525
2900	13.836	97.389	85.421	34.707	11.537	-7.393	-0.557
3000	13.843	97.858	85.828	36.091	11.052	-8.033	-0.585
3100	13.850	98.312	86.223	37.476	10.421	-8.650	-0.611
3200	13.857	98.752	86.608	38.861	9.776	-9.257	-0.633
3300	13.864	99.179	86.983	40.247	9.062	-9.854	-0.653
3400	13.872	99.593	87.347	41.634	8.269	-10.414	-0.669
3500	13.880	99.995	87.703	43.021	7.385	-10.951	-0.684
3600	13.890	100.386	88.050	44.410	6.385	-11.460	-0.696
3700	13.900	100.767	88.389	45.799	5.304	-11.896	-0.703
3800	13.910	101.138	88.719	47.190	4.158	-12.217	-0.697
3900	13.922	101.499	89.042	48.581	3.055	-12.437	-0.692
4000	13.935	101.852	89.358	49.974	1.904	-12.560	-0.686
4100	13.950	102.196	89.667	51.369	0.704	-12.575	-0.680
4200	13.965	102.532	89.969	52.764	-0.536	-12.491	-0.673
4300	13.982	102.861	90.265	54.162	-1.758	-13.116	-0.667
4400	14.000	103.183	90.555	55.561	-2.912	-13.287	-0.660
4500	14.020	103.498	90.839	56.952	-4.066	-13.443	-0.653
4600	14.041	103.806	91.118	58.345	-5.212	-13.583	-0.645
4700	14.064	104.108	91.391	59.740	-6.358	-13.718	-0.638
4800	14.088	104.405	91.659	61.138	-7.504	-13.846	-0.630
4900	14.113	104.695	91.922	62.538	-8.650	-13.964	-0.623
5000	14.140	104.981	92.181	63.940	-9.796	-14.074	-0.615
5100	14.168	105.261	92.434	65.346	-10.942	-14.179	-0.607
5200	14.198	105.536	92.684	66.754	-12.088	-14.280	-0.599
5300	14.228	105.807	92.929	68.164	-13.233	-14.377	-0.591
5400	14.259	106.073	93.170	69.579	-14.377	-14.472	-0.583
5500	14.294	106.335	93.407	71.000	-15.522	-14.563	-0.575
5600	14.328	106.593	93.640	72.430	-16.668	-14.653	-0.567
5700	14.363	106.847	93.869	73.870	-17.814	-14.742	-0.559
5800	14.400	107.097	94.095	75.318	-18.960	-14.830	-0.551
5900	14.438	107.344	94.318	76.764	-20.106	-14.917	-0.543
6000	14.475	107.587	94.537	78.219	-21.252	-15.003	-0.535

June 30, 1962; Sept. 30, 1966

Point Group [C_{2v}]
S°_{298.15} = [68.2] gibbs/mol
Ground State Quantum Weight = [3]
ΔH°_f° = 18.9 ± 7 kcal/mol
ΔH°_f°_{298.15} = 18.3 ± 7 kcal/mol

Electronic Levels and Quantum Weights		
ε, cm ⁻¹	g _i	
0	[3]	
[25,000]	[10]	

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	
932 (1)	
[300] (1)	
928 (1)	

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [110°]

Product of the Moments of Inertia: I_AI_BI_C = [9.433 x 10⁻¹¹⁵] g³cm⁶

σ = [2]

Heat of Formation.

G. DeMaris, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960), have reported the partial pressures of WO₂(g), WO₃(g) and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2185° to 2475°K. The adopted value, ΔH°_f°₂₉₈ (WO₂g) = 18.3 ± 7 kcal/mol, was calculated from ΔH°_f°₂₉₈ = -100.9 kcal/mol for W(c) + 2 O(g) → WO₂(g), which was obtained from third law treatment of their partial pressure data, using all JANAF functions. The third law drift is 15.0 ± 5.2 eu. Partial pressures of WO₂(g), WO₃(g) and O(g) at 2242°K have also been reported by W. A. Chupka, J. Berkowitz and C. F. Glease, J. Chem. Phys. **30**, 827 (1959), in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives ΔH°_f°₂₉₈ = -105.9 kcal/mol, which yields ΔH°_f°₂₉₈ (WO₂g) = 13.2 kcal/mol.

Heat Capacity and Entropy.

The WO₂(g) was assumed to have a C_{2v} symmetry with a bond angle O-W-O = 110°. The bond distance W-O was estimated to be the same as that in WO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectrum of WO₂ in a neon matrix by W. Weitzer, Jr., and D. McLeod, Jr., J. Mol. Spectry. **11**, 276 (1965). The bending vibrational frequency (300 cm⁻¹) was estimated by comparison with other dioxides. The electronic levels and quantum weights were estimated from W⁴⁺ ion by analogy with Mo⁴⁺ ion. The three principal moments of inertia are: I_A = 4.8776 x 10⁻³⁹, I_B = 1.1680 x 10⁻³⁸ and I_C = 1.6558 x 10⁻³⁸ g cm².

O₂W

Zirconium Dioxide (ZrO₂)

(Crystal) Mol. Wt. = 123.2188

O₂ZrZIRCONIUM DIOXIDE (ZrO₂) (CRYSTAL) MOL. WT. = 123.2188

$$\Delta H_f^0 = -261.0 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 298.15 = -262.3 \pm 0.4 \text{ kcal. mole}^{-1}$$

$$\Delta H_c^0 = 1.42 \pm 0.1 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^0 = [20.8] \text{ kcal. mole}^{-1}$$

$$S^0 298.15 = [12.035 \pm 0.08] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_f = 1478 \pm 5^\circ \text{K.}$$

$$T_m = 2950^\circ \text{K.}$$

Heat of Formation.

The $\Delta H_f^0 298.15 = -263.1 \pm 0.5 \text{ kcal. mole}^{-1}$ measured (by combustion calorimetry) by O. L. Humphrey, J. Am. Chem. Soc. 75, 978 (1954) and E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., J. Phys. Chem. 58, 3040 (1954) respectively. Also the heat of formation was measured calorimetrically by B. Neumann, C. Kröger and H. Kunz, Z. anorg. Chem. 218, 579 (1934), by W. A. Roth, E. Böger, and H. Siemensen, ibid., 239, 321 (1938) and by A. Sievert, A. Gotta and S. Halberstadt, ibid., 187, 185 (1930) and was found -258.2, -258.8 and -256.1 kcal. mole⁻¹ respectively. However more weight was given to the Humphrey and Huber values.

Heat Capacity and Entropy.

The low temperature heat capacities, 54.3-295°K., were measured by K. K. Kelley, Ind. Eng. Chem. 35, 377 (1944). The heat capacities in the temperature range 298-1478°K. were calculated by using the J. P. Coughlin and E. O. King equation $C_p = 16.64 + 1.80 \times 10^{-5} T - 3.36 \times 10^{-8} T^2$ obtained from their measured enthalpy data in the range 398.8 - 1841°K., J. Am. Chem. Soc. 72, 2282 (1950). The values from the two sources join smoothly at 298°K. Above the transition 1478°K. the heat capacity was taken as constant at 17.80 cal. mole⁻¹ deg.⁻¹, Coughlin and King, loc. cit. The entropy was calculated at 54.30 using the Debye and Einstein function $D(\frac{345}{T}) + E(\frac{513}{T})$ given by Kelley, loc. cit. The value of $S_{54.3}^0 = 0.5507 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

T_f and ΔH_f^0 were taken from Coughlin and King loc. cit.

Melting Data.

The T_m and ΔH_m^0 were taken from Natl. Bur. Standards Circ. 500 Washington (1952).

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	4.000	INFINITE	-2.091	-260.999	-260.999	INFINITE
100	4.524	21.604	-1.934	-261.767	-257.504	562.748
200	10.224	13.173	-1.176	-262.210	-253.034	276.490
298	12.036	12.036	-1.000	-262.300	-248.502	182.148
300	13.447	12.036	-0.925	-262.299	-248.416	180.962
400	15.260	12.036	-0.866	-262.198	-243.802	133.201
500	16.196	12.036	-0.808	-262.024	-239.221	104.558
600	16.767	12.036	-0.750	-261.832	-234.678	85.477
700	17.155	12.036	-0.692	-261.634	-229.166	68.652
800	17.485	12.036	-0.634	-261.431	-223.687	53.720
900	17.765	12.036	-0.576	-261.220	-218.231	40.739
1000	18.104	12.036	-0.518	-261.003	-212.798	28.340
1100	18.342	12.036	-0.460	-260.790	-207.390	17.572
1200	18.581	12.036	-0.402	-260.576	-201.996	8.722
1300	18.781	12.036	-0.344	-260.359	-196.611	3.999
1400	18.989	12.036	-0.286	-260.139	-191.237	2.065
1500	19.206	12.036	-0.228	-259.911	-185.866	1.005
1600	19.435	12.036	-0.170	-259.680	-180.496	0.596
1700	19.674	12.036	-0.112	-259.446	-175.126	0.338
1800	19.924	12.036	-0.054	-259.209	-169.756	0.204
1900	20.184	12.036	-0.000	-258.969	-164.386	0.138
2000	20.454	12.036	0.054	-258.726	-158.996	0.094
2100	20.734	12.036	0.108	-258.480	-153.586	0.064
2200	21.024	12.036	0.162	-258.231	-148.156	0.044
2300	21.324	12.036	0.216	-257.979	-142.706	0.034
2400	21.634	12.036	0.270	-257.724	-137.236	0.024
2500	21.954	12.036	0.324	-257.466	-131.746	0.014
2600	22.284	12.036	0.378	-257.206	-126.236	0.004
2700	22.624	12.036	0.432	-256.943	-120.706	0.004
2800	22.974	12.036	0.486	-256.677	-115.156	0.004
2900	23.334	12.036	0.540	-256.409	-109.586	0.004
3000	23.704	12.036	0.594	-256.139	-103.996	0.004
3100	24.084	12.036	0.648	-255.866	-98.386	0.004
3200	24.474	12.036	0.702	-255.590	-92.756	0.004
3300	24.874	12.036	0.756	-255.311	-87.106	0.004
3400	25.284	12.036	0.810	-255.029	-81.436	0.004
3500	25.704	12.036	0.864	-254.744	-75.746	0.004
3600	26.134	12.036	0.918	-254.456	-70.036	0.004
3700	26.574	12.036	0.972	-254.166	-64.306	0.004
3800	27.024	12.036	1.026	-253.872	-58.556	0.004
3900	27.484	12.036	1.080	-253.576	-52.786	0.004
4000	27.954	12.036	1.134	-253.276	-46.996	0.004

O₂Zr

Zirconium Dioxide (ZrO₂)

(Liquid)

Mol. Wt. = 123.2188

O₂Zr

MOL. WT. = 123.2188

(LIQUID)

ZIRCONIUM DIOXIDE (ZrO₂)

$$\Delta H_f^{298.15} = [244.55] \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = [20.8] \text{ kcal. mole}^{-1}$$

$$\Delta H_v^{298.15} = [149.2] \text{ kcal. mole}^{-1}$$

$$S^{298.15} = [17.04] \text{ cal. deg.}^{-1}$$

$$T_m = 2950^\circ \text{K.}$$

$$T_b = 4540^\circ \text{K.}$$

Heat of Formation:

The $\Delta H_f^{298.15} (l)$ was obtained from $\Delta H_f^{298.15} (c)$ by adding $\Delta H_m^{298.15}$ and the difference between $T_m^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

A glass transition was assumed at 2000°K. The heat capacity below 2000°K. was obtained from the heat capacity of the crystal. Above 2000°K. the heat capacity was assumed constant and estimated to be 21.0 cal. deg.⁻¹ mole⁻¹ or 7 cal. deg.⁻¹ per g-atom as suggested by O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry" Pergamon Press, New York (1958). The entropy was obtained in a manner analogous to that of the heat of formation.

Melting Data.

See ZrO₂(c) table.

Vaporization Data.

T_b was calculated as the temperature at which the free energy change of the reaction $\text{ZrO}_2(l) \rightarrow \text{ZrO}_2(g)$ approaches zero. The difference between $\Delta H_f^{298.15}$ for $\text{ZrO}_2(g)$ and $\text{ZrO}_2(l)$ is $\Delta H_v^{298.15}$.

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f	ΔF _f	Log K _p
0							
100	13.430	17.041	17.041	0.000	-244.550	-232.403	170.406
200	13.447	17.024	17.024	0.025	-244.569	-232.408	169.301
300	13.460	17.007	17.007	0.050	-244.588	-232.413	124.771
400	13.472	16.990	16.990	0.075	-244.607	-232.418	96.069
500	13.484	16.973	16.973	0.100	-244.626	-232.423	80.281
600	13.496	16.956	16.956	0.125	-244.645	-232.428	67.585
700	13.508	16.939	16.939	0.150	-244.664	-232.433	56.072
800	13.520	16.922	16.922	0.175	-244.683	-232.438	46.678
900	13.532	16.905	16.905	0.200	-244.702	-232.443	44.769
1000	13.544	16.888	16.888	0.225	-244.721	-232.448	39.938
1100	13.556	16.871	16.871	0.250	-244.740	-232.453	35.907
1200	13.568	16.854	16.854	0.275	-244.759	-232.458	32.404
1300	13.580	16.837	16.837	0.300	-244.778	-232.463	29.571
1400	13.592	16.820	16.820	0.325	-244.797	-232.468	27.043
1500	13.604	16.803	16.803	0.350	-244.816	-232.473	24.643
1600	13.616	16.786	16.786	0.375	-244.835	-232.478	22.403
1700	13.628	16.769	16.769	0.400	-244.854	-232.483	21.170
1800	13.640	16.752	16.752	0.425	-244.873	-232.488	19.636
1900	13.652	16.735	16.735	0.450	-244.892	-232.493	18.249
2000	13.664	16.718	16.718	0.475	-244.911	-232.498	16.994
2100	13.676	16.701	16.701	0.500	-244.930	-232.503	15.639
2200	13.688	16.684	16.684	0.525	-244.949	-232.508	14.780
2300	13.700	16.667	16.667	0.550	-244.968	-232.513	13.810
2400	13.712	16.650	16.650	0.575	-244.987	-232.518	12.920
2500	13.724	16.633	16.633	0.600	-245.006	-232.523	12.098
2600	13.736	16.616	16.616	0.625	-245.025	-232.528	11.339
2700	13.748	16.599	16.599	0.650	-245.044	-232.533	10.634
2800	13.760	16.582	16.582	0.675	-245.063	-232.538	9.979
2900	13.772	16.565	16.565	0.700	-245.082	-232.543	9.368
3000	13.784	16.548	16.548	0.725	-245.101	-232.548	8.798
3100	13.796	16.531	16.531	0.750	-245.120	-232.553	8.264
3200	13.808	16.514	16.514	0.775	-245.139	-232.558	7.763
3300	13.820	16.497	16.497	0.800	-245.158	-232.563	7.291
3400	13.832	16.480	16.480	0.825	-245.177	-232.568	6.848
3500	13.844	16.463	16.463	0.850	-245.196	-232.573	6.429
3600	13.856	16.446	16.446	0.875	-245.215	-232.578	6.033
3700	13.868	16.429	16.429	0.900	-245.234	-232.583	5.659
3800	13.880	16.412	16.412	0.925	-245.253	-232.588	5.304
3900	13.892	16.395	16.395	0.950	-245.272	-232.593	4.968
4000	13.904	16.378	16.378	0.975	-245.291	-232.598	4.640
4100	13.916	16.361	16.361	1.000	-245.310	-232.603	4.324
4200	13.928	16.344	16.344	1.025	-245.329	-232.608	4.023
4300	13.940	16.327	16.327	1.050	-245.348	-232.613	3.737
4400	13.952	16.310	16.310	1.075	-245.367	-232.618	3.464
4500	13.964	16.293	16.293	1.100	-245.386	-232.623	3.201
4600	13.976	16.276	16.276	1.125	-245.405	-232.628	2.949
4700	13.988	16.259	16.259	1.150	-245.424	-232.633	2.707
4800	13.999	16.242	16.242	1.175	-245.443	-232.638	2.474
4900	14.011	16.225	16.225	1.200	-245.462	-232.643	2.249
5000	14.023	16.208	16.208	1.225	-245.481	-232.648	2.032
5100	14.035	16.191	16.191	1.250	-245.500	-232.653	1.821
5200	14.047	16.174	16.174	1.275	-245.519	-232.658	1.615
5300	14.059	16.157	16.157	1.300	-245.538	-232.663	1.414
5400	14.071	16.140	16.140	1.325	-245.557	-232.668	1.217
5500	14.083	16.123	16.123	1.350	-245.576	-232.673	1.032
5600	14.095	16.106	16.106	1.375	-245.595	-232.678	0.856
5700	14.107	16.089	16.089	1.400	-245.614	-232.683	0.689
5800	14.119	16.072	16.072	1.425	-245.633	-232.688	0.530
5900	14.131	16.055	16.055	1.450	-245.652	-232.693	0.379
6000	14.143	16.038	16.038	1.475	-245.671	-232.698	0.234

June 30, 1961; Dec. 31, 1965

O₂Zr

Zirconium Dioxide (ZrO_2)
(Ideal Gas) Mol. Wt. = 123.2188

O_2Zr

MOL. WT. = 123.2188

ZIRCONIUM DIOXIDE (ZrO_2) (IDEAL GAS)

T, °K.	C_p°	S° cal. mole ⁻¹ deg. ⁻¹	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$ kcal. mole ⁻¹	ΔF_i°	Log K _p
0	9.000	INFINITE	INFINITE	0	INFINITE	INFINITE
100	9.115	56.438	2.870	67.878	37.878	150.402
200	9.230	61.199	1.036	68.172	68.172	76.243
298	11.009	65.402	0.000	68.400	70.513	51.685
300	11.026	65.470	0.020	68.404	70.526	51.376
400	12.576	68.756	1.465	68.605	71.203	38.902
500	12.578	66.705	2.376	68.796	71.850	31.395
600	12.759	73.750	67.693	68.997	72.418	26.377
700	13.022	75.738	68.703	69.210	72.972	22.782
800	13.207	77.489	69.694	69.434	73.495	20.077
900	13.342	79.053	70.669	69.665	73.988	17.966
1000	13.442	80.464	71.561	69.907	74.454	16.271
1100	13.519	81.749	72.430	70.168	74.898	14.880
1200	13.578	82.928	73.256	71.399	75.267	13.707
1300	13.625	84.017	74.042	71.669	75.580	12.705
1400	13.663	85.028	74.791	71.951	75.871	11.843
1500	13.694	85.972	75.506	72.242	76.140	11.093
1600	13.720	86.856	76.188	72.543	76.388	10.434
1700	13.741	87.689	76.840	72.855	76.621	9.850
1800	13.759	88.475	77.465	73.178	76.832	9.328
1900	13.774	89.219	78.064	73.495	77.025	8.860
2000	13.787	89.926	78.640	73.808	77.204	8.436
2100	13.798	90.599	79.193	74.114	77.362	8.051
2200	13.808	91.241	79.726	74.466	77.508	7.682
2300	13.817	91.855	80.240	74.870	77.632	7.338
2400	13.824	92.443	80.737	75.296	77.737	7.021
2500	13.831	93.009	81.216	75.748	77.821	6.728
2600	13.837	93.550	81.680	81.054	76.813	6.456
2700	13.842	94.073	82.130	81.528	76.644	6.204
2800	13.847	94.576	82.565	81.967	76.457	5.967
2900	13.851	95.062	82.988	82.401	76.253	5.746
3000	13.855	95.532	83.498	82.897	76.040	5.539
3100	13.859	95.986	83.979	83.419	75.812	5.344
3200	13.862	96.426	84.435	83.945	75.570	5.161
3300	13.865	96.853	84.862	84.459	75.315	4.988
3400	13.868	97.267	85.268	84.945	75.045	4.824
3500	13.870	97.669	85.656	85.406	74.766	4.666
3600	13.872	98.060	86.038	85.846	74.472	4.521
3700	13.874	98.440	86.410	86.271	74.165	4.381
3800	13.876	98.810	86.779	86.682	73.844	4.247
3900	13.878	99.170	87.130	87.082	73.513	4.119
4000	13.879	99.522	87.476	87.469	73.175	3.996
4100	13.881	99.864	87.825	87.840	72.817	3.881
4200	13.882	100.199	88.169	88.199	72.445	3.770
4300	13.884	100.525	88.506	88.543	72.073	3.663
4400	13.885	100.845	88.838	88.875	71.695	3.561
4500	13.886	101.157	89.165	89.201	71.297	3.463
4600	13.887	101.462	89.487	89.520	70.885	3.368
4700	13.888	101.761	89.807	89.831	70.469	3.277
4800	13.889	102.053	89.266	90.131	68.515	3.119
4900	13.890	102.339	89.550	90.419	66.208	2.908
5000	13.891	102.620	89.789	90.695	63.867	2.705
5100	13.892	102.895	90.043	90.965	61.493	2.509
5200	13.892	103.165	90.293	91.231	59.097	2.320
5300	13.893	103.429	90.538	91.494	56.683	2.138
5400	13.894	103.689	90.779	91.752	54.250	1.962
5500	13.894	103.944	91.017	92.006	51.800	1.792
5600	13.895	104.194	91.250	92.254	49.334	1.628
5700	13.895	104.440	91.479	92.494	46.854	1.470
5800	13.896	104.682	91.704	92.728	44.360	1.316
5900	13.896	104.920	91.926	92.957	41.854	1.167
6000	13.897	105.153	92.145	93.180	39.337	1.023

June 30, 1961; Dec. 31, 1965

Point Group C_{2v}
 $S_{298.15}^\circ = 65.402$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_f^\circ = -67.9 \pm 11$ kcal. mole⁻¹
 $\Delta H_f^\circ = -68.4 \pm 11$ kcal. mole⁻¹
 Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

$(\omega, \text{cm.}^{-1})$
 884 (1)
 137 (1)
 818 (1)

Bond Distance: $O-Zr = 1.711 \text{ \AA}$
 Bond Angle: $O-Zr-O = 109^\circ$
 Product of the Moments of Inertia: $I_A I_B I_C = 5.679836 \times 10^{-115} \text{ g.}^3 \text{ cm.}^6$
 $\sigma^- = 2$

Heat of Formation.

The ΔH_f° 298.15 = -68.4 ± 11 kcal. mole⁻¹ was calculated from the ΔH_f° 298.15 = 193.867 ± 11.25 kcal. mole⁻¹ for the reaction $ZrO_2(c) \rightarrow ZrO_2(g)$. The value of ΔH_f° 298.15 was obtained by the third law method using the determined vapor pressures (at the range 2331-2480°K) by W. A. Chapka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. 25, 1207 (1957). They observed the variation of the ZrO_2^+ ion intensity over ZrO_2 and reported equilibrium constants for the reaction $ZrO_2(c) \rightarrow ZrO_2(g)$ in the range 2331-2480°K. The third law drift is 80 ± 25 e.u.

Heat Capacity and Entropy.

The vibrational frequencies $\nu_1 = 884$, $\nu_2 = 1371$, $\nu_3 = 818$ and angle $O-Zr-O = 109^\circ$ were obtained from M. J. Linevsky, Spectroscopic Studies of the Vaporization of Refractory Materials, Technical Report Nr. AFML TR-64-420 Air Force Materials Lab. Research and Technology Division, Wright Patterson Air Force Base, Ohio (1965). The bond distances (r_e) $O-Zr = 1.711 \text{ \AA}$ was obtained from U. Uhler and L. Akerlund, Arkiv Fysik 10, 431 (1955). The three principal moments of inertia are: $I_A = 1.03083 \times 10^{-38}$, $I_B = 3.8828 \times 10^{-39}$, $I_C = 1.41809 \times 10^{-38}$ g. cm.²

O_2Zr

T, °K	C _p	gbbal/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔG°	Log K _p
0							
100	16.320	16.354	16.354	0.000	-186.700	-169.378	124.159
200	16.350	16.455	16.354	0.030	-186.698	-169.271	123.314
300	16.380	16.556	16.354	0.050	-186.698	-169.271	123.314
400	16.410	16.657	16.354	0.070	-186.698	-169.271	123.314
500	16.440	16.758	16.354	0.090	-186.698	-169.271	123.314
600	16.470	16.859	16.354	0.110	-186.698	-169.271	123.314
700	16.500	16.960	16.354	0.130	-186.698	-169.271	123.314
800	16.530	17.061	16.354	0.150	-186.698	-169.271	123.314
900	16.560	17.162	16.354	0.170	-186.698	-169.271	123.314
1000	16.590	17.263	16.354	0.190	-186.698	-169.271	123.314
1100	16.620	17.364	16.354	0.210	-186.698	-169.271	123.314
1200	16.650	17.465	16.354	0.230	-186.698	-169.271	123.314
1300	16.680	17.566	16.354	0.250	-186.698	-169.271	123.314
1400	16.710	17.667	16.354	0.270	-186.698	-169.271	123.314
1500	16.740	17.768	16.354	0.290	-186.698	-169.271	123.314
1600	16.770	17.869	16.354	0.310	-186.698	-169.271	123.314
1700	16.800	17.970	16.354	0.330	-186.698	-169.271	123.314
1800	16.830	18.071	16.354	0.350	-186.698	-169.271	123.314
1900	16.860	18.172	16.354	0.370	-186.698	-169.271	123.314
2000	16.890	18.273	16.354	0.390	-186.698	-169.271	123.314
2100	16.920	18.374	16.354	0.410	-186.698	-169.271	123.314
2200	16.950	18.475	16.354	0.430	-186.698	-169.271	123.314
2300	16.980	18.576	16.354	0.450	-186.698	-169.271	123.314
2400	17.010	18.677	16.354	0.470	-186.698	-169.271	123.314
2500	17.040	18.778	16.354	0.490	-186.698	-169.271	123.314
2600	17.070	18.879	16.354	0.510	-186.698	-169.271	123.314
2700	17.100	18.980	16.354	0.530	-186.698	-169.271	123.314
2800	17.130	19.081	16.354	0.550	-186.698	-169.271	123.314
2900	17.160	19.182	16.354	0.570	-186.698	-169.271	123.314
3000	17.190	19.283	16.354	0.590	-186.698	-169.271	123.314

TUNGSTEN OXIDE (WO_{2.72}) (CRYSTAL) OPW = 227.3684

ΔH_f⁰ = Unknown
ΔH_f⁰_{298.15} = -186.70 ± 0.5 kcal/mol

S_{298.15}⁰ = [16.35] gibbs/mol

Heat of Formation.

The adopted heat of formation, -186.7 ± 0.5 kcal/mol, is derived from recent equilibrium data which are in excellent agreement; the results are summarized below. In addition R. C. Griffiths, *J. Electrochem. Soc.* **105**, 398 (1958), has measured the heat of combustion to WO₃(c) which yields ΔH_f⁰₂₉₈(WO_{2.72}, c) = -185.4 ± 1 kcal/mol when recalculated with ΔH_f⁰₂₉₈(WO₃, c) = -201.46 kcal/mol. This result is less certain because of the incomplete characterization of the final products. The EMF data reported by Ye. I. Gerasimov, I. A. Vasil'eva, T. P. Chusova, V. A. Gaidarikh, and M. A. Timofeeva, *Zh. Fiz. Khim.* **36**, 358 (1962), give the value of -186.89 kcal/mol for the heat of formation at 298° K. R. J. Ackermann and E. G. Rauh, *J. Phys. Chem.* **67**, 2596 (1963), have investigated the tungsten-oxygen system by mass effusion, mass spectroscopy, and X-ray diffraction. In the temperature range from 1300° to 1600° K, they have derived indirectly from their measurements the heat of formation, -182.2 kcal/mol (corresponding to -187.2 kcal/mol at 298° K, using the JANAP functions).

Author	Reaction*	Temp. (°K)	No. of Points	ΔH _f ⁰ ₂₉₈ (kcal/mol) 3rd law 2nd law	Drift (eu)	ΔH _f ⁰ ₂₉₈ (WO _{2.72} , c)** (kcal/mol)
1. Bouquet (1964) et al.	A	830 - 1046	5	4.085 2.951	1.2 ± 0.2	-186.65
2. St. Pierre (1962) et al.	B	1173 - 1423	-	-	-45.739	-186.68
3. Vasil'eva (1960) et al.	A	904 - 1068	4	4.279 2.678	1.6 ± 0.3	-186.83
4. Griffiths (1958)	A	873 - 1173	24	4.314 4.314	-0.01 ± 0.06	-186.87

*Reaction A: 100/72 WO_{2.72}(c) + H₂(g) = 100/72 WO₂(c) + H₂O (g)
B: WO₂ (c) + 0.72 O₂(g) = WO_{2.72}(c)

** Based on the 3rd law value wherever possible.

1. J. Bouquet and G. Frechon, *Compt. rend.* **259**, 3869 (1964)
2. G. R. St. Pierre, M. T. Eklund, M. J. Pool, and R. Speiser, *Trans. AIME* **224**, 259 (1962)
3. I. A. Vasil'eva, Ye. I. Gerasimov and Yu. P. Simanov, *Zh. Fiz. Khim.* **34**, 1611 (1960)
4. R. C. Griffiths, *J. Electrochem. Soc.* **105**, 418 (1958).

Heat Capacity and Entropy.

The monoclinic unit cell of WO_{2.72} corresponds to W₁₀O₆₉, as shown by the X-ray diffraction studies of A. Magneli, G. Anderson, B. Blomberg and L. Kihlberg, *Anal. Chem.* **24**, 1998 (1952). The tabulated heat capacities of WO_{2.72}(c) were estimated from those of WO₂(c) and WO₃(c), because all three have similar monoclinic structures as identified by Magneli et al.

The entropy (S₂₉₈⁰ = 16.35 eu) was calculated from ΔS₂₉₈⁰ = 7.96 ± 0.09 eu for reaction A, using all JANAP values. The value of ΔS₂₉₈⁰ was derived from the second law analysis of Griffiths' data, loc. cit.

Tungsten Oxide (W_{02.90})
(Crystal)

GFW = 230.2483

TUNGSTEN OXIDE (W_{02.90}) (CRYSTAL)

OPW = 230.2483

02.90W

T, K	Cp	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100	17.060	17.536	17.536	.000	-196.000	-177.716	130.269
200	17.100	17.662	17.636	.032	-195.968	-177.603	129.383
300	17.120	17.757	17.723	.035	-195.933	-177.487	128.500
400	17.130	17.823	17.789	.034	-195.900	-177.362	127.617
500	17.140	17.873	17.839	.034	-195.862	-177.237	126.734
600	17.150	17.913	17.879	.034	-195.824	-177.112	125.851
700	17.160	17.948	17.914	.034	-195.786	-176.987	124.968
800	17.170	17.978	17.944	.034	-195.748	-176.862	124.085
900	17.180	17.998	17.964	.034	-195.710	-176.737	123.202
1000	17.190	18.018	17.984	.034	-195.672	-176.612	122.319
1100	17.200	18.038	18.004	.034	-195.634	-176.487	121.436
1200	17.210	18.058	18.024	.034	-195.596	-176.362	120.553
1300	17.220	18.078	18.044	.034	-195.558	-176.237	119.670
1400	17.230	18.098	18.064	.034	-195.520	-176.112	118.787
1500	17.240	18.118	18.084	.034	-195.482	-175.987	117.904
1600	17.250	18.138	18.104	.034	-195.444	-175.862	117.021
1700	17.260	18.158	18.124	.034	-195.406	-175.737	116.138
1800	17.270	18.178	18.144	.034	-195.368	-175.612	115.255
1900	17.280	18.198	18.164	.034	-195.330	-175.487	114.372
2000	17.290	18.218	18.184	.034	-195.292	-175.362	113.489
2100	17.300	18.238	18.204	.034	-195.254	-175.237	112.606
2200	17.310	18.258	18.224	.034	-195.216	-175.112	111.723
2300	17.320	18.278	18.244	.034	-195.178	-174.987	110.840
2400	17.330	18.298	18.264	.034	-195.140	-174.862	109.957
2500	17.340	18.318	18.284	.034	-195.102	-174.737	109.074
2600	17.350	18.338	18.304	.034	-195.064	-174.612	108.191
2700	17.360	18.358	18.324	.034	-195.026	-174.487	107.308
2800	17.370	18.378	18.344	.034	-194.988	-174.362	106.425
2900	17.380	18.398	18.364	.034	-194.950	-174.237	105.542
3000	17.390	18.418	18.384	.034	-194.912	-174.112	104.659

Heat of Formation.
The adopted heat of formation, -196.0 ± 3 kcal/mol, is a weighted average of those derived from equilibrium data, in addition the following results have been reported.
R. C. Griffiths, J. Electrochem. Soc. 105, 398 (1958), has measured the heat of combustion to W₀₃(c), which yields -195.6 kcal/mol when recalculated with ΔH°₂₉₈(W₀₃, c) = -201.46 kcal/mol. This result is less certain because of the incomplete characterization of the final products. R. J. Ackermann and E. O. Raub, J. Phys. Chem. 67, 2596 (1963), have investigated the tungsten-oxygen system by mass effusion, mass spectroscopy, and X-ray diffraction. In the temperature range from 1300° to 1600°K, they have derived indirectly two values of ΔH°(W_{02.90}, c) -190.9 and -188.0 kcal/mol (corresponding to -196.1 and -193.3 kcal/mol, respectively, at 298.15°K, using all JANAF functions).

Author	Reaction*	Temperature (°K)	No. of Points	ΔH° ₂₉₈ (kcal/mol)	Drift (eu)	ΔH° ₂₉₈ (W _{02.90} , c) (kcal/mol)
1. Bouquet (1963) et al.	A	773-898	5	0.270	2.168	-195.4
3. Vasil'eva (1960) et al.	A	897-993	4	0.240	2.178	-195.4
4. Griffiths (1959)	A	873-1073	18	0.284	1.504	-195.4
1. Bouquet (1964) et al.	B	844-954	5	0.754	2.657	-197.9
3. Vasil'eva (1960) et al.	B	915-1021	5	0.834	1.585	-197.9
4. Griffiths (1959)	B	873-1073	18	0.589	3.368	-197.7
1. Bouquet (1964) et al.	C	737-798	5	5.013	6.762	-198.0
2. St. Pierre (1962) et al.	D	1023-1273	-	-	-7.97	-193.5
2. St. Pierre (1962) et al.	E	1173-1322	-	-	-13.67	-200.4

* Reaction A: W₀₃(c) + 0.1 H₂(g) = W_{02.90}(c) + 0.1 H₂O(g)
B: W_{02.90}(c) + 0.18 H₂(g) = W_{02.72}(c) + 0.18 H₂O(g)
C: W_{02.90}(c) + 0.9 H₂(g) = W₀₂(c) + 0.9 H₂O(g)
D: W_{02.90}(c) + 0.05 O₂(g) = W₀₃(c)
E: W_{02.72}(c) + 0.09 O₂(g) = W_{02.90}(c)
** Based on the third law value wherever possible and ΔH°₂₉₈(W_{02.72}, c) = -186.7 kcal/mol.
1. J. Bouquet and G. Perrichon, Compt. rend. 252, 3869 (1964); 252, 694 (1963)
2. G. R. St. Pierre, W. T. Bithers, M. J. Pool and R. Speiser, Trans. AIME 224, 259 (1962)
3. I. A. Vasil'eva, Ya. I. Perasimov and Yu P. Simanov, Zh. Fiz. Khim. 34, 1811 (1960)
4. R. C. Griffiths, J. Electrochem. Soc. 106, 418 (1959)

Heat Capacity and Entropy.

The monoclinic unit cell of W_{02.90} corresponds to W₂₀O₅₉ as shown by the X-ray diffraction studies of A. Magnell, O. Anderson, B. Blomberg and L. Kihlberg, Anal. Chem. 24, 1998 (1952). The tabulated heat capacities and the entropy (S°₂₉₈ = 17.536 eu) were estimated from those of W₀₂(c) and W₀₃(c), because all three have the similar monoclinic structure as identified by Magnell et al.

Sept. 30, 1966

02.90W

QFW = 231.2082

(CRYSTAL)

TUNGSTEN OXIDE (WO_{2.96})

T, °K	C _p ^o	gibbs/mol S ^o - (G ^o - H ²⁹⁸)/T	H ^o - H ²⁹⁸	kcal/mol ΔH ^o	ΔG ^o	Log K _p
0						
100						
200						
298	17.300	17.900	•000	-199.560	-180.946	132.637
300	17.360	18.007	•032	-199.558	-180.831	131.735
400	15.480	23.298	1.876	-199.355	-174.615	95.405
500	12.000	27.619	3.705	-199.009	-168.467	73.637
600	22.050	31.746	6.061	-198.582	-162.397	59.153
700	22.780	35.202	8.304	-198.111	-156.402	48.831
800	23.280	38.278	10.608	-197.621	-150.480	41.109
900	23.750	41.046	12.958	-197.118	-144.616	35.118
1000	24.070	43.562	15.347	-196.607	-138.808	30.336
1100	24.430	45.874	17.772	-196.087	-133.055	26.436
1200	24.740	48.013	20.231	-195.559	-127.347	23.193
1300	25.060	50.006	22.721	-195.023	-121.684	20.457
1400	25.360	51.874	25.242	-194.478	-116.064	18.118
1500	25.620	53.633	27.791	-193.926	-110.482	16.097
1600	25.880	55.294	30.366	-193.368	-104.936	14.334
1700	26.180	56.872	32.969	-192.801	-99.426	12.782
1800	26.480	58.377	35.602	-192.226	-93.951	11.407
1900	26.780	59.817	38.265	-191.640	-88.507	10.181
2000	27.080	61.198	40.958	-191.044	-83.095	9.080
2100	27.380	62.527	43.681	-190.438	-77.712	8.088
2200	27.680	63.807	46.434	-189.824	-72.360	7.188
2300	27.980	65.044	49.217	-189.196	-67.034	6.370
2400	28.280	66.241	52.030	-188.560	-61.733	5.622
2500	28.580	67.402	54.873	-187.914	-56.467	4.936
2600	28.880	68.529	57.766	-187.257	-51.220	4.305
2700	29.180	69.624	60.669	-186.595	-45.999	3.723
2800	29.480	70.691	63.582	-185.936	-40.804	3.185
2900	29.780	71.731	66.505	-185.269	-35.634	2.685
3000	30.080	72.745	69.538	-184.605	-30.480	2.220

ΔH^o_C = Unknown

ΔH^o_{298.15} = -199.56 ± 3 kcal/mol

S^o_{298.15} = [17.90] gibbs/mol

Heat of Formation.

The adopted value, ΔH^o₂₉₈ (WO_{2.96}, c) = -199.56 kcal/mol, was obtained by third law treatment of ΔH^o = 191,600 + 54.0 T (cal/mol) in the temperature range from 1300 - 1550°K, using all JANAF functions. The equation for ΔH^o was reported by R. J. Ackermann and E. G. Rauh, J. Phys. Chem. **67**, 2596 (1963), based on studies by mass spectroscopy and x-ray diffraction. In this study ΔH^o was obtained by comparison of the Gibbs energies of sublimation (to gaseous WO₃, WO₂, W₂O₇, W₂O₉ and W₂O₁₂) over the two systems W-WO₂(c) and WO_{2.96}(c); thus WO_{2.96}(c) was related to WO₂(c) through the gaseous species.

J. E. Battles, Ph. D. Thesis, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," The Ohio State University, (1964), has reported partial pressures of W₂O₉(g) and W₂O₁₂(g) in equilibrium with WO₃ - WO_{2.96}(c). In light of Ackermann and Rauh's observation, the condensed phase was presumed to have the composition of WO_{2.96}(c). The pressure data are in reasonable agreement with the studies of Ackermann and Rauh as summarized below. Values of ΔH^o₂₉₈ for WO_{2.96}(c) derived from the data of Battles are based on the same author's data for W₂O₉(g), and W₂O₁₂(g) in order to relate WO_{2.96} to WO₂ directly.

Investigator	Reaction	Temperature (°K)	ΔH ^o ₂₉₈ (kcal/mol)	3rd law	2nd law	Drift (cal)	ΔH ^o ₂₉₈ (WO _{2.96} , c)* (kcal/mol)
1. Ackermann & Rauh	A	1300-1550	60.82	56.32	3.2 ± 0.6	-199.57	
2. Ackermann & Rauh	B	1300-1550	41.37	38.35	2.094 ± 0.09	-199.58	
3. Battles	B	1274-1418	40.82	43.28	-1.854 ± 0.05	-199.72	
4. Ackermann & Rauh	C	1300-1550	35.81	33.58	1.551 ± 0.09	-199.60	
5. Battles	C	1333-1418	35.37	38.74	-2.461 ± 0.1	-199.95	

Reaction: A: WO_{2.96}(c) = 0.44 W₂O₉(g) + 0.04 W₂O₁₂(g)

B: WO_{2.96}(c) = 0.29333 W₂O₉(g) + 0.04 W₂O₁₂(g)

C: WO_{2.96}(c) = 0.22 W₂O₁₂(g) + 0.04 W₂O₉(g)

* Third law value adopted in calculation.

Heat Capacity and Entropy.

The tabulated heat capacities and the entropy at 298.15°K were estimated from those of WO₂(c) and WO₃(c). Ackermann and Rauh, loc. cit., have found that the composition WO_{2.96} probably represents the azeotropic composition of the WO₃-x solid solution and is the only single phase which evaporates congruently below 1550°K.

Ozone (O₃)

(Ideal Gas) Mol. Wt. = 48.000

T, °K.	C _p ^o	S ^o - (F° - H ₂₉₈ °)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH _f ^o	Log K _p
0	0.000	INFINITE	2.474	34,739	INFINITE	INFINITE
100	6.257	47.259	0.002	34,739	34,739	0.000
200	6.379	47.259	0.002	34,739	34,739	0.000
298	6.379	47.259	0.002	34,739	34,739	0.000
300	6.379	47.259	0.002	34,739	34,739	0.000
400	6.379	47.259	0.002	34,739	34,739	0.000
500	6.379	47.259	0.002	34,739	34,739	0.000
600	6.379	47.259	0.002	34,739	34,739	0.000
700	6.379	47.259	0.002	34,739	34,739	0.000
800	6.379	47.259	0.002	34,739	34,739	0.000
900	6.379	47.259	0.002	34,739	34,739	0.000
1000	6.379	47.259	0.002	34,739	34,739	0.000
1100	6.379	47.259	0.002	34,739	34,739	0.000
1200	6.379	47.259	0.002	34,739	34,739	0.000
1300	6.379	47.259	0.002	34,739	34,739	0.000
1400	6.379	47.259	0.002	34,739	34,739	0.000
1500	6.379	47.259	0.002	34,739	34,739	0.000
1600	6.379	47.259	0.002	34,739	34,739	0.000
1700	6.379	47.259	0.002	34,739	34,739	0.000
1800	6.379	47.259	0.002	34,739	34,739	0.000
1900	6.379	47.259	0.002	34,739	34,739	0.000
2000	6.379	47.259	0.002	34,739	34,739	0.000
2100	6.379	47.259	0.002	34,739	34,739	0.000
2200	6.379	47.259	0.002	34,739	34,739	0.000
2300	6.379	47.259	0.002	34,739	34,739	0.000
2400	6.379	47.259	0.002	34,739	34,739	0.000
2500	6.379	47.259	0.002	34,739	34,739	0.000
2600	6.379	47.259	0.002	34,739	34,739	0.000
2700	6.379	47.259	0.002	34,739	34,739	0.000
2800	6.379	47.259	0.002	34,739	34,739	0.000
2900	6.379	47.259	0.002	34,739	34,739	0.000
3000	6.379	47.259	0.002	34,739	34,739	0.000
3100	6.379	47.259	0.002	34,739	34,739	0.000
3200	6.379	47.259	0.002	34,739	34,739	0.000
3300	6.379	47.259	0.002	34,739	34,739	0.000
3400	6.379	47.259	0.002	34,739	34,739	0.000
3500	6.379	47.259	0.002	34,739	34,739	0.000
3600	6.379	47.259	0.002	34,739	34,739	0.000
3700	6.379	47.259	0.002	34,739	34,739	0.000
3800	6.379	47.259	0.002	34,739	34,739	0.000
3900	6.379	47.259	0.002	34,739	34,739	0.000
4000	6.379	47.259	0.002	34,739	34,739	0.000
4100	6.379	47.259	0.002	34,739	34,739	0.000
4200	6.379	47.259	0.002	34,739	34,739	0.000
4300	6.379	47.259	0.002	34,739	34,739	0.000
4400	6.379	47.259	0.002	34,739	34,739	0.000
4500	6.379	47.259	0.002	34,739	34,739	0.000
4600	6.379	47.259	0.002	34,739	34,739	0.000
4700	6.379	47.259	0.002	34,739	34,739	0.000
4800	6.379	47.259	0.002	34,739	34,739	0.000
4900	6.379	47.259	0.002	34,739	34,739	0.000
5000	6.379	47.259	0.002	34,739	34,739	0.000
5100	6.379	47.259	0.002	34,739	34,739	0.000
5200	6.379	47.259	0.002	34,739	34,739	0.000
5300	6.379	47.259	0.002	34,739	34,739	0.000
5400	6.379	47.259	0.002	34,739	34,739	0.000
5500	6.379	47.259	0.002	34,739	34,739	0.000
5600	6.379	47.259	0.002	34,739	34,739	0.000
5700	6.379	47.259	0.002	34,739	34,739	0.000
5800	6.379	47.259	0.002	34,739	34,739	0.000
5900	6.379	47.259	0.002	34,739	34,739	0.000
6000	6.379	47.259	0.002	34,739	34,739	0.000

OZONE (O₃)

(IDEAL GAS)

MOL. WT. = 48.000

ΔH_f^o = 34.8 ± 0.4 kcal. mole⁻¹ΔH_f^o 298.15 = 34.2 ± 0.4 kcal. mole⁻¹S_{298.15}^o = 57.080 cal. deg.⁻¹ mole⁻¹Point group C_{2v}

Vibrational Levels and Multiplicities

(ω), cm. ⁻¹
1110 (1)
705 (1)
1043 (1)

Ground state multiplicity = 1

No α₁ available

Rotational constants: A₀₀₀ = 3.55361 cm.⁻¹ B₀₀₀ = 0.44530 cm.⁻¹ C₀₀₀ = 0.39477 cm.⁻¹
 X₁₁ = -3.8 cm.⁻¹ X₂₃ = -5.5 cm.⁻¹ X₃₁ = -9.0 cm.⁻¹
 X₁₂ = -2.0 cm.⁻¹

Heat of Formation

P. Glöckner, E. Wassmuth, and L. A. Schryver, Z. phys. Chem. 158, 297 (1932), measured ΔE for the reaction O₃(g) → 3/2 O₂(g) in a calorimeter calibrated by means of the reaction CO(g) + 1/2 O₂(g) → CO₂(g), and found the ratio of the ΔE values for these reactions to be 0.5077 ± 0.0024. The temperature of the experiments is not reported and is assumed to have been 18°C. From the above ratio, ΔH_f^o 298.15 is calculated to be 33.89 ± 0.36 cal. mole⁻¹. A. Kailan and S. Jahn, Z. anorg. Chem. 88, 243 (1910), measured ΔH at an unspecified temperature for the reaction O₃(g) → 3/2 O₂(g) in an electrically calibrated calorimeter. If the temperature of the experiments is assumed to have been 18°C and the modern joule-calorie conversion factor is used, ΔH_f^o 298.15 is found to be 34.3 ± 0.6 kcal. mole⁻¹. Variability in the O₃ content of the feed gas is allowed for in the uncertainty. The value adopted here is 34.2 ± 0.4 kcal. mole⁻¹.

Heat Capacity and Entropy

J. S. Gordon, private communication, April, 1961, has calculated the thermodynamic functions from 298.15° to 6000°K by the method of R. E. Pennington and K. A. Kobe, J. Chem. Phys. 22, 1442 (1954), which takes vibration-rotation interaction and anharmonicity into account. Gordon's data are from L. Pierce, J. Chem. Phys. 24, 139 (1956). The functions below 298.15°K have been calculated for a rigidly rotating harmonic oscillator.

Lead Metasilicate (PbSiO₃)
(Crystal)

Mol. Wt. = 283.2742

O₃PbSi

MOL. WT. = 283.2742

(CRYSTAL)

LEAD METASILICATE (PbSiO₃)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH _f ⁰ kcal. mole ⁻¹	ΔF _f ⁰	Log K _p
0	0.000	INFINITE	-	-272.011	-	INFINITE
100	10.480	8.893	3.587	-272.011	-200.441	39.822
200	17.343	18.523	8.824	-272.011	-193.991	35.329
298	21.520	26.273	10.754	-272.011	-187.589	31.535
300	21.590	26.406	10.887	-272.011	-187.589	31.535
400	26.776	38.776	17.762	-272.011	-181.232	28.290
500	26.740	38.776	17.762	-272.011	-174.714	25.484
600	26.380	43.806	16.426	-272.011	-168.635	23.033
700	29.500	48.269	13.231	-272.011	-162.283	20.862
800	30.250	52.260	11.010	-272.011	-155.761	18.863
900	31.150	55.818	9.342	-272.011	-148.070	17.077
1000	31.190	59.118	8.074	-272.011	-140.112	15.474

Heat of Formation.

The heat of the reaction PbO (red) + SiO₂ → PbSiO₃ (c) was reported by K. K. Kelley, U. S. Bureau of Mines, Report Investigation 5901 (1962). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAP values for PbO (c) (March 31, 1962) and for SiO₂ (c) (Dec. 31, 1962). The above ΔH_f⁰ = -3.75 ± 0.12 kcal. mole⁻¹.

Heat Capacity and Entropy.

In the low temperature region (53.25-298.15°K.) the C_p values are those determined by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). Above 298.15 C_p values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.25°K. using the Debye and Einstein functions D($\frac{h\nu}{kT}$) + E($\frac{h\nu}{kT}$) + 2E($\frac{h\nu}{kT}$) + E($\frac{h\nu}{kT}$) given by E. G. King, J. Am. Chem. Soc. 81, 799-800 (1959). The S_{53.25} = 3.682 cal. deg. mole⁻¹.

Melting Data.

T_m was taken from Oeller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).

June 30, 1965

O₃PbSi

SULFUR TRIOXIDE (SO₃) (IDEAL GAS) MOL. WT. = 80.0622

T, °K.	C _p	S° - (H° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	Log K _p
0	∞	∞	∞	∞	∞
100	18.45	50.733	2.796	93.220	INFINITE
200	18.45	50.733	2.796	93.220	201.504
298	12.108	61.344	1.084	94.165	90.555
300	12.142	61.344	1.084	94.165	88.689
400	13.784	61.344	1.084	94.165	64.580
500	15.082	68.367	2.768	96.052	36.850
600	16.075	71.209	4.328	96.481	29.837
700	17.861	75.031	7.667	106.811	24.801
800	18.823	78.105	9.448	110.009	20.825
900	17.817	80.001	68.753	109.891	15.154
1000	18.419	81.745	69.856	109.763	13.173
1100	18.458	83.357	70.915	109.626	11.457
1200	18.458	84.853	71.930	109.483	10.000
1300	18.458	86.253	72.904	109.341	8.508
1400	18.458	87.563	73.838	109.197	7.371
1500	19.046	88.795	74.735	109.051	6.377
1600	19.219	89.958	75.596	108.905	5.502
1700	19.374	91.051	76.419	108.760	4.748
1800	19.516	92.083	77.203	108.622	4.030
1900	19.645	93.056	77.952	108.488	3.405
2000	19.762	93.974	78.673	108.356	2.861
2100	19.869	94.844	79.366	108.226	2.329
2200	19.967	95.666	80.034	108.099	1.806
2300	20.056	96.444	80.683	107.973	1.434
2400	20.136	97.177	81.312	107.848	1.041
2500	20.208	97.866	81.922	107.724	.678
2600	20.272	98.512	82.509	107.601	.343
2700	20.328	99.117	83.074	107.479	.058
2800	20.376	99.689	83.623	107.358	-.228
2900	20.418	100.225	84.157	107.238	-.528
3000	20.455	100.725	84.673	107.118	-.780
3100	20.488	101.196	85.172	107.000	-.916
3200	20.517	101.638	85.652	106.883	1.233
3300	20.543	102.052	86.117	106.767	1.477
3400	20.566	102.440	86.569	106.652	1.643
3500	20.586	102.803	87.005	106.538	1.829
3600	20.603	103.144	87.426	106.425	2.005
3700	20.618	103.464	87.832	106.313	2.179
3800	20.631	103.764	88.224	106.202	2.349
3900	20.642	104.044	88.601	106.092	2.517
4000	20.651	104.304	88.964	105.983	2.679
4100	20.658	104.544	89.312	105.875	2.821
4200	20.663	104.764	89.645	105.768	2.957
4300	20.667	104.964	90.000	105.662	3.086
4400	20.670	105.144	90.348	105.557	3.209
4500	20.672	105.304	90.689	105.452	3.328
4600	20.673	105.444	91.016	105.348	3.446
4700	20.674	105.564	91.326	105.244	3.564
4800	20.675	105.664	91.621	105.140	3.682
4900	20.676	105.744	91.901	105.036	3.798
5000	20.677	105.804	92.152	104.932	3.916
5100	20.678	105.844	92.384	104.828	4.034
5200	20.679	105.874	92.599	104.724	4.152
5300	20.680	105.894	92.799	104.620	4.270
5400	20.681	105.904	92.984	104.516	4.388
5500	20.682	105.914	93.154	104.412	4.506
5600	20.683	105.924	93.309	104.308	4.624
5700	20.684	105.934	93.449	104.204	4.742
5800	20.685	105.944	93.574	104.100	4.860
5900	20.686	105.954	93.684	104.000	4.978
6000	20.687	105.964	93.779	103.900	5.096

Dec. 31, 1960; Sept. 30, 1965

Point Group D_{3h}
ΔH_f° 0 = -93.22 ± 0.17 kcal. mole⁻¹
ΔH_f° 298.15 = -94.59 ± 0.17 kcal. mole⁻¹
S_{298.15}° = 61.344 cal. mole⁻¹ deg.⁻¹
Ground State Quantum Weight = 1

Vibrational Frequencies and Degeneracies

ω, cm. ⁻¹	Deg.
1068 (1)	1
495 (1)	1
1391 (2)	2
529 (2)	2

Bond Distance: S-O = 1.43 Å
Bond Angle: O-S-O = 120°
Product of the Moments of Inertia: I_AI_BI_C = 1.0813 X 10⁻¹¹⁴ g.³ cm.⁶
Θ = 6

Heat of Formation

The heat of formation was calculated from the reaction SO₂ + 1/2 O₂ → SO₃ for which three sets of equilibrium constants are available. A summary of the second and third law treatment of the data is given below.

Ref.	Temp. Range	Points	2nd law		3rd law		Drift
			ΔH _f ° kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	ΔH _f ° kcal. mole ⁻¹	cel. mole ⁻¹ deg. ⁻¹	
1	933-945°K	5	-27.67 ± 2.7	-23.608	-23.608	3.7 ± 2.9	-0.8 ± 0.1
2	801-1170°K	8	-23.45 ± 0.1	-23.661	-23.614	-1.5 ± 0.6	-0.9 ± 0.2
3	850-1001°K	11	-22.74 ± 0.6	-23.638	-23.638	-0.9 ± 0.2	
4	801-1170°K	23*	-23.40 ± 0.2				

References

1. G. B. Taylor and S. Lehnner, Z. Physik. Chem. **B30**, (1931).
2. M. Bodenstein and W. Pohl, Z. Elektrochem. **11**, 373 (1905).
3. A. P. Kapustinaky and L. M. Shumovskiy, Acta Physicochem. URSS **4**, 791 (1956).
4. Combination of above references, with one point omitted due to failure of a statistical test.

The combined set was adopted though it appears that the three sets are not in excellent agreement, and the combination heavily favors Ref. 2. Although there is a definite trend in all the data it cannot be considered definitive enough for use in the modification of the SO₃ functions.

Heat Capacity and Entropy

The bond length and angles were taken from the electron diffraction data of K. J. Palmer, J. Am. Chem. Soc. **50**, 2360 (1938). The vibrational frequencies were taken from the infrared studies of R. W. Lovejoy, J. H. Colwell, D. F. Eggers and G. D. Halsey, J. Chem. Phys. **36**, 612 (1962), which are in excellent accord with those of R. Bent and W. R. Laidner, Spectrochim. Acta **19**, 931 (1963) using different techniques. These values differ from the assignment used by W. Stockmayer, G. M. Kavanagh and H. S. Mickley, J. Chem. Phys. **12**, 408 (1944) in their analysis of the thermodynamic properties of SO₃.

The individual moments of inertia were I_A=I_B = 8.148 X 10⁻³⁹ g. cm.² and I_C = 16.296 X 10⁻³⁹ g. cm.²

Dititanium Trioxide (Ti_2O_3)
(Crystal)

GFW = 143.7982

T, °K	Cp°	S°	gibbs/mol $-(G^\circ - H^\circ_{298})/T$	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	INFINITE	3.431	-361.505	-361.505	INFINITE
100	6.308	21.477	20.797	2.025	-361.368	-361.368	18.611
200	17.266	18.829	18.829	1.000	-361.490	-361.490	342.034
298	23.352	18.973	18.929	1.043	-363.488	-362.692	251.294
300	28.718	26.027	19.810	2.647	-363.197	-355.752	249.651
400	31.250	33.735	21.959	5.493	-362.284	-349.032	183.460
500	32.630	39.562	24.335	9.136	-361.551	-342.431	143.920
600	33.510	44.661	26.882	12.445	-360.781	-332.452	117.452
700	34.130	48.178	29.392	15.829	-360.014	-323.954	98.656
800	34.590	50.226	31.820	19.265	-359.271	-316.550	84.592
900	34.960	51.829	34.146	22.743	-358.561	-309.399	73.675
1000	35.270	53.037	36.368	26.255	-357.886	-297.429	64.959
1100	35.530	53.917	38.487	29.796	-357.121	-291.127	57.842
1200	35.770	54.508	40.508	33.361	-356.270	-285.011	51.908
1300	35.980	54.829	42.437	36.948	-355.346	-278.670	46.882
1400	36.180	54.981	44.281	40.557	-354.364	-272.796	42.585
1500	36.360	55.069	46.044	44.184	-353.339	-266.624	38.869
1600	36.540	55.091	47.734	47.829	-352.270	-260.112	35.425
1700	36.710	55.056	49.356	51.491	-351.163	-253.266	32.769
1800	36.870	54.961	50.914	55.170	-350.025	-246.025	30.236
1900	37.030	54.814	52.414	58.865	-348.851	-238.192	27.873
2000	37.181	54.617	53.859	62.576	-347.642	-230.689	25.708
2100	37.330	54.380	55.253	66.301	-346.397	-222.556	23.716
2200	37.475	54.103	56.600	70.042	-345.117	-213.763	21.852
2300	37.616	53.786	57.902	73.796	-343.801	-204.256	19.338
2400	37.756	53.436	59.163	77.566	-342.450	-194.094	16.841
2500	37.910	53.059	60.385	81.350	-341.064	-183.282	14.681
2600	38.050	52.651	61.571	85.148	-339.642	-171.812	12.829
2700	38.190	52.214	62.722	88.960	-338.184	-160.004	11.113
2800	38.330	51.751	63.841	92.786	-336.692	-147.986	9.626
2900	38.470	51.261	64.929	96.626	-335.167	-135.766	8.282
3000	38.610	50.746	65.981	100.481	-333.608	-123.351	7.081

Dec. 31, 1960; March 31, 1967; June 30, 1967

DITITANIUM TRIOXIDE (Ti_2O_3)

(CRYSTAL)

GFW = 143.7982

$S^\circ_{298.15} = 18.83$ gibbs/mol	$\Delta H^\circ_{298.15} = -361.50 \pm 2$ kcal/mol	$\Delta H^\circ_{298.15} = -363.49 \pm 2$ kcal/mol
$T_f = 473^\circ\text{K}$	$\Delta H^\circ_f = 0.215$ kcal/mol	
$T_m = 2112^\circ\text{K}$	$\Delta H^\circ_m = [26.4]$ kcal/mol	

Heat of Formation

G. L. Humphrey, J. Am. Chem. Soc. 73, 1887 (1951), determined the enthalpy change $\Delta H^\circ_{298} = -88.11 \pm 0.1$ kcal/mol for the reaction $\text{Ti}_2\text{O}_3(\text{c}) + 1/2\text{O}_2(\text{g}) = 2\text{TiO}_2(\text{rutile})$ using bomb calorimetry. Based on this result and $\Delta H^\circ_{298}(\text{rutile}) = -225.8$ kcal/mol, the adopted value of ΔH°_{298} for $\text{Ti}_2\text{O}_3(\text{c})$ is calculated to be -363.49 ± 2 kcal/mol. A value of $\Delta H^\circ_{298}(\text{Ti}_2\text{O}_3, \text{c}) = -362.8 \pm 0.6$ kcal/mol was reported by S. M. Ariya, M. P. Morozova, and E. Vol'f, Russ. J. Inorg. Chem. (English transl.) 2, 16 (1957), who measured the heat of combustion of various compositions in the Ti_2O_3 system. Ariya et al. used an estimated correction for the formation of TiO_{2-x} , while Humphrey obtained values of 0.1 - 1.3 kcal/mol by grinding the product and returning it with white oil. Most of the assigned uncertainty arises from this problem. [See $\text{TiO}_2(\text{rutile})$ for further details.]

Heat Capacity and Entropy

The low temperature heat capacities, 53 - 296°K, were measured by C. H. Shonate, J. Am. Chem. Soc. 68, 310 (1946). The data indicate a small anomaly in Cp near 240°K. High temperature enthalpies, 375 - 1750°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by drop calorimetry. The heat capacities, 298 - 473°K, derived by Naylor, loc. cit., are joined smoothly with the low temperature Cp at 298°K. Cp values above 473°K are calculated from the heat capacity equation for the β phase derived by Naylor.

S. Nomura, T. Kawakubo, and T. Yanagi, J. Phys. Soc. Japan, 16, 706 (1961), measured the specific heat in the range 70 - 250°K with a conduction-type calorimeter. A broad anomaly in the specific heat was observed from 160 to 200°K. Below this region the Cp values are unreasonably small, but near 200°K the data are closer to the adopted values.

The S°_{298} is calculated from the adopted low temperature Cp based on $S^\circ_{50} = 0.442$ eu. A. D. Pearson, J. Phys. Chem. Solids, 5, 316 (1958), studied the crystal structure of Ti_2O_3 by X-ray method and found that the agreement between calculated and observed density values is good; in other words, there are no significant vacant sites in Ti_2O_3 crystal lattice. This was later confirmed by S. C. Abrahams, Phys. Rev. 130, 2230 (1963). Therefore we do not add vacancy entropy to S°_{298} . Because of the magnetic transition ($\alpha \rightarrow \beta$) at 473°K, we have assumed that no spin-magnetic entropy is likely below 50°K. See Transition Data for more information.

Transition Data

Tf and ΔH°_f were obtained from B. F. Naylor, loc. cit. S. Nomura, T. Kawakubo and T. Yanagi, J. Phys. Soc. Japan 16, 706 (1961), derived the much smaller $\Delta H^\circ_f = 0.036$ kcal/mol from their observations with a conduction-type calorimeter. These authors suggested that the discrepancy may be due to non-stoichiometry on to impurities in the sample studied by Naylor.

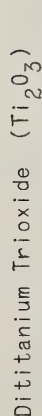
Single-crystal neutron diffraction studied by S. C. Abrahams, Phys. Rev. 130, 2230 (1963), indicate that Ti_2O_3 undergoes an antiferromagnetic ordering of small magnetic moment, associated with the Ti^{3+} cations, below a Neel temperature of about 660°K. The temperature of this transition has been reported variously as about 450 to 600°K based on other properties. A. D. Pearson, J. Phys. Chem. Solids 5, 316 (1958), found no change in the Ti_2O_3 corundum-type structure, but noted a rapid change in the lattice parameters between 430 and 473°K. Observations of corresponding changes in magnetic susceptibility, resistivity and thermoelectric power have been summarized by the same authors and by J. B. Goodenough, Phys. Rev. 117, 1442 (1960). Goodenough attempted to interpret the earlier observations in terms of strong cation-cation interactions.

The magnetic nature of the transition suggests that any spin-magnetic entropy in Ti_2O_3 would be included in ΔH°_f and in the observed Cp values for α and β phases. Magnetic contributions are thus unlikely below 50°K.

Melting Data

See Ti_2O_3 table for details.

03Ti2



GFW = 143.7982

(LIQUID)

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
100							
200							
298	37,500	22,952	22,952	.000	- 342.087	- 322.646	236.506
300	37,500	23,184	22,953	.069	- 342.059	- 322.526	234.960
400	37,500	33,972	24,424	3,819	- 340.612	- 316.235	172.782
500	37,500	42,340	27,201	7,569	- 339.250	- 310.301	135.632
600	37,500	49,177	30,311	11,319	- 337.965	- 304.633	110.943
700	37,500	54,556	32,441	15,499	- 337.752	- 299.425	90.407
800	37,500	58,965	34,441	18,819	- 335.621	- 293.886	80.286
900	37,500	64,382	36,305	22,569	- 334.564	- 288.732	70.114
1000	37,500	68,333	42,014	26,319	- 333.582	- 283.693	62.001
1100	37,500	71,907	44,571	30,069	- 332.669	- 278.787	55.382
1200	37,500	75,172	46,272	33,569	- 332.658	- 274.011	49.200
1300	37,500	78,172	48,272	37,569	- 331.658	- 269.801	43.200
1400	37,500	80,951	51,437	41,319	- 331.662	- 263.992	41.211
1500	37,500	83,538	53,492	45,069	- 330.709	- 259.192	37.764
1600	37,500	85,958	55,446	48,819	- 329.800	- 254.451	34.756
1700	37,500	88,572	57,388	52,569	- 328.733	- 249.717	32.760
1800	37,500	92,402	60,787	60,069	- 327.379	- 245.137	27.669
1900	37,500	94,326	62,416	63,819	- 335.575	- 235.689	25.755
2000	37,500	96,156	63,950	67,569	- 334.893	- 230.710	24.010
2100	37,500	97,569	65,922	71,319	- 334.525	- 225.851	22.566
2200	37,500	99,163	68,322	75,069	- 334.525	- 220.851	20.966
2300	37,500	101,163	69,666	78,819	- 332.858	- 215.946	19.666
2400	37,500	102,694	69,666	82,569	- 332.200	- 211.112	18.455
2500	37,500	104,165	70,965	86,319	- 331.588	- 206.282	17.340
2600	37,500	105,948	72,637	90,069	- 330.269	- 201.454	16.353
2700	37,500	108,260	74,615	97,569	- 329.641	- 194.594	15.464
2800	37,500	108,260	74,615	97,569	- 329.641	- 194.594	15.464
2900	37,500	109,531	75,758	101,319	- 329.021	- 187.191	13.637
3000	37,500	109,531	75,758	101,319	- 329.021	- 187.191	13.637

DITITANIUM TRIOXIDE (Ti₂O₃)

(LIQUID)

S°_{298.15} = [22.952] gibbs/mol

Tm = 2112 ± 10°K

ΔH°_{298.15} = [-342.087] kcal/mol

ΔHm° = [26.4] kcal/mol

Heat of Formation

The heat of formation, ΔH°₂₉₈, for Ti₂O₃(l) is obtained from that of the crystal by adding ΔHm° and the difference between H°₂₁₁₂ - H°₂₉₈ for Ti₂O₃(c) and Ti₂O₃(l).

Heat Capacity and Entropy

The heat capacity of Ti₂O₃(l) is estimated on the basis of 7.5 gibbs/g-atom. The S°₂₉₈ is derived in a manner analogous to that of the heat of formation.

Melting Data

The adopted Tm was determined by P. G. Wahlbeck and P. W. Gilles, J. Am. Ceram. Soc. **49**, 18 (1966). ΔHm° is estimated based on the assumption that at Tm the entropy of melting is 2.5 eu/g-atom. Other Tm values reported are listed as follows:

Tm, °K	Source
2073	T. H. Schofield and A. E. Bacon, J. Inst. Metals 54 , 47 (1956).
2093	G. Brauer and W. Lüttke, J. Inorg. Nucl. Chem. 16 , 67 (1960).
2103	H. Nishimura and H. Kimura, J. Japan Inst. Metals (Sendai) 20 , 524 (1956).
2173	E. Junker, Z. Anorg. Allgem. Chem. 228 , 97 (1936).
2193	R. C. DeVries and R. Roy, Bull. Am. Ceram. Soc. 33 , 370 (1954).



Tungsten Trioxide (WO₃)

GFW = 231.8482

(Crystal)

TUNGSTEN TRIOXIDE (WO₃)

(CRYSTAL)

OPW = 231.8482

T, °K	Cp°	gibbs/mol S° - (G° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	∞000	INFINITE	2.951	-200.110	-200.110	INFINITE
100	7.277	4.508	31.096	-201.014	-195.026	426.229
200	13.909	11.826	19.649	-201.444	-188.832	206.345
298	17.481	18.143	∞000	-201.450	-182.626	133.869
300	17.520	18.252	∞032	-201.458	-182.510	132.958
400	19.528	24.546	1.525	-200.450	-176.501	74.507
500	21.186	28.158	3.942	-200.501	-170.601	74.507
600	22.255	32.122	6.118	-200.469	-163.661	59.686
700	22.978	35.610	8.382	-199.993	-157.706	46.266
800	23.480	38.713	10.706	-199.499	-151.803	41.471
900	24.000	41.544	12.984	-198.984	-145.940	35.540
1000	24.390	44.040	15.403	-198.479	-139.994	30.592
1100	23.653	46.663	18.235	-197.630	-134.188	26.661
1200	24.044	48.738	21.555	-197.212	-128.437	23.392
1300	24.435	50.678	25.004	-196.759	-122.724	20.632
1400	24.827	52.423	28.577	-196.269	-117.047	18.272
1500	25.218	54.230	32.357	-195.762	-111.404	16.234
1600	25.609	55.870	36.775	-195.295	-105.784	14.451
1700	26.001	57.434	41.831	-194.768	-100.215	12.884
1800	26.400	58.931	47.511	-194.174	-94.668	11.494
1900	26.800	60.354	53.811	-193.619	-89.153	10.255
2000	27.200	61.754	60.734	-193.074	-83.668	9.143
2100	27.600	63.091	68.209	-192.469	-78.212	8.140
2200	28.000	64.384	76.231	-191.846	-72.788	7.231
2300	28.400	65.638	84.817	-191.200	-67.392	6.404
2400	28.800	66.856	93.956	-190.535	-62.040	5.646
2500	29.200	68.039	103.654	-189.851	-56.683	4.955
2600	29.600	69.192	113.911	-189.145	-51.368	4.318
2700	30.000	70.316	124.725	-188.424	-46.081	3.730
2800	30.400	71.414	136.093	-187.698	-40.820	3.186
2900	30.800	72.487	147.011	-186.965	-35.586	2.682
3000	31.200	73.539	157.477	-186.221	-30.379	2.213

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

 $\Delta H_f^\circ = -200.11 \pm 0.2$ kcal/mol $\Delta H_f^\circ_{298.15} = -201.46 \pm 0.2$ kcal/mol $\Delta H^\circ = 0.355$ kcal/mol $\Delta H_m^\circ = 17.55$ kcal/mol $\Delta H_f^\circ_{298.15}$ (to monomer) = 131.46 kcal/mol $\Delta H_f^\circ_{298.15}$ (to dimer) = 82.36 kcal/mol $\Delta H_f^\circ_{298.15}$ (to trimer) = 40.26 kcal/mol $\Delta H_f^\circ_{298.15}$ (to tetramer) = 33.91 kcal/mol

Heat of Formation.

The selected heat of formation, $\Delta H_f^\circ_{298}(\text{WO}_3, c) = -201.46 \pm 0.2$ kcal/mol, was determined by A. D. Meh, J. Am. Chem. Soc. **81**, 1582 (1959), using bomb calorimetry. G. Huff, E. Squitieri and P. E. Snyder, J. Am. Chem. Soc. **70**, 3380 (1948), have reviewed the literature heat of formation data and also measured calorimetrically the heat of formation, -201.84 ± 0.1 kcal/mol, which is in good agreement with the value selected. Other combustion values were reported as $\Delta H_f^\circ_{298} = -199 \pm 1$ kcal/mol by R. C. Griffiths, J. Electrochem. Soc. **105**, 398 (1958); and $\Delta H_f^\circ_{298} = -205.3$ kcal/mol by I. A. Vasil'eva, V. I. Gerasimov, and Y. P. Simanov, Zh. Fiz. Khim. **31**, 882 (1957). R. C. Griffiths, J. Electrochem. Soc. **106**, 418 (1959), also derived the heat of formation, -202.8 ± 1.4 kcal/mol from equilibrium data.

Heat Capacity and Entropy.

The low temperature (53-296.7°K) heat capacities and high temperature (399.6 - 1835.8°K) enthalpy changes have been measured by E. G. King, W. W. Kellner, and A. U. Christensen, U.S. Bur. Mines R.I. 5664 (1960); and these data have been used to derive the tabulated heat capacities. Low temperature and high temperature values were joined smoothly at 298.15°K. The entropy was calculated from the heat capacities based on $S^\circ_1 = 1.31$ eu.

King et al. were apparently unaware of the transition near 593°K which was reported by J. A. Perri, E. Banks, and B. Post, J. Appl. Phys. **28**, 1272 (1957), and they did not take sufficient points in that region to fix the precise enthalpy curve. We have adopted only one curve through the region because of the insufficiency of the data and also because the heat effects appear to be small or gradual.

Transition and Melting Data.

The heat of transition, the transition point, the heat of melting and the melting point were derived from the high temperature enthalpy data of King et al., loc. cit.

The melting point, $1746 \pm 1^\circ\text{K}$, has also been quoted by S. J. Schneider, NBS Monograph **68**, "Compilation of the Melting Points of the Metal Oxides," October 10, 1963.

In the high temperature X-ray diffractometric studies, Perri et al., loc. cit., indicate that WO_3 undergoes a phase transition from monoclinic to orthorhombic at approximately 593°K and from orthorhombic to tetragonal at 993°K.

Heat of Sublimation.

The values of ΔH_s° at 298.15°K are calculated as the heat of sublimation of one mole of crystal to one mole of monomer, 1/2 mole of dimer, 1/3 mole of trimer and 1/4 mole of tetramer, respectively.

Lead Orthosilicate (Pb_2SiO_4)
(Crystal) Mol. Wt. = 506.4636



LEAD ORTHOSILICATE (Pb_2SiO_4) (CRYSTAL)

T, °K.	C_p	S°	$-(F^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0	+0.00	+0.00	INFINITE	- 6.198	- 327.311	- 327.311	INFINITE
100	17.636	17.210	69.708	- 5.250	- 326.690	- 320.263	699.901
200	27.239	32.672	47.489	- 2.963	- 325.258	- 311.554	340.434
298	32.740	44.654	44.654	+0.00	- 329.320	- 302.839	221.976
300	32.800	44.857	44.655	0.001	- 329.318	- 302.835	220.488
400	33.300	55.794	44.656	3.552	- 328.670	- 298.182	124.590
500	39.140	63.212	48.610	7.301	- 328.670	- 285.051	100.665
600	41.430	70.561	51.669	11.335	- 328.099	- 276.377	83.491
700	43.050	77.077	54.862	15.564	- 329.756	- 267.428	70.636
800	44.050	82.893	57.982	19.921	- 329.039	- 258.576	59.697
900	44.450	88.000	61.000	24.388	- 328.478	- 249.724	50.697
1000	45.200	92.848	64.000	28.848	- 327.479	- 241.132	46.199
1100	45.600	97.175	66.822	33.389	- 326.640	- 232.540	40.798
1200	45.900	101.155	69.520	37.963	- 325.782	- 224.021	36.240
1300	46.300	104.829	72.097	42.573	- 324.900	- 215.577	31.977
1400	46.500	108.450	74.622	47.140	- 324.000	- 207.190	28.977
1500	47.000	111.522	76.918	51.507	- 323.069	- 198.690	26.039
1600	47.300	114.565	79.177	56.622	- 322.133	- 190.642	23.441
1700	47.570	117.441	81.344	61.365	- 321.288	- 182.343	21.064
1800	47.850	120.167	83.426	66.345	- 320.435	- 173.495	18.604
1900	48.100	122.850	85.426	71.426	- 319.578	- 164.604	16.042
2000	48.400	125.236	87.357	75.758	- 318.758	- 155.060	

$\Delta H_f^\circ 0 = -327.3 \pm 3.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -329.3 \pm 3.5 \text{ kcal. mole}^{-1}$
 $S_{298.15}^\circ = 44.654 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_m = 1016^\circ\text{K.}$

Heat of Formation.

The heat of the reaction $2\text{PbO}(c) + \text{SiO}_2(c) \rightarrow \text{Pb}_2\text{SiO}_4(c)$ was reported by O. Kubaschewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon Press, New York (1958). This value for the heat of reaction of the oxides has been converted to the heat of formation using JANAF values for $\text{PbO}(c)$ (March 31, 1962) and for $\text{SiO}_2(c)$ (Dec. 31, 1962). The above $\Delta H_f^\circ 298.15 = -7.00 \pm 3.5 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

In the low temperature region (53.07 - 298.15°K.) the C_p values are those determined by E. O. King, J. Am. Chem. Soc., 81, 799-800 (1959). Above 298.15°K. values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.07°K. using the Debye and Einstein functions $D(\frac{h\nu}{kT}) + 2E(\frac{h\nu}{kT}) + E(\frac{h\nu}{kT})$ given by E. O. King, J. Am. Chem. Soc., 81, 799-800 (1959). The $S_{53.07}^\circ = 8.248 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

T_m was taken from Geller, Creamer and Bunting, J. Research Natl. Bureau of Standards, 13, 237 (1934).



Trilead Tetroxide (Pb_3O_4)
(Crystal) Mol. Wt. = 685.63

INTERIM TABLE

T, °K.	C_p	S°	$-(F^\circ - H^\circ_{298})/T$	$H^\circ - H^\circ_{298}$	ΔH°_f	ΔF°_f	Log K _p
0	.000	.000	INFINITE	7.144	-173.373	-173.373	INFINITE
100	20.800	19.087	78.517	5.843	-176.867	-165.830	362.405
200	31.100	37.071	53.516	3.780	-178.382	-156.260	174.626
298	35.136	50.334	39.965	.000	-178.311	-147.263	107.943
300	35.150	50.611	50.395	.065	-178.308	-147.092	107.151
400	35.920	60.859	51.783	3.618	-178.133	-137.712	75.239
500	36.697	68.927	54.429	7.249	-178.983	-128.377	56.111
600	37.480	75.627	57.628	10.958	-178.954	-119.046	43.368
700	38.260	81.623	60.459	14.748	-178.233	-109.205	34.094
800	39.040	86.683	63.421	18.610	-178.127	-99.353	27.141
900	39.820	91.326	66.267	22.553	-177.954	-89.515	21.736
1000	40.600	95.562	68.988	26.574	-177.705	-79.699	17.417
1100	41.380	99.468	71.584	30.473	-177.381	-69.916	13.890
1200	42.160	103.002	74.104	34.850	-176.973	-60.161	10.956
1300	42.940	106.508	76.427	39.105	-176.490	-50.446	8.480
1400	43.720	109.718	78.691	43.438	-175.940	-40.773	6.365
1500	44.500	112.761	80.862	47.849	-175.323	-31.135	4.546
1600	45.280	115.658	82.947	52.338	-174.649	-21.505	2.943
1700	46.060	118.427	84.953	56.805	-173.913	-11.996	1.542
1800	46.840	121.082	86.887	61.550	-173.128	-2.498	.303
1900	47.620	123.635	88.754	66.273	-172.289	6.957	.000
2000	48.400	126.097	90.560	71.074	-171.397	16.368	1.769

March 31, 1962

TRILEAD TETROXIDE (Pb_3O_4) (Crystal)

Mol. Wt. = 685.63

ΔH°_f 298.15 = -175.31 \pm 0.49 kcal. mole⁻¹

S° 298.15 = 50.4 \pm 1.6 cal. deg.⁻¹ mole⁻¹

Heat of Formation. Calculated from ΔH°_f 298.15 = -147.27 kcal. mole⁻¹ for the reaction: $3\text{Pb}(c) + 2\text{O}_2(g) = \text{Pb}_3\text{O}_4(c)$ given by R. W. Millar, J. Am. Chem. Soc., 51, 207 (1929).

Heat Capacity and Entropy. C_p (71.5° to 292.6°K.) reported by R. W. Millar, loc. cit. Above 298.15°K., heat capacity values were estimated by comparison with C_p values for the other lead oxides. The two heat capacity curves were joined smoothly at 298.15°K. by graphical extrapolation.

0 Pb_3

0 Pb_3



MOL. WT. = 183.3036

ZIRCONIUM ORTHOSILICATE ($ZrSiO_4$) (CRYSTAL)

$\Delta H_f^\circ = -481.1 \pm 0.7 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = -483.7 \pm 0.7 \text{ kcal. mole}^{-1}$
 $T_d = 1811^\circ K.$

ZIRCONIUM ORTHOSILICATE ($ZrSiO_4$)

$S_{298.15}^\circ = 20.083 \pm 0.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $T_d = 1811^\circ K.$

Heat of Formation.
 The $\Delta H_f^\circ 298.15$ was calculated from the $\Delta H_f^\circ 298.15$ of its constituent oxides $ZrO_2(c) + SiO_2(c) = ZrSiO_4(c)$ and from the $\Delta H_f^\circ 298.15$ of $ZrO_2(c)$ (June 30, 1961) and $SiO_2(c)$ (Dec. 31, 1962) in JANAP tables. The $\Delta H_f^\circ 298.15 = -4.736 \text{ kcal. mole}^{-1}$ was based on the free energy of formation of its constituent oxides at the decomposition temperature $1811^\circ K.$

Heat Capacity and Entropy.
 At low temperatures C_p were used from K. K. Kelley, J. Am. Chem. Soc. 63, 2750 (1941). From $298-940^\circ K.$ C_p was calculated by using the J. P. Coughlin and E. O. King equation $C_p = 31.48 + 3.92 \times 10^{-5} T - 8.08 \times 10^{-9} T^2$, J. Am. Chem. Soc., 72, 2262 (1950), which joined smoothly with the low temperature data. Above $940^\circ K.$ the data was estimated by extending the curve smoothly. The entropy was calculated at $52.7^\circ K.$ using the Debye and Einstein functions $D(\frac{h\nu}{kT}) + 28(\frac{h\nu}{kT}) + 28(\frac{h\nu}{kT}) + E(\frac{12\pi^2}{h\nu})$ given by K. K. Kelley, J. Am. Chem. Soc., 63, 2750 (1941). $S_{52.7}^\circ = 0.65404 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Temperature of Decomposition.
 T_d is the temperature at which $\Delta F_T^\circ = 0$ for the reaction $ZrSiO_4(c) \rightarrow ZrO_2(c) + SiO_2(c)$. $T_d = 1811^\circ K.$ was taken from C. E. Curtis and H. G. Sowaan, J. Am. Soc., 36, 190 (1953).

Zirconium Orthosilicate ($ZrSiO_4$) (Crystal)
 Mol. Wt. = 183.3036

T, °K.	C_p	S°	$-(F^\circ - H_{300}^\circ)/T$	$H^\circ - H_{300}^\circ$	ΔH_f°	ΔF_T°	Log K _p
0	0.000	INFINITE	INFINITE	3.562	-481.062	-481.062	INFINITE
100	7.513	11.689	22.098	2.034	-483.400	-485.337	106.415
200	17.513	11.689	22.098	2.034	-483.400	-485.337	508.473
298	23.580	20.083	20.083	0.000	-483.736	-456.386	334.674
300	23.600	20.229	20.083	0.044	-483.736	-456.216	332.937
400	27.600	21.716	21.060	2.607	-483.740	-447.036	244.236
500	30.100	23.090	23.019	5.469	-483.741	-437.679	191.587
600	31.950	25.057	25.330	8.596	-483.221	-428.775	156.174
700	33.180	27.479	27.742	11.895	-482.833	-419.731	131.040
800	34.100	29.173	30.145	15.222	-482.402	-410.748	112.206
900	34.720	30.226	32.488	18.664	-481.967	-401.815	97.509
1000	35.260	30.910	34.749	22.461	-481.485	-392.955	85.672
1100	35.550	30.283	36.919	25.700	-481.024	-384.105	76.311
1200	35.780	30.387	38.997	29.267	-481.529	-375.266	68.342
1300	35.890	30.255	40.985	32.951	-481.075	-366.429	61.599
1400	35.900	30.000	42.866	36.443	-480.580	-357.626	55.856
1500	36.000	31.398	44.703	40.041	-480.220	-348.856	50.926
1600	36.000	33.723	46.447	43.641	-479.820	-340.109	46.455
1700	36.000	35.905	48.116	47.241	-491.563	-331.280	42.587
1800	36.000	37.963	49.718	50.841	-491.143	-322.462	39.078
1900	36.000	39.909	51.256	54.441	-490.762	-312.872	35.941
2000	36.000	41.750	52.733	58.041	-490.389	-303.101	33.120
2100	36.000	43.512	54.159	61.641	-490.052	-293.742	30.569
2200	36.000	45.187	55.532	65.241	-490.629	-284.238	28.235
2300	36.000	46.787	56.856	68.841	-490.324	-274.683	26.100
2400	36.000	48.320	58.136	72.441	-490.051	-265.139	24.143
2500	36.000	49.789	59.373	76.041	-489.750	-255.697	22.344
2600	36.000	51.201	60.570	79.641	-489.477	-246.087	20.684
2700	36.000	52.560	61.730	83.241	-489.216	-236.578	19.149
2800	36.000	53.869	62.854	86.841	-489.065	-227.077	17.723
2900	36.000	55.132	63.946	90.441	-489.224	-217.581	16.397
3000	36.000	56.353	65.006	94.041	-489.453	-208.095	15.159



T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	.000	.000	INFINITE	- 5.423	- 584.430	- 584.430	INFINITE
100	11.022	5.065	56.695	- 5.165	- 586.409	- 575.974	1299.769
200	27.355	18.095	34.033	- 3.184	- 587.545	- 565.014	517.418
298	36.990	30.935	30.935	.000	- 587.750	- 553.995	406.016
300	37.150	31.144	30.936	.069	- 587.747	- 553.685	403.359
400	43.700	42.651	32.484	4.147	- 587.300	- 542.383	296.344
500	46.400	42.939	35.594	8.873	- 586.540	- 531.240	232.205
600	44.000	41.546	39.250	13.396	- 586.702	- 520.359	189.504
800	40.500	37.683	44.640	23.234	- 583.940	- 509.120	159.048
900	51.000	41.644	50.204	28.294	- 583.992	- 498.706	136.240
1000	51.600	87.048	53.622	33.426	- 583.173	- 488.093	118.525
					- 582.403	- 477.570	104.373
1100	52.200	91.995	56.899	38.617	- 581.674	- 467.119	92.808
1200	52.700	96.954	60.807	43.158	- 581.007	- 457.132	83.102
1300	53.100	101.797	62.993	47.156	- 582.796	- 446.666	74.991
1400	53.600	104.754	65.627	54.498	- 581.603	- 435.588	67.998
1500	54.000	108.466	68.547	59.878	- 580.835	- 425.177	61.968

Dec. 31, 1960; Mar. 31, 1967

TRITITANIUM PENTOXIDE, ALPHA (α -Ti₃O₅)

(CRYSTAL)

QPM = 223.697

$\Delta H_f^\circ = -584.63 \pm 0.7$ kcal/mol
 $\Delta H_f^\circ_{298.15} = -587.75 \pm 3.0$ kcal/mol
 $\Delta H_f^\circ = [2.81]$ kcal/mol

$S^\circ_{298.15} = 30.935$ gibbs/mol
 $T_f = 450^\circ\text{K}$

Heat of Formation

The enthalpy change, $\Delta H^\circ_{298} = -49.65 \pm 0.05$ kcal/mol, for the reaction $\text{Ti}_3\text{O}_5(\text{c}) + 1/2 \text{O}_2(\text{g}) = 3 \text{TiO}_2(\text{rutile})$ has been measured by G. L. Humphrey, J. Am. Chem. Soc. 73, 1587 (1951), using combustion bomb calorimetry. Based on the reported ΔH°_{298} and $\Delta H^\circ_{298}(\text{rutile}) = -225.8$ kcal/mol, the value of ΔH°_{298} for $\text{Ti}_3\text{O}_5(\text{a})$ is derived as -587.75 ± 0.7 kcal/mol. A value of -587.0 ± 1.0 kcal/mol was obtained by S. M. Araya, M. F. Morozova, and E. Vol'f, Russ. J. Inorg. Chem. (English transl.) 2, 16 (1957), from a similar calorimetric study on Ti-O compounds of various compositions. The latter authors observed that their combustion product had a composition of about $\text{Ti}_{1.99}\text{O}_5$ so they applied an approximate correction to their data. Presumably, the rutile in Humphrey's combustion was also deficient in oxygen, but we have not attempted to make a correction (see TiO_2 (rutile) table for further details).

Heat Capacity and Entropy

Low temperature heat capacities, 53.1 - 296.6°K, were measured by C. H. Shomate, J. Am. Chem. Soc. 68, 310 (1946). High temperature enthalpies, 350.5 - 1340°K, were determined by B. F. Naylor, J. Am. Chem. Soc. 68, 1077 (1946), by use of drop calorimetry. The heat capacities, 298 - 450°K, derived by Naylor are too high to join smoothly at 298°K with the low temperature data, hence they are not used. The Cp values above 296.6°K are obtained by graphical extrapolation of the adopted low temperature Cp.

The samples used by both Shomate and Naylor were prepared by reduction of titanium dioxide with carbon at 1350°C. Analysis of the product gave 99.1% Ti_3O_5 , 0.2% TiO and 0.7% SiO_2 . X-ray lines from the sample were weak and fuzzy but no data were given. Thus comparison with subsequent studies is not possible. According to Naylor, the enthalpy measurements showed a transition at about 450°K. When Ti_3O_5 was heated above this temperature, it did not return to the original state on cooling. Enthalpies were then systematically higher by up to 10 percent. The change in the enthalpy curve seemed to depend upon both the temperature and time of heating above Tt. Regrinding was the only method found for returning the sample to its original state. Possible explanations are presented in the Transition Data.

S°_{298} is calculated from $S^\circ_{50} = 0.88$ eu using the low temperature Cp reported by Shomate, loc. cit. It is pertinent to ask if there should be entropy contributions due to vacancies in the crystal lattice or to spin-magnetic effects below 50°K. S. Asbrink and A. Magnelli, Acta Cryst. 12, 575 (1959), showed that the X-ray crystallographic density is greater than the experimental density by less than 1%, thus the entropy due to the presence of vacancies is considered to be negligible. We also assume that any spin-magnetic entropy is related to the $\alpha \rightarrow \beta$ transition, by analogy with the $\alpha \rightarrow \beta$ transition of Ti_2O_3 . Consistent with this assumption is the observation that the entropy of $\beta\text{-Ti}_3\text{O}_5$ is already larger than the sum of entropies for $\beta\text{-Ti}_2\text{O}_3$ and TiO_2 .

Transition Data

See $\text{Ti}_3\text{O}_5(\beta)$ table.

Trititanium Pentoxide, Beta (β -Ti₃O₅)
(Crystal)

GFW = 223.697

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0							
100							
200							
298	44.165	35.913	35.913	.000	-585.354	-552.983	405.347
300							
300	44.160	36.186	35.914	.082	-585.338	-552.783	402.702
400	45.726	37.555	37.555	4.082	-585.318	-552.684	394.705
500	47.760	39.130	40.073	5.079	-585.318	-551.533	382.333
600	46.493	37.550	44.720	13.698	-583.004	-521.164	189.634
700	47.397	37.792	48.511	19.397	-582.308	-510.912	159.514
800	48.201	38.194	52.202	23.177	-581.653	-490.760	119.651
900	48.909	38.596	55.912	26.974	-581.044	-470.611	89.787
1000	49.509	39.002	59.624	32.978	-580.454	-450.465	60.051
1100	50.614	39.897	62.343	37.999	-579.898	-430.322	30.324
1200	51.418	40.726	65.008	43.101	-579.372	-410.184	1.006
1300	52.222	41.573	67.633	48.283	-578.875	-390.054	
1400	53.030	42.430	70.224	53.545	-578.405	-370.000	
1500	53.830	43.299	72.790	58.888	-577.959	-350.000	
1600	54.634	44.178	75.334	64.311	-577.538	-330.000	
1700	55.439	45.066	77.857	69.815	-577.138	-310.000	
1800	56.243	45.964	80.360	75.398	-576.755	-290.000	
1900	57.047	46.872	82.844	81.060	-576.388	-270.000	
2000	57.851	47.789	85.309	86.808	-576.044	-250.000	
2100	58.655	48.717	87.766	92.634	-575.722	-230.000	
2200	59.459	49.654	90.214	98.539	-575.422	-210.000	
2300	60.264	50.600	92.654	104.516	-575.142	-190.000	
2400	61.068	51.554	95.089	110.565	-574.882	-170.000	
2500	61.872	52.516	97.514	116.739	-574.642	-150.000	

TRITITANIUM PENTOXIDE, BETA (β -Ti₃O₅) (CRYSTAL)

OPW = 223.697

ΔH°_{298.15} = [-585.354] kcal/mol

ΔH° = [2.81] kcal/mol

ΔH° = [33] kcal/mol

T_g = 450°K

T_m = 2047 ± 10°K

S°_{298.15} = [35.913] gibbs/mol

Heat of Formation

The value of ΔH°₂₉₈(β) is obtained from ΔH°₂₉₈(α) by adding ΔH° and the difference between H°₄₅₀ - H°₂₉₈ for Ti₃O₅(α) and Ti₃O₅(β).

Heat Capacity and Entropy

The heat capacities are derived from the enthalpy data, 452 - 1340°K, measured by B. P. Naylor, J. Am. Chem. Soc. 69, 1077 (1946). The Cp values beyond the experimental range are obtained by linear extrapolation.

The S°₂₉₈ is calculated in a manner analogous to that of the heat of formation. For a discussion pertaining to the entropy uncertainty, see the Transition Data.

Transition Data

Tt and ΔH° are based on the β-phase enthalpy data of Naylor, loc. cit., and on the selected enthalpies of the α-phase. ΔH° is thus subject to an unknown error since the β-phase enthalpies correspond to a somewhat different state than do the α-phase values (see α-Ti₃O₅). The enthalpy data also show unusual scatter in the range 452-530°K. Because of these uncertainties, the more recent X-ray studies are summarized below.

S. Abrink and A. Magnelli, *Acta Cryst.* 16, 575 (1959), found that monoclinic α-Ti₃O₅ transforms to a β form of the anosovite type (slightly deformed pseudo-brookite) at about 393°K, i. e., over 50° lower than Naylor's value. P. O. Wahlbeck and P. W. Gilles, *J. Am. Ceram. Soc.* 49, 180 (1966), confirmed that the transition occurs between 373 and 473°K but did not measure the temperature accurately. In both studies only the α form was observed on cooling the samples to room temperature. Abrink and Magnelli noted the following in X-ray studies at elevated temperatures. In a wide region around 393°K, the powder reflections of the unstable phase disappeared, while the general characteristics of the stable one formed within considerably less than one hour. Complete development of some reflections of the stable phase took several hours, while some lines appeared with anomalous intensities at temperatures approaching the transformation point, thus "foreshadowing" the change of structure. Small contents of Fe or Mg stabilized the β form at room temperature.

These observations suggest that the transformation may be considered as a "perit" which occurs over a range of temperatures. The anomalous enthalpy data observed by Naylor may arise from slow completion of the transition and from stabilization of part of the sample in the β form due to impurities. The latter suggestion is consistent with Naylor's observation that regrounding returned the sample to its normal α form. Correction of the enthalpy data based on these assumptions does not appear practical. Pending new data for a well-characterized sample, we must rely on the results of Naylor.

Melting Data.

P. O. Wahlbeck and P. W. Gilles, *J. Am. Ceram. Soc.* 49, 180 (1966), found that Ti₃O₅ melts incongruently at 2047 ± 10°K which is adopted. ΔH° is estimated assuming that at T_m the entropy of melting is 2 eu/g-atom. Melting points of 2173 and 1983°K were reported by R. DeVries and R. Roy, *Bull. Am. Ceram. Soc.* 33, 370 (1954), and O. Bräuer and W. Litke, *J. Inorg. Nucl. Chem.* 16, 67 (1960), respectively.

Trititanium Pentoxide (Ti₃O₅)
(Liquid) GFW = 223.697

T, °K	C _p ^a	S ^b	-(C _p ^a -H ₂₉₈)/T	H ^c -H ₂₉₈	ΔH ^c	ΔG ^c	Log K _p
0							
100							
200							
298	56.000	36.679	36.679	.000	- 560.754	- 329.204	387.920
300	56.000	36.680	36.680	.104	- 560.716	- 329.212	385.385
400	56.000	35.135	40.878	5.704	- 558.747	- 518.744	293.428
500	56.000	27.631	55.024	11.304	- 556.913	- 508.959	222.466
600	56.000	22.841	69.669	16.904	- 555.198	- 499.532	181.954
700	56.000	19.874	86.926	22.504	- 553.124	- 487.853	148.954
800	56.000	17.421	106.821	28.104	- 550.769	- 472.702	114.768
900	56.000	15.287	130.587	33.704	- 548.129	- 464.095	101.428
1000	56.000	13.447	157.144	39.304	- 545.193	- 455.606	90.520
1100	56.000	11.795	179.953	44.904	- 542.054	- 447.187	81.506
1200	56.000	10.407	199.961	50.504	- 538.730	- 438.139	73.730
1300	56.000	9.254	217.216	56.104	- 535.156	- 428.413	67.187
1400	56.000	8.290	231.841	61.704	- 531.354	- 418.113	61.484
1500	56.000	7.476	244.284	67.304	- 527.331	- 407.231	56.463
1600	56.000	6.788	254.703	72.904	- 523.086	- 395.774	51.505
1700	56.000	6.203	263.438	78.504	- 518.613	- 383.814	46.487
1800	56.000	5.711	270.000	84.104	- 513.313	- 371.360	41.428
1900	56.000	5.301	275.612	89.704	- 507.295	- 358.473	36.203
2000	56.000	4.954	280.391	95.304	- 500.536	- 345.156	30.865
2100	56.000	4.666	284.438	100.904	- 493.034	- 331.484	25.428
2200	56.000	4.431	287.760	106.504	- 484.754	- 317.484	19.895
2300	56.000	4.241	290.431	112.104	- 475.686	- 303.189	14.268
2400	56.000	4.091	292.596	117.704	- 465.829	- 288.614	8.542
2500	56.000	3.976	294.304	123.304	- 455.186	- 273.777	2.724
2600	56.000	3.891	295.612	128.904	- 443.754	- 258.614	- 3.203
2700	56.000	3.831	296.562	134.504	- 431.536	- 243.187	- 7.428
2800	56.000	3.791	297.191	140.104	- 418.531	- 227.484	- 10.855
2900	56.000	3.766	297.535	145.704	- 404.829	- 211.428	- 13.484
3000	56.000	3.751	297.691	151.304	- 390.429	- 195.024	- 15.203
3100	56.000	3.746	297.704	156.904	- 375.331	- 178.268	- 16.024
3200	56.000	3.751	297.596	162.504	- 359.536	- 161.187	- 15.866
3300	56.000	3.766	297.304	168.104	- 343.131	- 143.777	- 14.614
3400	56.000	3.791	296.812	173.704	- 326.131	- 126.024	- 13.105
3500	56.000	3.831	296.062	179.304	- 308.536	- 107.928	- 11.268
3600	56.000	3.891	295.000	184.904	- 290.331	- 89.428	- 9.669
3700	56.000	3.976	293.612	190.504	- 270.536	- 70.536	
3800	56.000	4.091	291.904	196.104	- 249.131	- 51.268	
3900	56.000	4.241	289.904	201.704	- 226.131	- 31.614	
4000	56.000	4.431	287.596	207.304	- 201.536	- 11.505	

Mar. 31, 1967

TRITITANIUM PENTOXIDE (Ti₃O₅) (LIQUID)S_{298.15}^o = [39.679] gibbs/molT_m = 2047 ± 10°KΔH_{298.15}^o = [-560.754] kcal/molΔH_m^o = [33] kcal/mol

OPW = 223.697

Heat of Formation

The ΔH_{298.15(1)}^o is obtained from ΔH_{298.15(β)}^o by adding ΔH_m^o and the difference between H₂O₄₇^o - H₂^o₂₉₈ for Ti₃O₅(β) and Ti₃O₅(1).

Heat Capacity and Entropy

The heat capacity is estimated on the basis of 7.0 gibbs/g-atom. S₂₉₈^o is obtained in a manner analogous to that of the heat of formation.

Melting Data

See Ti₃O₅(β) table for details.

Diphosphorus Trioxide, Dimeric

(Ideal Gas) Mol. Wt. = 219.90 INTERIM TABLE

T, °K.	C _p ^o	S ^o	cal. mole ⁻¹ deg ⁻¹	-(F ^o -H ₂₉₈)/T	H ^o -H ₂₉₈	ΔH _f ^o	ΔF _f ^o	Log K _p
0	∞	∞	∞	∞	∞	∞	∞	∞
100	11.239	59.176	59.176	59.176	59.176	59.176	59.176	INFINITE
200	24.210	70.884	85.432	2.610	-511.044	-502.908	-495.031	1099.051
298	34.402	82.584	82.584	∞	-512.540	-486.831	-478.940	356.840
300	34.556	82.798	82.585	3.064	-512.551	-486.671	-478.940	354.323
400	43.319	103.386	80.954	8.216	-513.111	-469.185	-460.071	265.071
500	47.996	111.902	90.417	12.891	-513.135	-460.365	-451.691	167.691
600	49.789	116.444	94.036	17.786	-513.156	-451.098	-442.992	140.992
700	51.036	120.170	97.040	22.831	-513.177	-442.007	-434.711	128.711
800	51.936	123.216	99.419	27.982	-513.196	-433.056	-426.368	118.118
900	52.594	125.752	101.453	33.268	-513.212	-424.242	-418.023	108.943
1000	53.096	127.889	103.206	38.649	-513.227	-415.537	-409.766	100.556
1100	53.486	129.579	104.794	44.127	-513.240	-407.021	-401.592	92.929
1200	53.793	130.951	106.166	49.699	-513.251	-398.683	-393.496	85.956
1300	54.041	132.061	107.361	55.361	-513.260	-390.506	-385.561	79.561
1400	54.241	132.941	108.419	61.099	-513.267	-382.571	-377.766	73.699
1500	54.406	133.619	109.354	66.899	-513.272	-374.866	-370.191	68.354
1600	54.544	134.119	110.199	72.649	-513.276	-367.371	-362.826	63.519
1700	54.661	134.479	110.889	78.359	-513.279	-360.076	-355.631	59.189
1800	54.761	134.719	111.459	84.019	-513.281	-352.956	-348.596	55.319
1900	54.846	134.869	111.919	89.629	-513.282	-346.086	-341.726	51.899
2000	54.918	134.941	112.289	95.189	-513.283	-339.446	-335.191	48.899
2100	54.981	134.981	112.589	100.709	-513.284	-333.026	-328.871	46.299
2200	55.031	135.001	112.819	106.189	-513.285	-326.816	-322.761	44.009
2300	55.071	135.011	112.979	111.629	-513.286	-320.806	-316.851	42.009
2400	55.109	135.019	113.059	117.029	-513.287	-314.986	-311.131	40.259
2500	55.146	135.024	113.149	122.389	-513.288	-309.346	-305.601	38.729
2600	55.181	135.028	113.249	127.709	-513.289	-303.876	-301.231	37.309
2700	55.214	135.031	113.359	133.009	-513.290	-298.566	-296.991	35.989
2800	55.246	135.034	113.479	138.279	-513.291	-293.406	-291.931	34.759
2900	55.277	135.037	113.609	143.519	-513.292	-288.396	-287.001	33.609
3000	55.308	135.039	113.749	148.729	-513.293	-283.526	-282.231	32.529
3100	55.338	135.041	113.899	153.909	-513.294	-278.796	-277.581	31.509
3200	55.367	135.043	114.059	159.059	-513.295	-274.206	-273.171	30.549
3300	55.395	135.045	114.229	164.179	-513.296	-269.746	-268.831	29.639
3400	55.422	135.047	114.409	169.269	-513.297	-265.406	-264.591	28.769
3500	55.449	135.049	114.589	174.329	-513.298	-261.176	-260.461	27.939
3600	55.475	135.051	114.779	179.359	-513.299	-257.056	-256.441	27.149
3700	55.500	135.053	114.969	184.359	-513.300	-253.046	-252.531	26.399
3800	55.524	135.055	115.169	189.329	-513.301	-249.146	-248.721	25.679
3900	55.548	135.057	115.379	194.269	-513.302	-245.346	-244.921	24.979
4000	55.571	135.059	115.599	199.179	-513.303	-241.646	-241.321	24.299
4100	55.594	135.061	115.829	204.059	-513.304	-238.046	-237.821	23.639
4200	55.617	135.063	116.069	208.909	-513.305	-234.546	-234.421	23.009
4300	55.639	135.065	116.319	213.729	-513.306	-231.146	-231.121	22.409
4400	55.661	135.067	116.579	218.519	-513.307	-227.846	-227.921	21.829
4500	55.683	135.069	116.839	223.279	-513.308	-224.646	-224.821	21.279
4600	55.705	135.071	117.109	228.009	-513.309	-221.546	-221.821	20.749
4700	55.727	135.073	117.379	232.709	-513.310	-218.546	-218.921	20.239
4800	55.749	135.075	117.659	237.379	-513.311	-215.646	-216.121	19.749
4900	55.771	135.077	117.939	242.019	-513.312	-212.846	-213.421	19.279
5000	55.793	135.079	118.219	246.629	-513.313	-210.146	-210.821	18.829
5100	55.815	135.081	118.509	251.209	-513.314	-207.546	-208.321	18.399
5200	55.837	135.083	118.799	255.759	-513.315	-205.046	-205.901	17.979
5300	55.859	135.085	119.089	260.279	-513.316	-202.646	-203.591	17.579
5400	55.881	135.087	119.379	264.769	-513.317	-200.346	-201.381	17.189
5500	55.903	135.089	119.669	269.229	-513.318	-198.146	-199.481	16.809
5600	55.925	135.091	119.959	273.659	-513.319	-196.046	-197.581	16.439
5700	55.947	135.093	120.249	278.059	-513.320	-194.046	-195.781	16.079
5800	55.969	135.095	120.539	282.429	-513.321	-192.146	-194.081	15.729
5900	55.991	135.097	120.829	286.769	-513.322	-190.346	-192.481	15.389
6000	56.013	135.099	121.119	291.079	-513.323	-188.646	-190.981	15.049

Dec. 31, 1960; Sept. 30, 1961; Dec. 31, 1962

DIPHOSPHORUS TRIOXIDE, DIMERIC (P₂O₅) (Ideal gas)

Mol. Wt. = 219.90

ΔH_f^o 298.15 = -512.5 ± 8 kcal. mole⁻¹

S_{298.15}^o = 82.6 cal. deg⁻¹ mole⁻¹

Point group = T_d

Vibrational Frequencies and Degeneracies

ω cm ⁻¹	ω cm ⁻¹
613 (1)	465 (2)
613 (1)	643 (3)
302 (3)	919 (3)
370 (3)	1029 (2)
407 (3)	636 (3)

Bond Lengths and Angles: P-O distance = 1.65 ± 0.02 Å

P-O-P angle = 127.5 ± 1.0° O-P-O angle = 99° ± 1° O'' = 12

Product of Moments of Inertia: I_AI_BI_C = 4.832 X 10⁻¹¹² g.³ cm.⁶

Heat of Formation. ΔH_f^o 298.15 for liquid P₂O₅ was measured by W. E. Koerner and F. Daniels, J. Chem. Phys. 20, 113 (1952). The measurement was made by burning samples of red phosphorus in nitric oxide in a flow calorimeter. Calculation of the heat of formation of the gas was made using ΔH_v^o 298.15 = 11.46 kcal. mole⁻¹ as reported by T. D. Farr, Tenn. Valley Authority, Chem. Engr. Report No. 8 (1950).

Heat Capacity and Entropy. The vibrational levels are from the Raman data of H. Gerding, H. van Bredede and H. C. J. de Decker, Rec. Trav. Chim. 61, 549 (1942), and infra-red spectra data of T. A. Sidorov and N. N. Sobolev, Optics and Spect. 2, 710 (1957). Bond lengths and angles are from electron diffraction data by G. C. Hampson and A. J. Stosick, J. Am. Chem. Soc. 80, 1814 (1958).

T, K	Cp°	S°	-(G°-H°)/T	H°-H° ₂₉₈	ΔH°	Log Kp
0	-0.00	-0.00	INFINITE	-7.443	-276.750	INFINITE
100	19.449	67.918	127.934	-6.002	-271.907	596.231
200	31.427	85.631	102.516	-3.377	-265.586	290.219
298	36.726	99.298	99.298	-0.000	-259.319	190.086
300	36.793	99.326	99.299	0.028	-259.203	188.829
400	40.814	119.469	103.649	7.910	-246.833	107.691
500	41.642	126.990	106.930	12.036	-240.849	67.729
600	42.515	133.451	110.268	16.228	-234.968	73.300
800	42.515	139.106	113.453	20.463	-229.119	62.609
1000	42.937	148.643	119.630	29.013	-217.783	47.557
1100	43.069	152.742	122.457	33.314	-212.170	42.154
1200	43.171	156.494	124.139	37.626	-206.590	37.625
1300	43.251	159.953	125.666	41.947	-201.045	33.799
1400	43.316	163.131	127.010	46.276	-195.538	30.000
1500	43.366	166.131	128.111	50.610	-190.034	27.688
1600	43.408	168.951	129.068	54.948	-184.559	25.210
1700	43.443	171.593	130.706	59.291	-179.097	23.025
1800	43.472	174.057	132.114	63.637	-173.652	21.084
1900	43.496	176.376	133.346	67.986	-168.222	19.369
2000	43.510	178.650	134.482	72.336	-162.787	17.780
2100	43.537	180.774	135.525	76.689	-157.361	16.377
2200	43.553	182.800	136.492	81.043	-151.946	15.094
2300	43.570	184.736	137.386	85.397	-146.525	13.923
2400	43.584	186.593	138.211	89.750	-141.104	12.852
2500	43.590	188.370	139.074	94.113	-135.684	11.861
2600	43.600	190.079	139.875	98.475	-130.251	10.946
2700	43.608	191.725	140.618	102.835	-124.820	10.103
2800	43.615	193.311	141.306	107.196	-119.379	9.318
2900	43.620	194.846	141.946	111.556	-113.938	8.582
3000	43.629	196.321	142.540	115.921	-108.495	7.902
3100	43.634	197.751	143.090	120.284	-103.054	7.261
3200	43.640	199.137	143.604	124.648	-97.613	6.659
3300	43.644	200.480	144.081	128.999	-92.172	6.092
3400	43.648	201.789	144.521	133.346	-86.731	5.550
3500	43.652	203.048	144.933	137.742	-81.290	5.030
3600	43.656	204.278	145.304	142.107	-75.849	4.569
3700	43.659	205.474	145.687	146.473	-70.408	4.106
3800	43.662	206.638	146.044	150.839	-64.967	3.645
3900	43.665	207.770	146.376	155.196	-59.526	3.201
4000	43.668	208.878	146.695	159.572	-54.085	2.771
4100	43.670	209.956	146.971	163.939	-48.644	2.395
4200	43.672	211.009	147.236	168.306	-43.203	2.017
4300	43.674	212.036	147.480	172.673	-37.762	1.656
4400	43.676	213.038	147.709	177.040	-32.321	1.302
4500	43.678	214.022	147.919	181.408	-26.880	0.952
4600	43.680	214.982	148.116	185.776	-21.439	0.666
4700	43.681	215.921	148.296	190.144	-15.998	0.363
4800	43.683	216.841	148.451	194.513	-10.557	0.073
4900	43.684	217.744	148.590	198.882	-5.116	-0.219
5000	43.686	218.624	148.715	203.249	0.325	-0.473
5100	43.687	219.489	148.780	207.618	5.784	-0.731
5200	43.688	220.338	148.831	211.987	11.243	-0.979
5300	43.689	221.170	148.866	216.356	16.702	-1.219
5400	43.690	221.986	148.886	220.725	22.161	-1.452
5500	43.691	222.788	148.892	225.094	27.620	-1.672
5600	43.692	223.576	148.886	229.463	33.079	-1.886
5700	43.693	224.349	148.866	233.832	38.538	-2.094
5800	43.694	225.109	148.831	238.201	43.997	-2.295
5900	43.695	225.859	148.775	242.570	49.456	-2.489
6000	43.695	226.590	148.700	246.940	54.915	-2.685

Sept. 30, 1966

Point Group [D_{2h}]
S°_{298.15} = [99.3] gibbs/mol
Ground State Quantum Weight = [1.]

ΔH°₀ = -278.8 kcal/mol
ΔH°_{298.15} = -278.2 ± 10 kcal/mol

Vibrational Frequencies and Degeneracies

ω, cm ⁻¹	ω, cm ⁻¹
[600] (4)	[300] (8)
[1721] (6)	[1721] (6)

Bond Distances: W-O = [1.81] Å
Bond Angle: O-W-O = [109.47°], W-O_{bridge}-W = [70.53°]
Product of the Moments of Inertia: I_AI_BI_C = [5.917 × 10⁻¹¹²] g³ cm⁶ σ = [4]

Heat of Formation.

The adopted value, ΔH°₂₉₈ (W₂O₃, g) = -278.2 kcal/mol, was reduced from ΔH°_{f,450} = -272.5 kcal/mol, reported by R. J. Ackermann and E. G. Hauh, J. Phys. Chem. 67, 2596 (1963). They have studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1800°K by mass spectrometry, mass effusion, and X-ray diffraction, and also have determined ΔH°_f (W₂O₃, g) = -272.500 ± 54.987 (cal/mol) from partial pressure measurements over the W-W₂O₃(c) system.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," The Ohio State University, 1964, has also studied the same system in the temperature range from 1418 to 1527° K. Third law calculation of the partial pressure data gives ΔH°₂₉₈ = 144.0 kcal/mol for 3 W₂O₃(c) = W₂O₃(g) + W(c) which yields ΔH°₂₉₈ (W₂O₃, g) = -278.8 kcal/mol, using all JANAF functions. This value is in good agreement with the value adopted.

J. H. Norman and H. G. Staley, J. Chem. Phys. 43, 3804 (1965), have obtained ΔH°_{f,1800} = -127 kcal/mol for 2 W₂O₃(g) = W₂O₃(g) by mass spectrometric study of the vapor over W₂O₃ dissolved in CaO-Al₂O₃-SiO₂. The value of ΔH°_f was determined by the second law method from ion intensities and leads to ΔH°_{f,298} (W₂O₃, g) = -275 kcal/mol, using all JANAF functions (dated Sept. 30, 1966). The absolute pressure values reported by Norman and Staley appear to be quite inconsistent with the JANAF functions, since they lead to ΔH°_f (W₂O₃, g) = -246 kcal/mol by the third law method.

Investigator	Chemical Reaction	Temperature (°K)	ΔH° ₂₉₈ (kcal/mol)	Drift (eu)	ΔH° _f (W ₂ O ₃ , g) (kcal/mol)
Ackermann & Hauh	3 W ₂ O ₃ (c) = W ₂ O ₃ (g) + W(c)	1300-1800	144.54	0.01	-278.2*
Battles	3 W ₂ O ₃ (c) = W ₂ O ₃ (g) + W(c)	1418-1527	142.66	0.85 ± 0.40	-278.8*
Norman & Staley	2 W ₂ O ₃ (g) = W ₂ O ₃ (g)	1700-1900	-135	-106	-275 **

* Third law value adopted in calculation.
** Second law value adopted in calculation.

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 600 cm⁻¹ (4), 300 cm⁻¹ (8), and 1721 cm⁻¹ (6) in order to give the entropy at 1450°K, S₁₄₅₀ = 164.66 eu, corresponding to ΔS_{f,1450} = 54.98 eu which was reported by Ackermann and Hauh. The adopted value, S°₂₉₈ (W₂O₃, g) = 99.3 eu, was reduced from the entropy at 1450°K, using JANAF functions. Second law calculation of the partial pressure data of Battles gives ΔS°_{f,1470} = 63.5 eu for 3 W₂O₃(c) = W₂O₃(g) + W(c). This yields S°₂₉₈ (W₂O₃, g) = 97.9 eu.

The molecular configuration for W₂O₃(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atom, and two of these tetrahedra share a common oxygen edge to form a planar four-member ring. The bond distance W-O was estimated as 1.81 Å and the bond angle O-W-O = 109.47° and W-O_{bridge}-W = 70.53°. The three principal moments of inertia are: I_A = 3.481 × 10⁻³⁷, I_B = 1.363 × 10⁻³⁷ and I_C = 1.247 × 10⁻³⁷ g cm².

Tritungsten Octaoxide (W_3O_8)
(Ideal Gas) GFW = 679.5452

TRITUNGSTEN OCTAOXIDE (W_3O_8)
(IDEAL GAS)

T, °K	Cp°	gibbs/mol S°	(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	+0.00	INFINITE	INFINITE	- 9.552	- 406.385	- 406.385	INFINITE
100	26.940	75.456	156.609	- 8.115	- 408.192	- 388.491	870.901
200	42.309	99.703	122.369	- 4.529	- 408.830	- 424.488	424.488
298	49.301	118.036	118.036	+0.00	- 408.700	- 378.468	277.425
300	49.398	118.341	118.037	+0.91	- 408.694	- 378.282	275.578
400	53.445	133.157	120.029	- 5.251	- 408.145	- 201.186	156.623
500	55.875	145.366	123.912	- 10.727	- 407.396	- 358.322	126.071
600	57.403	155.699	128.371	- 16.387	- 406.579	- 348.583	106.834
700	58.101	162.475	137.390	- 28.068	- 404.974	- 329.500	90.015
800	59.101	172.475	141.684	- 34.004	- 404.220	- 320.108	77.733
900	59.594	179.466	141.684	- 39.982	- 403.512	- 310.798	67.925
1000	59.956	185.765	145.783	- 45.992	- 402.850	- 301.564	59.915
1100	60.230	191.493	149.682	- 52.079	- 402.232	- 293.249	47.618
1200	60.408	200.588	156.912	- 58.799	- 401.666	- 285.106	38.626
1300	60.741	206.084	160.265	- 64.147	- 401.145	- 274.162	31.979
1400	60.850	210.279	163.463	- 70.227	- 400.673	- 265.082	28.910
1500	60.939	214.009	166.511	- 76.216	- 400.249	- 256.082	26.062
1600	61.076	221.395	172.218	- 88.518	- 399.550	- 246.106	21.905
1800	61.129	224.699	174.894	- 94.629	- 399.278	- 239.145	18.377
2000	61.175	227.835	177.463	- 100.744	- 399.058	- 229.196	15.346
2100	61.214	230.821	179.934	- 106.864	- 398.989	- 221.264	14.005
2200	61.248	233.677	182.392	- 112.987	- 398.981	- 213.532	12.635
2300	61.278	236.393	184.805	- 119.113	- 398.719	- 193.403	11.609
2400	61.304	239.001	186.817	- 125.242	- 398.714	- 184.466	10.534
2500	61.327	241.504	188.955	- 131.374	- 398.766	- 175.549	9.529
2600	61.348	243.910	191.023	- 137.508	- 398.868	- 166.637	8.588
2700	61.363	246.122	193.032	- 143.642	- 399.015	- 157.729	7.671
2800	61.383	248.158	194.965	- 149.781	- 399.315	- 148.778	6.805
2900	61.397	250.012	196.847	- 155.920	- 399.713	- 139.778	6.085
3000	61.411	252.694	198.674	- 162.060	- 400.253	- 130.798	5.341
3100	61.423	254.708	200.449	- 168.202	- 400.966	- 121.811	4.635
3200	61.444	256.548	202.185	- 174.347	- 401.857	- 113.777	3.958
3300	61.464	258.548	203.855	- 180.489	- 402.997	- 105.708	3.278
3400	61.489	260.817	213.081	- 186.633	- 404.364	- 97.026	2.635
3500	61.461	262.164	207.085	- 192.779	- 406.005	- 88.527	2.024
3600	61.469	263.696	208.639	- 198.926	- 408.003	- 76.343	1.442
3700	61.483	265.220	210.135	- 205.072	- 410.352	- 66.990	0.898
3800	61.499	266.821	211.580	- 211.221	- 413.077	- 59.588	0.371
3900	61.489	268.817	213.081	- 217.359	- 436.048	- 47.026	0.147
4000	61.494	270.374	214.694	- 223.519	- 436.416	- 37.052	0.031
4100	61.499	271.492	215.875	- 229.668	- 436.797	- 27.055	1.442
4200	61.509	272.821	217.550	- 235.818	- 437.182	- 17.058	0.958
4300	61.524	274.374	219.181	- 241.969	- 437.582	- 7.038	0.531
4400	61.513	276.236	219.845	- 248.120	- 437.995	- 2.960	0.137
4500	61.517	277.618	221.113	- 254.272	- 438.413	12.991	- 0.31
4600	61.520	278.970	222.356	- 260.424	- 438.839	23.042	1.095
4700	61.527	280.158	223.576	- 266.576	- 439.277	33.162	1.964
4800	61.530	282.857	225.943	- 272.728	- 439.719	43.182	2.837
4900	61.533	284.100	227.093	- 278.881	- 440.168	53.189	3.704
5000	61.533	285.319	228.223	- 285.034	- 440.625	63.265	4.521
5100	61.536	286.519	229.188	- 291.188	- 441.099	73.353	5.343
5200	61.541	287.684	230.083	- 297.341	- 441.586	83.441	6.165
5300	61.543	288.836	231.949	- 303.494	- 442.030	93.551	6.986
5400	61.545	289.966	232.547	- 309.650	- 442.508	103.647	7.807
5500	61.547	291.075	233.982	- 315.804	- 442.989	113.776	8.628
5600	61.547	291.075	233.982	- 321.959	- 443.480	123.889	9.449
5700	61.551	293.234	236.002	- 328.113	- 443.971	134.014	10.270
5800	61.552	295.287	238.598	- 334.268	- 444.462	144.139	11.091
5900	61.552	296.287	240.424	- 340.424	- 444.965	154.333	11.912
6000	61.554	299.321	237.558	- 346.579	- 1027.180	170.750	6.220

Sept. 30, 1966

GFW = 679.5452

Point Group [D_{2d}] $\Delta H_f^\circ = -406.4$ kcal/mol

$S_{298.15}^\circ = [118.0]$ gibbs/mol $\Delta H_f^\circ = -408.7 \pm 10$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω, cm^{-1}	ω, cm^{-1}
[800] (6)	[199] (3)
[350] (4)	[150] (6)
[242] (8)	

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47°]

Product of the Moments of Inertia: $I_A I_B I_C = [7.65 \times 10^{-111}] \text{ g}^3 \text{ cm}^6$

$\sigma = [4]$

Heat of Formation.

R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2586 (1963), have studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion and X-ray diffraction, and also have determined the $\Delta H_f^\circ(W_3O_8, g) = -400,900 \pm 9054$ T (cal/mol) from partial pressure measurements over W-WO₂ (c). The adopted value, $\Delta H_f^\circ(W_3O_8, g) = -408.7$ kcal/mol, was reduced from $\Delta H_f^\circ(W_3O_8, g) = -400.9$ kcal/mol, using JANAF functions.

Investigator	Chemical Reaction	Temperature (°K)	ΔH_f° (kcal/mol)	Drift (eu)	ΔH_f° (W_3O_8, g) (kcal/mol)
Ackermann & Rauh	4 WO ₂ (c) = W ₃ O ₈ (g)+W(c)	1300-1600*	155.05	155.09	-408.7
		2nd law	155.05		
		3rd law			

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm⁻¹ (6), 350 cm⁻¹ (4), 242 cm⁻¹ (8), 199 cm⁻¹ (3) and 150 cm⁻¹ (6) in order to give the entropy at 1450°K, $S_{1450}^\circ = 208.18$ eu, corresponding to $\Delta H_f^\circ = -90.54$ eu, which was reported by Ackermann and Rauh.

The molecular configuration for W₃O₈(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, the three tetrahedra are connected by two common edges, and also the three tungsten atoms are in the same axis. The bond distance W-O was estimated as 1.81 Å and the bond angle $\angle OWO = 109.47^\circ$. The three principal moments of inertia are: $I_A = I_B = 4.060 \times 10^{-37}$ and $I_C = 4.641 \times 10^{-38} \text{ g cm}^2$.

08W3

Point Group [D_{3h}]

$\Delta H_f^\circ = -480.7 \text{ kcal/mol}$
 $\Delta H_{298.15}^\circ = -483.6 \pm 10 \text{ kcal/mol}$

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies		
ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
[800] (6)	[200] (6)	
[396] (3)	[150] (6)	
[350] (6)		

Bond Distances: W-O = [1.91] Å

Bond Angles: O-W-O = [109.47°], W-O-bridge-W = [130.53°]

Product of the Moments of Inertia: $I_{A,B,C} = [3.865 \times 10^{-110}] \text{ g cm}^2$

$\sigma = [6]$

Heat of Formation.

The adopted value, $\Delta H_{298}^\circ(\text{WO}_3\text{g}) = -483.6 \text{ kcal/mol}$, was reduced from $\Delta H_{1450}^\circ(\text{WO}_3\text{g}) = -474.1 \text{ kcal/mol}$ of R. J. Ackermann and E. G. Reau, *J. Phys. Chem.* **67**, 2598 (1963), who studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600 °K by mass spectrometry, mass effusion, and X-ray diffraction, and determined $\Delta H^\circ(\text{WO}_3\text{g}) = -474.100 \pm 110.267 \text{ (cal/mol)}$ from partial pressure measurements over W-WO₂(c). They reviewed the previous determinations 1, 2, 3, 4 of the thermodynamic properties of sublimation of WO₃, and also pointed out that it was not possible to make quantitative observations on stoichiometric WO₃ in vacuo, since it is a "bivalent" system and the ion current is not constant until the composition of the sample reaches WO_{2.96}. This is probably the cause of previous discrepancies in sublimation studies.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide", The Ohio State University, 1964, has also studied the partial pressure of W₂O₅(g) over W-WO₂(c) in the temperature range from 1399° to 1527°K. Third law calculation of the partial pressure data gives $\Delta H_{298}^\circ = -148.2 \text{ kcal/mol}$ for $4.5 \text{ WO}_2(\text{c}) = \text{W}_2\text{O}_5(\text{c}) + 1.5 \text{ W}(\text{c})$, which yields $\Delta H_{298}^\circ(\text{WO}_3\text{g}) = -486.0 \text{ kcal/mol}$, using all JANAF functions.

J. H. Norman and H. G. Staley, *J. Chem. Phys.* **43**, 3904 (1965), have obtained $\Delta H_{1600}^\circ = -240 \text{ kcal/mol}$ for $3 \text{ WO}_2(\text{c}) = \text{W}_2\text{O}_5(\text{c})$ by mass spectrometric study of the vapor over WO₃ dissolved in CaO-Al₂O₃-SiO₂. The value of ΔH° was determined by the second law method from ion intensities and leads to $\Delta H_{298}^\circ(\text{WO}_3\text{g}) = -463.4 \text{ kcal/mol}$. Using all JANAF functions (dated September 30, 1966). The absolute pressure values reported by Norman and Staley also appear to be quite inconsistent with the JANAF functions, since they lead to -443 kcal/mol by the third law method.

Reference 1. K. Uno, *J. Chem. Soc. Japan* **62**, 990 (1941).

2. J. Berkowitz, W. A. Chupka, and M. O. Inghram, *J. Chem. Phys.* **27**, 85 (1957).

3. P. E. Blackburn, J. Hosh, and H. L. Johnston, *J. Phys. Chem.* **62**, 769 (1958); P. E. Blackburn, WADC TR 59-575, part 1, Mar. 1960; and part 2, Dec. 1960.

4. G. Meyer, J. P. Oosterom, and J. L. DeRoos, *Rec. Trav. Chim.* **78**, 412 (1959).

Investigator	Chemical Reaction	Temperature		Drift	$\Delta H_{298}^\circ(\text{WO}_3\text{g})$ (kcal/mol)
		2nd law	3rd law	(eu)	
Ackermann & Reau	$4.5 \text{ WO}_2(\text{c}) = \text{W}_2\text{O}_5(\text{c}) + 1.5 \text{ W}(\text{c})$	1300-1600	150.61	150.64	-483.6 *
Battles	$4.5 \text{ WO}_2(\text{c}) = \text{W}_2\text{O}_5(\text{c}) + 1.5 \text{ W}(\text{c})$	1369-1527	148.20	148.20	-486.0 *
Norman & Staley	$3 \text{ WO}_2(\text{c}) = \text{W}_2\text{O}_5(\text{c})$	1700-1900	-253.4	-233	-463.4 **

* Third law value adopted in calculation

** Second law value adopted in calculation

Heat Capacity and Entropy.

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1} (6), 396 cm^{-1} (3), 330 cm^{-1} (9), 200 cm^{-1} (6), and 150 cm^{-1} (6) in order to give the entropy at 1450°K , $S_{1450}^\circ = 219.14 \text{ eu}$, corresponding to $\Delta S_{1450}^\circ = 110.28 \text{ eu}$, reported by Ackermann and Reau. The adopted value, $S_{298}^\circ(\text{WO}_3\text{g}) = 120.6 \text{ eu}$, was reduced from the entropy at 1450°K , using JANAF functions. Second law calculation of the partial pressure data of Battles gives $\Delta S_{1455}^\circ = 71.7 \text{ eu}$ for $4.5 \text{ WO}_2(\text{c}) = \text{W}_2\text{O}_5(\text{c}) + 1.5 \text{ W}(\text{c})$. This yields $S_{298}^\circ(\text{WO}_3\text{g}) = 122.4 \text{ eu}$.

The molecular configuration for W₂O₅(g) is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atom, and that each tetrahedron shares two oxygen atoms to form a planar six-member ring. The bond distance W-O is estimated as 1.91 Å and the bond angles O-W-O = 109.47° and W-O-bridge-W = 130.53°. The three principal moments of inertia are: $I_A = I_B = 2.805 \times 10^{-37}$ and $I_C = 4.913 \times 10^{-37} \text{ g cm}^2$.

T, °K	C _p ^o	S ^o	-(G°-H°)/T	H°-H° ₂₉₈	ΔH ^o	ΔG ^o	Log K _p
0	∞	∞	∞	9.956	-480.652	-480.652	INFINITE
100	26.614	76.161	161.514	8.595	-482.822	-471.121	1020.634
200	44.668	100.980	129.233	4.851	-483.709	-468.472	501.941
298	54.284	120.394	100.000	0.000	-483.600	-468.687	307.551
300	54.401	120.929	120.600	0.099	-483.593	-466.600	325.348
400	58.219	137.015	122.760	5.702	-482.956	-474.356	237.321
500	61.048	150.337	120.982	11.677	-482.073	-472.305	166.989
600	62.806	161.634	131.860	17.876	-481.105	-470.460	149.403
700	64.195	171.608	146.811	24.218	-480.127	-368.738	124.692
800	64.742	180.003	161.683	30.656	-479.179	-387.184	108.174
900	65.301	187.662	186.374	37.159	-478.265	-375.735	91.241
1000	65.711	194.565	150.054	43.711	-477.397	-364.387	76.637
1100	66.020	200.843	155.117	50.268	-476.577	-353.131	70.161
1200	66.259	206.598	160.171	56.913	-475.803	-341.939	62.276
1300	66.446	211.909	163.026	63.548	-475.082	-330.813	55.615
1400	66.597	216.839	166.696	70.201	-474.409	-319.745	49.614
1500	66.719	221.438	170.194	76.867	-473.786	-308.716	44.080
1600	66.819	225.747	173.634	83.544	-473.213	-297.730	40.468
1700	66.903	229.801	176.125	90.230	-472.689	-286.778	36.660
1800	66.971	233.627	178.781	96.924	-472.221	-275.857	33.406
1900	67.033	237.250	181.511	103.624	-471.807	-264.959	30.477
2000	67.084	240.686	184.324	110.330	-471.447	-254.083	27.765
2100	67.128	243.963	187.203	117.041	-471.130	-243.218	25.312
2200	67.166	247.087	190.135	123.754	-470.866	-232.380	23.095
2300	67.200	250.074	193.066	130.474	-470.649	-221.544	21.051
2400	67.229	252.934	195.977	137.106	-470.463	-210.703	19.187
2500	67.255	255.670	198.811	143.759	-470.307	-200.869	17.474
2600	67.278	258.317	201.570	150.444	-470.167	-191.059	15.892
2700	67.299	260.887	204.270	157.173	-470.043	-181.273	14.427
2800	67.317	263.396	206.906	163.946	-469.934	-171.504	13.067
2900	67.334	265.867	209.488	170.768	-469.840	-161.752	11.800
3000	67.349	268.300	212.029	177.531	-469.761	-152.016	10.616
3100	67.363	270.705	214.560	184.248	-469.697	-142.294	9.508
3200	67.375	272.998	217.096	190.916	-469.646	-132.590	8.467
3300	67.386	275.171	219.637	197.543	-469.604	-122.902	7.488
3400	67.396	277.234	221.229	204.122	-469.572	-113.227	6.564
3500	67.406	278.197	222.776	210.657	-469.549	-103.571	5.690
3600	67.414	280.074	224.290	217.146	-469.534	-93.934	4.862
3700	67.422	281.881	225.763	223.593	-469.528	-84.314	4.082
3800	67.430	283.618	227.206	229.999	-469.530	-74.714	3.360
3900	67.436	285.283	228.568	236.241	-469.538	-65.134	2.693
4000	67.443	286.876	229.746	242.424	-469.550	-55.578	2.085
4100	67.448	288.406	230.856	248.549	-469.564	-46.046	1.525
4200	67.454	289.871	231.902	254.618	-469.579	-36.548	1.010
4300	67.459	291.278	232.900	260.633	-469.594	-27.084	0.530
4400	67.464	292.629	233.851	266.596	-469.609	-17.654	0.083
4500	67.468	293.934	234.759	272.509	-469.624	-8.264	-0.320
4600	67.472	295.194	235.624	278.374	-469.638	1.176	-0.754
4700	67.476	296.419	236.450	284.191	-469.652	11.576	-1.150
4800	67.480	297.600	237.236	289.959	-469.666	21.926	-1.505
4900	67.483	298.746	237.984	295.679	-469.679	32.226	-1.810
5000	67.486	299.856	238.696	301.350	-469.692	42.476	-2.065
5100	67.489	300.931	239.364	306.974	-469.705	52.676	-2.280
5200	67.492	301.971	240.000	312.553	-469.718	62.826	-2.455
5300	67.495	302.984	240.574	318.088	-469.730	72.926	-2.590
5400	67.497	303.969	241.154	323.579	-469.742	82.976	-2.685
5500	67.500	304.924	241.729	329.024	-469.754	92.976	-2.740
5600	67.502	310.064	242.300	334.424	-469.766	102.926	-2.765
5700	67.504	311.239	242.874	339.779	-469.778	112.826	-2.770
5800	67.506	312.413	243.449	345.089	-469.789	122.676	-2.765
5900	67.508	313.587	244.024	350.354	-469.799	132.476	-2.740
6000	67.510	314.761	244.600	355.574	-469.809	142.226	-2.695

June 30, 1962; Mar. 31, 1963; Sept. 30, 1966

Diphosphorus Pentoxide, Dimeric ((P₂O₅)₂)
(Crystal) Mol. Wt. = 283.8892

010P4

MOL. WT. = 283.8892

DIPHOSPHORUS PENTOXIDE, DIMERIC ((P₂O₅)₂) (CRYSTAL)

ΔH_f°	-697.0 ± 2.1 kcal. mole ⁻¹
ΔH_f°	-702.7 ± 2.1 kcal. mole ⁻¹
ΔH_f°	-702.15 ± 0.08 kcal. mole ⁻¹
ΔH_f°	-702.15 ± 0.08 kcal. mole ⁻¹
T_g	$631^\circ K.$

Heat of Formation.

The heat of formation (ΔH_f° 298.15) of P₄O₁₀(c) has been reported by many investigators. The most recent value, ΔH_f° 298.15 = -719.4 ± 2.0 kcal. mole⁻¹ for the reaction P₄(w, white, c) + 5O₂(g) = P₄O₁₀(hex., c), was determined by E. F. Egan, Jr. and B. B. Luff, "Heats of Formation of Phosphorus Oxides", June 1, 1963 to Nov. 30, 1963, Tennessee Valley Authority, Office of Agriculture and Chemical Development, Fundamental Research Branch, Wilson Dam, Alabama. This ΔH_f° 298.15 value was derived from energy of combustion, ΔE_c = -716.397 kcal. mole⁻¹, which is an average value of many measurements using three different sample forms, i.e. uncoated phosphorus, lucite-coated phosphorus and cellulose acetate-coated phosphorus. The adopted ΔH_f° 298.15 (P₄O₁₀, c) value was recalculated based on the P(red, V, c) as reference state.

The heat of combustion of white phosphorus was determined as -713.2 ± 1.0 kcal. mole⁻¹ by W. S. Holmes, Trans. Paraday Soc. 58, 1916 (1962), yielding ΔH_f° 298.15 (P₄O₁₀, c) = -696.5 ± 1.3 kcal. mole⁻¹, based on P(red, V, c) as reference state. The heat of formation of P₂O₅ from red phosphorus was reported to be -355 ± 2 kcal. mole⁻¹ by W. S. Koerner and P. Daniels, J. Chem. Phys. 20, 115 (1952). The product, P₂O₅, was considered to be a mixture of two forms, i.e. crystalline and amorphous. The other ΔH_f° 298.15 (P₄O₁₀, c) values reported by early investigators were reviewed by Egan and Luff, loc. cit.

Heat Capacity and Entropy.

The heat capacities (18-324°K.) and $S_{298.15}^\circ$ adopted were taken from R. J. L. Andon, J. P. Counsell, R. McKerrell and J. P. Martin, Trans. Faraday Soc. 59, 2702 (1963). The Cp values above 324°K. were obtained by graphical extrapolation. The $S_{298.15}^\circ$ value was calculated based on S_{10}° = 0.35 e.u.

Low temperature (15-310°K.) and high temperature (298.15-623.15°K.) heat capacities were also measured by Thermal Laboratory, The Dow Chemical Company, private communication, June 18, 1962, and M. Prandien, J. Res. Natl. Bur. Std. 10, 35 (1933), respectively. The low temperature data were not adopted because they are less satisfactory than the data of Andon et al. The high temperature data were not used because the sample employed for enthalpy measurements was not explicitly reported as pure hexagonal form.

Sublimation Data.

The value of ΔH_g° 298.15 was derived from the vapor pressure data by both the second and third law analyses. See the P₄O₁₀(g) table for details. T_g is the temperature at which the free energy change of the reaction P₄O₁₀(hex. c) = P₄O₁₀(g) approaches zero. Sublimation temperature for P₄O₁₀(c) was derived to be 532°K., 636°K. (average of three determinations) and 623.7°K. (average of two determinations) by M. Prandien, loc. cit. from the vapor pressure data reported by J. M. Hoeflake and M. P. Schaffer, Rec. trav. chim. 45, 191 (1926); A. Saite, Z. physik. Chem. 149, 337 (1930); and A. Saite and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924), respectively.

T, °K.	C _p	S°	-(F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f °	ΔF _f °	Log K _p
0	0.000	INFINITE	INFINITE	0.000	-696.994	-696.994	INFINITE
100	18.550	89.040	-7.441	-699.947	-680.441	-680.441	1487.032
200	36.940	97.260	-6.332	-701.810	-660.134	-660.134	721.326
298	50.600	94.680	-5.000	-702.700	-639.450	-639.450	468.707
300	50.830	94.994	-4.994	-702.707	-639.458	-639.458	465.531
400	62.200	71.218	5.616	-702.727	-617.815	-617.815	337.542
500	71.700	86.135	61.708	-701.964	-596.660	-596.660	260.787
600	80.300	99.982	66.530	-700.535	-575.725	-575.725	209.698
700	88.200	112.920	70.720	-700.535	-555.725	-555.725	173.284
800	94.800	125.153	78.103	-700.535	-535.725	-535.725	151.683
900	100.800	136.675	83.977	-700.535	-515.725	-515.725	128.333
1000	105.800	147.560	89.796	-700.535	-495.725	-495.725	109.586
1100	110.200	157.858	95.520	-700.535	-475.725	-475.725	94.349
1200	114.200	167.598	101.244	-700.535	-455.725	-455.725	81.724
1300	116.200	176.797	106.955	-700.535	-435.725	-435.725	71.144
1400	118.300	185.487	111.923	-700.535	-415.725	-415.725	62.125
1500	120.000	193.710	117.103	-700.535	-395.725	-395.725	54.368

Diphosphorus Pentoxide, Dimeric ((P₂O₅)₂)
(Ideal Gas) Mol. Wt. = 283.8892

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	H° - H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	∞	INFINITE	7.308	-670.975	-670.975	INFINITE	
100	16.835	64.368	127.411	-634.4	-634.4	1440.018	
200	22.818	51.487	107.577	-608.979	-608.979	1440.018	
298	25.126	45.925	96.925	-600	-600	459.308	
300	45.125	96.805	96.926	-0.84	-0.84	456.245	
400	54.377	111.161	98.422	5.066	5.066	332.812	
500	60.462	124.013	102.279	10.867	10.867	256.705	
600	65.043	135.484	106.875	17.165	17.165	209.300	
700	68.149	145.757	111.709	23.853	23.853	174.020	
800	70.339	155.011	116.453	30.766	30.766	153.374	
900	72.067	163.404	121.300	37.894	37.894	130.346	
1000	73.329	171.066	125.959	45.166	45.166	111.957	
1100	74.304	178.102	130.329	52.550	52.550	96.940	
1200	75.059	184.602	134.585	60.020	60.020	84.449	
1300	75.681	190.635	138.667	67.559	67.559	73.900	
1400	76.175	196.263	142.571	75.152	75.152	64.876	
1500	76.581	201.532	146.338	82.791	82.791	57.071	
1600	76.918	206.486	149.944	90.466	90.466	50.255	
1700	77.200	211.158	153.409	98.173	98.173	44.253	
1800	77.439	215.577	156.741	105.905	105.905	38.929	
1900	77.642	219.770	159.949	113.659	113.659	34.175	
2000	77.817	223.757	163.041	121.433	121.433	29.906	
2100	77.969	227.557	166.023	129.222	129.222	26.049	
2200	78.101	231.188	168.903	137.026	137.026	22.550	
2300	78.216	234.662	171.687	144.842	144.842	19.363	
2400	78.318	237.993	174.381	152.668	152.668	16.446	
2500	78.408	241.192	176.990	160.505	160.505	13.767	
2600	78.489	244.269	179.519	168.350	168.350	11.300	
2700	78.560	247.232	181.972	176.202	176.202	9.019	
2800	78.625	250.091	184.354	184.062	184.062	6.905	
2900	78.682	252.851	186.669	191.927	191.927	5.043	
3000	78.735	255.519	188.920	199.798	199.798	3.410	
3100	78.782	258.101	191.110	207.674	207.674	2.007	
3200	78.825	260.603	193.243	215.554	215.554	1.199	
3300	78.864	263.030	195.321	223.439	223.439	0.687	
3400	78.900	265.384	197.347	231.327	231.327	0.358	
3500	78.933	267.672	199.324	239.219	239.219	0.188	
3600	78.963	269.896	201.254	247.113	247.113	0.085	
3700	78.991	272.060	203.136	255.011	255.011	0.043	
3800	79.017	274.167	204.980	262.912	262.912	0.025	
3900	79.041	276.220	206.780	270.815	270.815	0.013	
4000	79.063	278.221	208.541	278.720	278.720	0.006	
4100	79.083	280.174	210.265	286.627	286.627	0.002	
4200	79.102	282.080	211.952	294.536	294.536	0.000	
4300	79.119	283.941	213.605	302.447	302.447	0.000	
4400	79.137	285.760	215.224	310.360	310.360	0.000	
4500	79.152	287.539	216.811	318.275	318.275	0.000	
4600	79.167	289.270	218.368	326.191	326.191	0.000	
4700	79.180	290.981	219.895	334.108	334.108	0.000	
4800	79.193	292.649	221.393	342.027	342.027	0.000	
4900	79.205	294.282	222.864	349.947	349.947	0.000	
5000	79.216	295.882	224.308	357.868	357.868	0.000	
5100	79.227	297.451	225.727	365.790	365.790	0.000	
5200	79.237	298.989	227.121	373.713	373.713	0.000	
5300	79.246	300.499	228.492	381.637	381.637	0.000	
5400	79.255	301.980	229.839	389.562	389.562	0.000	
5500	79.263	303.434	231.164	397.488	397.488	0.000	
5600	79.271	304.866	232.467	405.415	405.415	0.000	
5700	79.279	306.263	233.750	413.342	413.342	0.000	
5800	79.286	307.625	235.012	421.271	421.271	0.000	
5900	79.293	308.950	236.254	429.200	429.200	0.000	
6000	79.300	310.233	237.478	437.129	437.129	0.000	

Dec. 31, 1962; Dec. 31, 1965

DIPHOSPHORUS PENTOXIDE, DIMERIC ((P₂O₅)₂) (IDEAL GAS)

MOL. WT. = 283.8892

Point group T_d
 $\Delta H_f^0 = [96.5] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^0 = -677.4 \pm 2.1 \text{ kcal. mole}^{-1}$
 Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies					
ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹	ω , cm ⁻¹
424 (1)	650 (2)	[750] (3)	764 (3)		
721 (1)	952 (2)	1015 (3)	1015 (3)		
1437 (1)	[170] (3)	329 (3)	1390 (3)		
278 (2)	[470] (3)	573 (3)			

Bond Distances: $P-O = 1.40 \pm 0.03 \text{ \AA}$ $P-O = 1.60 \pm 0.01 \text{ \AA}$ $P-P = 2.85 \pm 0.03 \text{ \AA}$
 Bond Angle: $\text{Optical } P-O = 117 \pm 1^\circ$ $O-P-O = 101 \pm 1^\circ$ $P-O-P = 124^\circ 30' \pm 1^\circ$ $\sigma = 12$
 Product of the Moments of Inertia: $I_{AB}^2 C = 2.93798 \times 10^{-111} \text{ g}^3 \text{ cm}^6$

Heat of Formation.

The value of ΔH_f^0 298.15 (P₂O₅, g) was calculated from the heats of formation and sublimation for P₂O₅ (hex., c). The heat of sublimation (ΔH_s^0 298.15) was derived from vapor pressure data by the second and third law methods. The results obtained are presented as follows.

Investigator	Temperature, °K	Second Law Value	Third Law Value	Drift, e.u.
Hoeflake and Schaffer ¹	260 - 401	25.42 ± 0.07	25.33	-0.39 ± 0.13
Southard and Nelson ²	216.2-300.4	25.59 ± 0.06	25.35	-0.16 ± 0.14
	283.6-389.3	25.45 ± 0.07	25.35	-0.10 ± 0.07

1. J. W. A. Hoeflake and P. E. C. Schaffer, Rec. trav. chim. 45, 191 (1926).

2. J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. 59, 911 (1937).

The value of ΔH_f^0 298.15 adopted was 25.34 ± 0.08 kcal. mole⁻¹. There are many vapor pressure measurements reported but only the above two over P₂O₅ (hex., c).

It has been shown that P₂O₅ has three solid phases and two liquid phases. The three solid phases are hexagonal, orthorhombic and tetragonal. As temperature increases, the thermal stability of P₂O₅ follows the same order. The metastable liquid, according to data of Hoeflake and Schaffer, loc. cit., is from hexagonal form. The stable liquid is from tetragonal form. W. L. Hill, G. T. Faust and S. B. Hendricks, J. Am. Chem. Soc. 65, 794 (1943) reported that molecules of P₂O₅ having the same structure as in the vapor are present in the hexagonal form of the solid. The vapor pressures of P₂O₅ over different condensed phases have been measured by many investigators and reviewed by T. D. Farr, "Phosphorus, Properties of the Elements and Some of Its Compounds", Tennessee Valley Authority, Wilson Dam, Alabama, 1950. The complexity of the solid state of P₂O₅ has also been discussed by A. Seitz and A. J. Rutgers, J. Chem. Soc. 125, 2573 (1924); A. Seitz, Z. physik. Chem. A149, 337 (1930); A. Smits, J. A. A. Ketselaar and J. L. Meyerling, *ibid.*, B41, 87 (1938); and A. Seitz, *ibid.*, B46, 43 (1940).

Heat Capacity and Entropy.

The molecular structure and constants were obtained from P. A. Akishin, N. G. Rambidi and E. Z. Zaslavin, Kristallografiya, 3, 360 (1959). The molecular structure of P₂O₅ (g) has also been studied by the electron diffraction method by L. R. Maxwell, S. B. Hendricks and L. S. Deming, J. Chem. Phys. 5, 626 (1937), and G. C. Hampson and A. J. Stoeck, J. Am. Chem. Soc. 60, 1814 (1938). The model of the P₂O₅ molecule was later confirmed by the x-ray method reported by H. C. J. Decker and C. H. MacGillivray, Rec. trav. chim. 60, 153 (1941); and spectroscopic studies reported by H. Gerding and K. C. J. Decker, Rec. trav. chim. 65, 191 (1945), and T. A. Sidorov and N. N. Sobolev, Opt. Spectr. (USSR) 2, 717 (1957). All vibrational frequencies were obtained from E. P. Egan, Jr., private communication, Feb. 23, 1960, except nine frequencies, i.e. 170 (3), 470 (3) and 750 (3) cm⁻¹ which were estimated in order to make the second and third law values of ΔH_f^0 298.15 agree. The three principal moments of inertia are: $I_A = I_B = I_C = 1.4322 \times 10^{-37} \text{ cm}^2$. The heat capacities (549-1098°C. or 822-1371°K.) of P₂O₅ (g) have been determined by M. Prandsen, J. Res. Natl. Bur. Std. 10, 35 (1933). His results are in fair agreement with the calculated ones.

Tungsten Trioxide, Tetrameric (WO₃)₄

(Ideal Gas) GFW = 927.3928

TUNGSTEN TRIOXIDE, TETRAMERIC ((WO₃)₄) (IDEAL GAS)

OPW = 927.3928

Point Group [D_{2h}] $\Delta H_f^\circ = -666.7$ kcal/mol $S_{298.15}^\circ = [144.6]$ gbbbs/mol $\Delta H_f^{298.15} = -670.2 \pm 10$ kcal/mol

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies

ω , cm ⁻¹	ω , cm ⁻¹
[800] (8)	[240] (8)
[300] (8)	[200] (18)

Bond Distance: W-O = [1.81] Å

Bond Angle: O-W-O = [109.47°], W-O₂-bridge-W = [160.53°]Product of the Moments of Inertia: $I_A I_B I_C = [3.854 \times 10^{-109}]$ g²cm⁶ $\sigma^\circ = [8]$

Heat of Formation

The adopted value, $\Delta H_f^{298}(\text{WO}_3, \text{g}) = -670.2$ kcal/mol, was reduced from $\Delta H_f^{1450}(\text{WO}_3, \text{g}) = -655.6$ kcal/mol of R. J. Ackermann and E. G. Rauh, J. Phys. Chem. **67**, 2598 (1963), who studied the sublimation behavior of the tungsten-oxygen system over the temperature range from 1300 to 1600°K by mass spectrometry, mass effusion and x-ray diffraction, and determined $\Delta H_f^\circ(\text{WO}_3, \text{g}) = -655.600 \pm 160.29$ T (cal/mol) from partial pressure measurements over the W-WO₃(c). They reviewed the previous determinations 1,2,3,4 of the thermodynamic properties of sublimation of WO₃, and also pointed out that it was not possible to make quantitative observations on stoichiometric WO₃ in vacuo, since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches WO_{2.98}. This is probably the cause of previous discrepancies in sublimation studies.

J. E. Battles, Ph. D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide", The Ohio State University, 1964, has also studied the partial pressure of WO₃(g) over W-WO₃(c) in the temperature range from 1449 to 1527°K. Third law calculation of the partial pressure data gives $\Delta H_f^{298} = -172.0$ kcal/mol for $6 \text{ WO}_2(\text{c}) = \text{W}_6\text{O}_{12}(\text{g}) + 2 \text{ W}(\text{c})$, which yields $\Delta H_f^{298}(\text{WO}_3, \text{g}) = -675.6$ kcal/mol, using all JANAF functions.

References 1. K. Ueno, J. Chem. Soc. Japan **62**, 990 (1941).2. J. Berkowitz, W. A. Chupke, and M. G. Inghram, J. Chem. Phys. **27**, 85 (1957).3. P. E. Blackburn, M. Hoch, and H. L. Johnston, J. Phys. Chem. **62**, 769 (1958).

P. E. Blackburn, WADC TR 59-575, part 1, Mar. 1960; and part 2, Dec. 1960.

4. G. Meyer, J. P. Oosterom, and J. L. DeRoos, Rec. Trav. Chim. **78**, 412 (1959).

Investigator	Chemical Reaction	Temperature (°K)	ΔH_f^{298} (kcal/mol)	Drift (eu)	$\Delta H_f^{298}(\text{WO}_3, \text{g})^\circ$ (kcal/mol)
Ackermann & Rauh	$6 \text{ WO}_2(\text{c}) = \text{W}_6\text{O}_{12}(\text{g}) + 2 \text{ W}(\text{c})$	1300 - 1600°	175.41	175.55	-670.2
Battles	$6 \text{ WO}_2(\text{c}) = \text{W}_6\text{O}_{12}(\text{g}) + 2 \text{ W}(\text{c})$	1449 - 1527°	176.16	172.01	-673.6

* Third law value adopted in calculation.

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1} (s), 300 cm^{-1} (s), 240 cm^{-1} (s), and 200 cm^{-1} (s) in order to give the entropy at 1450°K , $S_{1450}^\circ = 276.9$ eu, corresponding to $\Delta H_f^{1450} = -160.29$ eu, reported by Ackermann and Rauh. The adopted value, $S_{298}^\circ(\text{WO}_3, \text{g}) = 144.6$ eu, was reduced from the entropy at 1450°K , using JANAF functions. Second law calculation of the partial pressure data of Battles gives $\Delta H_f^{1487} = 82.3$ eu for $6 \text{ WO}_2(\text{c}) = \text{W}_6\text{O}_{12}(\text{g}) + 2 \text{ W}(\text{c})$. This yields $S_{298}^\circ(\text{WO}_3, \text{g}) = 147.4$ eu.

The molecular configuration for $\text{W}_6\text{O}_{12}(\text{g})$ is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedron shares two oxygen atoms to form a planar eight-member ring. The bond distance W-O is estimated as 1.81 Å and the bond angles O-W-O = 109.47° and W-O₂-bridge-W = 160.53° . The three principal moments of inertia are $I_A = I_B = 5.855 \times 10^{-37}$ g cm², and $I_C = 1.034 \times 10^{-36}$ g cm².

Mar. 31, 1963; Sept. 30, 1966

Phosphorus (P)

(Reference State) At. Wt. = 30.975

T, °K.	C _p	cal. mole ⁻¹ deg ⁻¹	S°	-(H°-H° ₂₉₈)/T	cal. mole ⁻¹	H°-H° ₂₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _f
0	2.000	1.000	INFINITE	=	.062	.000	.000	.000	.000
100	2.000	1.000	1.000	=	.062	.000	.000	.000	.000
200	2.000	1.000	1.000	=	.062	.000	.000	.000	.000
298	5.084	5.450	5.450	=	.000	.000	.000	.000	.000
300	5.079	5.450	5.450	.009	.000	.000	.000	.000	.000
400	5.540	7.011	5.655	.542	.000	.000	.000	.000	.000
500	5.652	8.263	6.037	1.113	.000	.000	.000	.000	.000
600	6.165	9.377	6.521	1.714	.000	.000	.000	.000	.000
700	6.500	10.352	7.000	2.347	.000	.000	.000	.000	.000
800	6.700	11.124	7.637	2.930	.000	.000	.000	.000	.000
900	6.816	11.700	8.150	3.466	.000	.000	.000	.000	.000
1000	6.860	12.100	8.675	3.955	.000	.000	.000	.000	.000
1100	6.819	11.520	9.024	24.746	.000	.000	.000	.000	.000
1200	6.434	11.905	10.915	25.169	.000	.000	.000	.000	.000
1300	6.407	12.261	12.543	25.633	.000	.000	.000	.000	.000
1400	6.407	12.581	13.964	26.076	.000	.000	.000	.000	.000
1500	6.407	12.899	15.216	26.524	.000	.000	.000	.000	.000
1600	6.475	13.187	16.330	26.971	.000	.000	.000	.000	.000
1700	6.482	13.459	17.330	27.419	.000	.000	.000	.000	.000
1800	6.486	13.715	18.233	27.867	.000	.000	.000	.000	.000
1900	6.484	13.956	19.054	28.316	.000	.000	.000	.000	.000
2000	6.484	14.186	19.805	28.766	.000	.000	.000	.000	.000
2100	6.504	14.408	20.496	29.216	.000	.000	.000	.000	.000
2200	6.509	14.618	21.133	29.667	.000	.000	.000	.000	.000
2300	6.513	14.816	21.723	30.118	.000	.000	.000	.000	.000
2400	6.516	15.010	22.273	30.570	.000	.000	.000	.000	.000
2500	6.522	15.195	22.786	31.021	.000	.000	.000	.000	.000
2600	6.526	15.372	23.267	31.474	.000	.000	.000	.000	.000
2700	6.529	15.543	23.718	31.927	.000	.000	.000	.000	.000
2800	6.533	15.708	24.144	32.380	.000	.000	.000	.000	.000
2900	6.537	15.867	24.545	32.833	.000	.000	.000	.000	.000
3000	6.540	16.021	24.923	33.287	.000	.000	.000	.000	.000
3100	6.544	16.170	25.286	33.741	.000	.000	.000	.000	.000
3200	6.547	16.314	25.628	34.196	.000	.000	.000	.000	.000
3300	6.550	16.454	25.954	34.650	.000	.000	.000	.000	.000
3400	6.553	16.590	26.265	35.106	.000	.000	.000	.000	.000
3500	6.557	16.722	26.562	35.561	.000	.000	.000	.000	.000
3600	6.560	16.850	26.846	36.017	.000	.000	.000	.000	.000
3700	6.563	16.975	27.118	36.473	.000	.000	.000	.000	.000
3800	6.566	17.097	27.379	36.929	.000	.000	.000	.000	.000
3900	6.569	17.216	27.629	37.386	.000	.000	.000	.000	.000
4000	6.572	17.331	27.871	37.843	.000	.000	.000	.000	.000
4100	6.575	17.444	28.103	38.300	.000	.000	.000	.000	.000
4200	6.578	17.555	28.326	38.758	.000	.000	.000	.000	.000
4300	6.581	17.662	28.542	39.216	.000	.000	.000	.000	.000
4400	6.584	17.766	28.751	39.674	.000	.000	.000	.000	.000
4500	6.587	17.867	28.952	40.133	.000	.000	.000	.000	.000
4600	6.589	17.971	29.147	40.591	.000	.000	.000	.000	.000
4700	6.592	18.070	29.336	41.050	.000	.000	.000	.000	.000
4800	6.595	18.167	29.519	41.510	.000	.000	.000	.000	.000
4900	6.598	18.262	29.697	41.969	.000	.000	.000	.000	.000
5000	6.601	18.355	29.869	42.429	.000	.000	.000	.000	.000
5100	6.604	18.446	30.036	42.890	.000	.000	.000	.000	.000
5200	6.607	18.535	30.199	43.350	.000	.000	.000	.000	.000
5300	6.609	18.623	30.357	43.811	.000	.000	.000	.000	.000
5400	6.612	18.709	30.511	44.272	.000	.000	.000	.000	.000
5500	6.615	18.794	30.660	44.733	.000	.000	.000	.000	.000
5600	6.618	18.877	30.806	45.195	.000	.000	.000	.000	.000
5700	6.621	18.959	30.949	45.657	.000	.000	.000	.000	.000
5800	6.623	19.039	31.088	46.119	.000	.000	.000	.000	.000
5900	6.626	19.118	31.223	46.581	.000	.000	.000	.000	.000
6000	6.629	19.195	31.355	47.044	.000	.000	.000	.000	.000

June 30, 1961

(REFERENCE STATE)

PHOSPHORUS (P)

AT. WT. = 30.975

The selected reference states are:

O to 704°K. Solid Phosphorus (Red.V)

704 to 6000°K. Ideal Diatomic Gas

For details see Phosphorus (Red.V) and P₂ (Ideal Gas).

P

Phosphorus, Red, V. (P)
(Crystal) At. Wt. = 30.975

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	$-(F^{\circ}-H_{298}^{\circ})/T$	$H^{\circ}-H_{298}^{\circ}$ kcal. mole ⁻¹	ΔF_f°	Log K _p
0	2.000	INFINITE	0.000	0.000	INFINITE
100	4.072	3.419	0.000	0.000	0.000
200	5.079	5.450	0.000	0.000	0.000
298	5.079	5.450	0.000	0.000	0.000
300	5.079	5.450	0.000	0.000	0.000
400	5.352	6.292	0.000	0.000	0.000
500	5.352	6.292	0.000	0.000	0.000
600	6.165	9.376	1.713	0.000	0.000
700	6.500	10.351	2.306	0.000	0.000
800	6.840	11.241	2.745	0.000	0.000
900	7.180	12.061	3.074	0.000	0.000
1000	7.520	12.841	3.314	0.000	0.000
1100	7.860	13.573	3.468	0.000	0.000
1200	8.200	14.272	3.548	0.000	0.000
1300	8.540	14.942	3.558	0.000	0.000
1400	8.880	15.587	3.498	0.000	0.000
1500	9.220	16.211	3.278	0.000	0.000
1600	9.560	16.817	2.908	0.000	0.000
1700	9.900	17.407	2.408	0.000	0.000
1800	10.240	17.982	1.788	0.000	0.000
1900	10.580	18.543	1.068	0.000	0.000
2000	10.920	19.090	0.268	0.000	0.000

AT. WT. = 30.975

(CRYSTAL)

PHOSPHORUS, RED, V. (P)

$\Delta H_f^{\circ} = 0$ kcal. mole⁻¹
 $\Delta H_g^{\circ} = 7.69 \pm 0.1$ kcal. mole⁻¹
 $T_m = 870^{\circ}\text{K}$
 $\Delta H_f^{\circ} = 0$ kcal. mole⁻¹
 $S_{298.15}^{\circ} = 5.45 \pm 0.02$ cal. deg.⁻¹ mole⁻¹
 $\Delta H_m^{\circ} = 4.5 \pm 0.2$ kcal. mole⁻¹

Heat of Formation

Zero by definition below 704°K. See P₂(g) sheet for details above 704°K.

Heat Capacity and Extrapolation

The only reliable low temperature measurements, 15 to 305°K, are reported by R. L. Potter, Dissertation, Massachusetts Institute of Technology (1946). A value at 10°K was obtained by graphical extrapolation and a T³ function was assumed from 0 to 10°K. High temperature heat capacities were obtained from a smooth curve joining the measurements of O. Kubaschewski and O. Schrag, Z. Elektrochem. 46, 875 (1940), in the range 573 to 773°K and that of V. Regnault, Ann. chim. phys. 9, 322 (1843) at 331°K with those of Potter. Measurements of A. Wigand, Ann. Physik, 22, 64 (1907), are too high. The uncertainty in the high temperature heat capacity is about 2%.

Melting

The values of ΔH_m and T_m were calculated from the functions of the solid and liquid. This may be compared with a reported triple point of 862.7°K by A. Smits and S. C. Bokhorst, Verh. Akad. Wetenschap. 23, 930 (1914).

Heat of Sublimation

Vapor pressure measurements on the triclinic allotrope, T. V. A. designation V, are reported by T. D. Farr, Tennessee Valley Authority Chemical Engineering Report No. 8 (1950). These data lead to a sublimation point of 704°K and ΔH_g° 298.15 of 30.77 ± 0.4 kcal. mole⁻¹ of P₄. A. Smits and S. C. Bokhorst, Z. phys. Chem. 91, 248 (1916), measured the vapor pressure of a sample whose preparation indicates that it was probably P, V. These results lead to ΔH_g° 298.15 = 30.6 ± 1 kcal. An unpublished value of 30.84 kcal. mole⁻¹ of P₄ by C. C. Stephenson is quoted by J. S. Kane, Thesis Univ. of California (1955).

D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941), show that the vapor density measurements of A. Stock, G. E. Gibson and E. Stamm, Ber. 45, 3527 (1912) are best explained by a vapor essentially composed of only P₄(g) below 800°K. This conclusion is supported by recent mass spectrometer measurements of J. S. Kane and J. H. Reynolds, J. Chem. Phys. 25, 342 (1956).

(Crystal) At. Wt. = 30.975

T. °K.	C _p	cal. mole ⁻¹ deg. ⁻¹	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	cal. mole ⁻¹	ΔH _f °	ΔF _f °	Log K _f
0	5.000	INFINITE	1.261			3.754	INFINITE		
100	5.051	9,278	1.528			3.754			
200	5.101	10,318	1.598			3.754			
298	5.168	9,818	1.600			4.173	2.871	2.104	
300	5.705	9,853	9,818	0.11		4.175	2.863	2.085	
400	6.050	11,523	10,046	1.599		4.230	2.817	1.320	
500	6.330	12,523	10,488	1.218		4.278	1.958	0.856	
600	6.330	14,079	10,993	1.651		4.310	1.489	0.542	
700	6.330	15,054	11,505	2.484		4.310	1.019	0.318	
800	6.330	15,900	12,003	3.117		16,140	0.760	1.300	
900	6.330	16,645	12,478	3.750		15,943	0.349	0.813	
1000	6.330	17,312	12,929	4.383		15,749	1.761	0.429	
1100	6.330	17,916	13,355	5.016		15,557	0.592	0.118	
1200	6.330	18,466	13,759	5.649		15,367	0.760	0.138	
1300	6.330	18,973	14,140	6.282		15,178	2.097	0.352	
1400	6.330	19,442	14,503	6.915		14,990	3.419	0.534	
1500	6.330	19,879	14,847	7.548		14,803	4.728	0.689	

PHOSPHORUS, WHITE (P)

(CRYSTAL)

AT. WT. = 30.975

$$\Delta H_f^\circ = 3.75 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_g^\circ = 3.52 \pm 0.05 \text{ kcal. mole}^{-1}$$

$$\Delta H_t^\circ = 124.62 \pm 0.2 \text{ cal. mole}^{-1}$$

$$\Delta H_m^\circ = 157.43 \pm 0.5 \text{ cal. mole}^{-1}$$

Heat Capacity and Extrapolation

Low temperature measurements, 15-315°K, were made by R. T. Maples, Dissertation, Massachusetts Institute of Technology (1949). A Debye θ temperature of 124 was used to extrapolate to 0°K. P. E. Young and J. H. Hildenbrand, *J. Am. Chem. Soc.* **54**, 859 (1942), obtained heat capacities from enthalpy measurements that are 4% higher than those from the low temperature calorimeter which are preferred because of the proximity to the melting point.

Transition

Observed by Maples.

Melting

The selected heat of fusion is that observed by Maples. Young and Hildenbrand obtain 125 cal. mole⁻¹ for the same quantity. Maples' value is consistent with vapor pressures and other thermochemical data; see P(11q) and P₄(g) sheets.

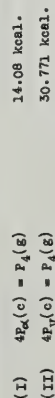
Heat of Sublimation

The vapor pressure measurements of P. S. Dainton and H. M. Kimberly, *Trans. Faraday Soc.* **46**, 912 (1950), are the most precise and lead to $\Delta H_{g,298.15}^\circ = 14.08 \pm 0.2 \text{ kcal. mole}^{-1}$ of P₄. Measurements of A. Jolibois, *Compt. rend.* **249**, 287 (1908), A. Smits and S. C. Bokhorst, *Z. Phys. Chem.* **91**, 246 (1916), and M. Gentszner, *Z. phys. Chem.* **95**, 89 (1913) lead to values that agree within the assigned uncertainty.

Heat of Formation

The heat of formation is obtained from the heats of sublimation represented by reaction I and II at 298.15°K.

See P, V sheet for details.



Of the calorimetric determinations only those of H. Giren, *Ann. Chim. Phys.* **30**, 203 (1903) result in a reliable value for the heat of formation, $4.4 \pm 0.4 \text{ kcal. mole}^{-1}$. A comprehensive review is given by H. J. Rodewald, *Helv. Chim. Acta* **43**, 878 (1960).

June 30, 1961

Phosphorus (P)

(Liquid) At. Wt. = 30.975

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH° _f	Log K _P
100					
200					
298	6.292	10.249	0.000	4.322	2.891
300	6.292	10.249	0.012	4.325	2.883
400	6.292	12.098	0.461	4.421	2.386
500	6.292	13.582	1.270	4.479	1.870
600	6.292	14.849	1.899	4.507	1.344
700	6.292	15.619	2.528	4.503	0.816
800	6.292	16.120	3.157	4.481	0.289
900	6.292	16.400	3.787	4.446	-0.240
1000	6.292	17.563	4.416	4.390	-0.769
1100	6.292	18.463	5.045	4.319	-1.298
1200	6.292	19.010	5.674	4.231	-1.827
1300	6.292	19.380	6.303	4.128	-2.356
1400	6.292	19.580	6.933	4.012	-2.885
1500	6.292	20.614	7.562	3.885	-3.414
1600	6.292	20.621	8.191	3.749	-3.943
1700	6.292	21.202	8.820	3.605	-4.472
1800	6.292	21.567	9.449	3.453	-5.001
1900	6.292	21.902	10.079	3.295	-5.530
2000	6.292	22.225	10.708	3.133	-6.059
2100	6.292	22.532	11.337	2.967	-6.588
2200	6.292	22.824	11.966	2.797	-7.117
2300	6.292	23.102	12.595	2.623	-7.646
2400	6.292	23.372	13.225	2.445	-8.175
2500	6.292	23.629	13.854	2.263	-8.704
2600	6.292	23.875	14.483	2.078	-9.233
2700	6.292	24.113	15.112	1.891	-9.762
2800	6.292	24.342	15.741	1.702	-10.291
2900	6.292	24.562	16.371	1.511	-10.820
3000	6.292	24.776	17.000	1.319	-11.349

PHOSPHORUS (P)

(LIQUID)

AT. WT. = 30.975

$$\Delta H_{f, 298.15}^{\circ} = 5.2 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$\Delta H_{f, 298.15}^{\circ} = 10.25 \pm 0.03 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^{\circ}, P_A \rightarrow P(lq) = 157.43 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_m^{\circ}, P_V \rightarrow P(lq) = 4.5 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$\Delta H_{f, 298.15}^{\circ} = 3.37 \pm 0.03 \text{ kcal. mole}^{-1}$$

$$P_c = [95.3] \text{ atm.}$$

Heat of Formation

Derived from the ΔH_m° by the following cycle:

$$(I) \quad P \quad 317.30 = P(lq) \quad 0.157 \text{ kcal.}$$

$$(II) \quad P_A \quad 298.15 = P_A \quad 317.30 \quad 0.113$$

$$(III) \quad P(lq) \quad 317.30 = P(lq) \quad 298.15 \quad -0.121$$

$$(IV) \quad P_V \quad 298.15 = P_A \quad 298.15 \quad 4.08$$

The $\Delta H_{f, 298.15}^{\circ}$ obtained from vapor pressure measurements on P_V and on the liquid is 4.32 kcal. mole⁻¹ in agreement with that derived from the melting point.

Heat Capacity

P. E. Young and J. H. Hildenbrand, J. Am. Chem. Soc. **64**, 839 (1942), obtained an equation from enthalpy measurements which decreased with temperature. However, a better fit to the thermochemical data results if a constant heat capacity is assumed.

Entropy

Derived from low temperature measurements on P_V , White. See P, White sheet for details.

Vaporization Phenomena

D. MacRae and C. C. Van Voorhis, J. Am. Chem. Soc. **43**, 547 (1921), determinations of the vapor pressure, 44 to 150°C, are the most precise and lead to a $\Delta H_{f, 298.15}^{\circ}$ of 13.504 ± 0.1 kcal. mole⁻¹ of P_4 . A vapor pressure equation derived by T. D. Farr, Tennessee Valley Authority Chemical Engineering Report No. 8 (1950) to fit the measurements reported in the literature leads to a value of 13.6 ± 0.1 kcal. mole⁻¹ of P_4 . The boiling point is calculated from the functions of $P(lq)$ and $P_A(g)$, and may be compared with the values of 552.7 and 553.7 resulting from Farr's equation and observations of A. Smits and S. C. Bokhorst, Proc. Akad. Wetenschap. **16**, 106 (1915) respectively.

Critical Phenomena

T_c determined and P_c estimated by W. Marchwald and R. Helmholz, Z. anorg. Chem. **124**, 81 (1922).

T, °K	C _p ^o	cal. mole ⁻¹ deg. ⁻¹	S ^o	-(H ^o -H ₂₉₈ ^o)/T	H ^o -H ₂₉₈ ^o	ΔH _f ^o	Log K _p
0	4.000	INFINITE	1.481	79.176	79.176	INFINITE	
100	4.948	33.552	43.397	79.582	76.376	-166.911	
200	4.968	39.434	48.88	79.760	79.060	-79.860	
298	4.968	38.980	49.000	79.795	69.798	-51.161	
300	4.968	38.980	49.009	79.795	69.736	-50.800	
400	4.968	40.440	39.175	5.06	79.759	66.388	-36.271
500	4.968	41.548	39.543	1.003	79.685	63.052	-27.559
600	4.968	42.454	39.955	1.500	79.581	59.734	-21.757
700	4.968	43.163	40.367	2.000	79.457	56.417	-17.000
800	4.968	43.683	40.767	2.499	79.308	53.100	-13.072
900	4.968	44.146	41.146	2.990	79.139	49.783	-10.000
1000	4.968	44.562	41.505	3.487	78.957	46.467	-8.000
1100	4.968	44.946	41.844	3.984	78.765	43.151	-6.000
1200	4.968	45.298	42.164	4.481	78.558	39.836	-4.000
1300	4.971	45.596	42.467	4.978	78.336	36.521	-2.000
1400	4.974	45.844	42.754	5.475	78.100	33.206	0.000
1500	4.979	46.048	43.026	5.972	77.850	29.891	2.000
1600	4.987	46.209	43.285	6.471	77.585	26.576	4.000
1700	4.999	46.339	43.530	6.970	77.306	23.261	6.000
1800	5.015	46.438	43.766	7.470	76.913	19.946	8.000
1900	5.036	46.510	43.993	7.973	76.416	16.631	10.000
2000	5.062	46.549	44.210	8.478	75.815	13.316	12.000
2100	5.094	46.556	44.417	8.986	75.108	10.001	14.000
2200	5.132	46.533	44.600	9.497	74.306	6.686	16.000
2300	5.175	46.483	44.761	10.012	73.410	3.371	18.000
2400	5.225	46.408	44.900	10.532	72.430	0.056	20.000
2500	5.279	46.300	45.017	11.057	71.375	-3.259	22.000
2600	5.339	46.167	45.110	11.586	70.246	-6.574	24.000
2700	5.407	46.000	45.188	12.120	69.043	-9.900	26.000
2800	5.481	45.800	45.243	12.660	67.768	-13.225	28.000
2900	5.562	45.567	45.275	13.207	66.421	-16.550	30.000
3000	5.651	45.300	45.280	13.777	65.003	-19.875	32.000
3100	5.749	45.000	45.250	14.383	63.516	-23.200	34.000
3200	5.857	44.667	45.188	15.027	61.963	-26.525	36.000
3300	5.975	44.300	45.093	15.710	60.350	-29.850	38.000
3400	6.101	43.900	44.957	16.433	58.675	-33.175	40.000
3500	6.236	43.467	44.775	17.200	56.940	-36.500	42.000
3600	6.380	43.000	44.543	18.013	55.145	-39.825	44.000
3700	6.533	42.500	44.260	18.875	53.290	-43.150	46.000
3800	6.696	42.000	43.927	19.788	51.385	-46.475	48.000
3900	6.869	41.500	43.550	20.750	49.430	-49.800	50.000
4000	7.052	41.000	43.127	21.763	47.435	-53.125	52.000
4100	7.245	40.500	42.650	22.825	45.400	-56.450	54.000
4200	7.448	40.000	42.127	23.938	43.325	-59.775	56.000
4300	7.661	39.500	41.550	25.099	41.210	-63.100	58.000
4400	7.884	39.000	40.927	26.308	39.055	-66.425	60.000
4500	8.127	38.500	40.250	27.565	36.860	-69.750	62.000
4600	8.390	38.000	39.527	28.869	34.625	-73.075	64.000
4700	8.663	37.500	38.750	30.220	32.350	-76.400	66.000
4800	8.946	37.000	37.927	31.618	30.035	-79.725	68.000
4900	9.239	36.500	37.050	33.062	27.680	-83.050	70.000
5000	9.542	36.000	36.127	34.551	25.285	-86.375	72.000
5100	9.855	35.500	35.150	36.085	22.840	-89.700	74.000
5200	10.178	35.000	34.127	37.665	20.345	-93.025	76.000
5300	10.511	34.500	33.050	39.290	17.800	-96.350	78.000
5400	10.854	34.000	31.927	40.960	15.205	-99.675	80.000
5500	11.207	33.500	30.750	42.675	12.560	-102.950	82.000
5600	11.570	33.000	29.527	44.435	9.865	-106.225	84.000
5700	11.943	32.500	28.250	46.240	7.120	-109.500	86.000
5800	12.326	32.000	26.927	48.090	4.325	-112.775	88.000
5900	12.719	31.500	25.550	49.985	1.480	-116.050	90.000
6000	13.122	31.000	24.127	51.925	-1.415	-119.325	92.000

June 30, 1962

PHOSPHORUS (P)

(IDEAL GAS)

MOL. WT. = 30.975

$\Delta H_f^o = 79.18 \pm 0.05$ kcal. mole⁻¹
 Ground State Configuration $4s^2 3s^2$

$\Delta H_f^o = 79.15 \pm 0.05$ kcal. mole⁻¹
 $S_{298.15}^o = 38.98$ cal. mole⁻¹ deg.⁻¹

Electronic Levels and Multiplicities

ϵ_1 , cm. ⁻¹	g_1	ϵ_2 , cm. ⁻¹	g_2
0	4	59,643	12
11,370	10	65,984	58
18,740	6	69,696	102
56,190	12	75,380	180
58,075	6	78,762	162
		80,835	202

Heat of Formation.

The ΔH_f^o 298.15 was derived by the following cycle:

- (1) $4 P_{red}(v)$ [298.15°] = $P_4(g)$ [298.15°] $\Delta H_f^o = 30.77$ kcal. mole⁻¹ of P_4 See $P_{red}(v)$ sheet under Heat of Sublimation.
- (2) $P_4(g)$ [298.15°] = $2P_2(g)$ [298.15°] $\Delta H_f^o = 54.59$ kcal. mole⁻¹ of P_4 See $P_2(g)$ sheet under Heat of Formation.
- (3) $2P_2(g)$ [298.15°] = $2P_2(g)$ [0°] $\Delta H_f^o = 2(-2.128)$ kcal. mole⁻¹ of P_4 See $P_2(g)$ table.
- (4) $2P_2(g)$ [0°] = $4P(g)$ [0°] $\Delta H_f^o = 2(116.075)$ kcal. mole⁻¹ of P_4 A. G. Daydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, 1953.
- (5) $4 P(g)$ [0°] = $4 P(g)$ [298.15°] $\Delta H_f^o = 4(1.481)$ kcal. mole⁻¹ of P_4 See $P(g)$ table.

D_0^o for reaction (4) was given by A. G. Daydon (loc. cit.). He reported a predissociation limit at 51,958 ± 9 cm.⁻¹. He considered the dissociation to be $P_2 \rightarrow P(^4S) + P(^2D)$. From the predissociation limit and the energy level of the excited $P(^2D)$ state [11,360.8 cm.⁻¹] Daydon (loc. cit.) obtained a $D_0^o = 5.033$ e.v. or 116.075 kcal. mole⁻¹. As a check, a graphical Birge-Sponer extrapolation by Daydon (loc. cit.) [$\sum_{j=1}^{\infty} (v_j - v_0)$] agrees with a $D_0^o = 5.0$ e.v.

The vapor equilibrium data of G. Freuner and I. Brockmoller, Z. physik. Chem. **81**, 129 (1913) gave a ΔH_f^o for reaction (4) which was much lower than the spectroscopic value i.e. 31.5(1073°K) vs. 116(0°) kcal. mole⁻¹ of P_2 . D. P. Stevenson and D. M. Yost, J. Chem. Phys. **9**, 403 (1941) reported that the vapor equilibrium measurements of G. Freuner and I. Brockmoller (loc. cit.) were doubtful while the measurements of A. Stook, G. E. Gibson, and E. Stamm Ber **45**, 3527 (1913) were correct. Stook et al. (loc. cit.) have shown that the reaction $P_2(g) \rightarrow 2P(g)$ is extremely slight even at 1473°K which is the highest temperature of the vapor equilibrium studies.

Heat Capacity and Entropy.

The thermodynamic functions were calculated from the electronic levels which were evaluated by averaging the spectroscopic values of W. C. Martin, J. Opt. Soc. Am. **49**, 1071, (1959).

Monophosphorus Monosulfide (PS)
(Ideal Gas) GFW = 63.0378

PS

T, °K	Cp°	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔHf°	ΔGf°	Log Kp
0	0.00	INFINITE	INFINITE	2.297	36.918	INFINITE	
100	7.302	47.280	6.205	-1.597	37.387	-72.307	
200	8.114	52.654	5.670	-0.813	37.436	-31.420	
298	8.423	55.958	5.558	-0.000	37.300	-24.516	
300	8.427	56.010	5.558	-0.016	37.297	-24.437	
400	8.506	58.461	5.196	1.267	36.507	-11.207	
500	8.718	60.395	5.025	1.735	35.975	-10.203	
600	8.793	61.991	57.640	2.610	35.292	-12.324	
700	8.845	63.351	58.361	3.492	34.741	-8.563	
800	8.883	64.534	59.061	4.379	34.200	-4.768	
900	8.913	65.582	59.728	5.266	33.669	-0.953	
1000	8.937	66.523	60.361	6.161	33.148	-2.931	
1100	8.956	67.376	60.961	7.056	32.641	-4.925	
1200	8.973	68.156	61.528	7.953	32.150	-6.937	
1300	8.988	68.874	62.066	8.851	31.678	-8.968	
1400	9.001	69.541	62.577	9.750	31.225	-11.020	
1500	9.013	70.162	63.062	10.651	30.789	-13.095	
1600	9.025	70.744	63.524	11.553	30.369	-15.195	
1700	9.035	71.292	63.965	12.456	29.964	-17.320	
1800	9.045	71.809	64.387	13.360	29.575	-19.470	
1900	9.055	72.298	64.790	14.265	29.200	-21.645	
2000	9.064	72.763	65.177	15.171	28.839	-23.845	
2100	9.073	73.205	65.549	16.077	28.492	-26.070	
2200	9.082	73.627	65.907	16.985	28.158	-28.320	
2300	9.091	74.031	66.251	17.894	27.836	-30.595	
2400	9.100	74.418	66.584	18.803	27.525	-32.895	
2500	9.109	74.790	66.904	19.714	27.225	-35.220	
2600	9.118	75.147	67.215	20.625	26.936	-37.570	
2700	9.126	75.492	67.515	21.537	26.658	-39.945	
2800	9.137	75.824	67.806	22.451	26.390	-42.345	
2900	9.148	76.145	68.088	23.365	26.132	-44.770	
3000	9.158	76.455	68.362	24.280	25.884	-47.220	
3100	9.170	76.755	68.628	25.197	25.646	-49.695	
3200	9.182	77.047	68.886	26.114	25.418	-52.195	
3300	9.195	77.330	69.138	27.033	25.199	-54.720	
3400	9.208	77.604	69.383	27.953	24.988	-57.270	
3500	9.223	77.871	69.621	28.873	24.784	-59.845	
3600	9.238	78.131	69.854	29.798	24.586	-62.445	
3700	9.254	78.385	70.081	30.722	24.394	-65.070	
3800	9.271	78.632	70.303	31.649	24.207	-67.720	
3900	9.289	78.873	70.520	32.577	24.024	-70.395	
4000	9.309	79.108	70.732	33.507	23.846	-73.095	
4100	9.329	79.338	70.939	34.438	23.672	-75.820	
4200	9.350	79.563	71.141	35.372	23.502	-78.570	
4300	9.372	79.784	71.340	36.309	23.336	-81.345	
4400	9.395	79.999	71.534	37.247	23.174	-84.145	
4500	9.418	80.211	71.725	38.187	23.016	-86.970	
4600	9.443	80.418	71.911	39.130	22.862	-89.820	
4700	9.469	80.621	72.095	40.076	22.712	-92.695	
4800	9.495	80.821	72.274	41.026	22.566	-95.595	
4900	9.522	81.017	72.451	41.980	22.424	-98.520	
5000	9.550	81.210	72.624	42.939	22.285	-101.470	
5100	9.578	81.399	72.794	43.895	22.150	-104.445	
5200	9.507	81.585	72.961	44.844	22.018	-107.445	
5300	9.537	81.769	73.126	45.806	21.889	-110.470	
5400	9.567	81.949	73.289	46.772	21.762	-113.520	
5500	9.598	82.127	73.447	47.740	21.638	-116.595	
5600	9.729	82.302	73.603	48.711	21.516	-119.695	
5700	9.760	82.474	73.757	49.686	21.396	-122.820	
5800	9.792	82.644	73.909	50.663	21.278	-125.970	
5900	9.823	82.812	74.059	51.644	21.162	-129.145	
6000	9.856	82.977	74.206	52.629	21.048	-132.345	

Dec. 31, 1960; June 30, 1961; June 30, 1967

MONOPHOSPHORUS MONOSULFIDE (PS)

(IDEAL GAS)

GFW = 63.0378

Ground State Configuration $2^1\Pi$

$S^0_{298.15} = 56 \pm 0.2$ gibbs/mol

$\Delta H^0_{298.15} = 36.9 \pm 10$ kcal/mol

$\Delta H^0_{298.15} = 37.3 \pm 10$ kcal/mol

Electronic Levels and Quantum Weights

e_i , cm ⁻¹	g_i	g_i
0	0	2
324	324	2
[20000]	2	2
22000	4	4
34594	2	2

$\omega_e = 743.5 \pm 3.8$ cm⁻¹ $\omega_e X_e = 3.8 \pm 0.9$ cm⁻¹ $\sigma = 1$

$B_e = [0.29]$ cm⁻¹ $\alpha_e = [0.0016]$ cm⁻¹ $r_e = [1.92]$ Å

Heat of Formation

The dissociation energy (D^0_0) of PS(g) is estimated to be 140 ± 25 kcal/mol by comparison with the corresponding quantity for PO(g) and from a linear Birge-Sponer extrapolation of the third excited ($C^2\Sigma$) electronic state potential function. It is assumed that the $C^2\Sigma$ state dissociates to S(g) in its ground (3P) state and P(g) in its first excited (3D) state. The fundamental vibrational frequency in the $C^2\Sigma$ state (ω_e) is 531.8 ± 2.5 cm⁻¹ and the corresponding anharmonic term ($\omega_e X_e$) is 2.6 ± 0.5 cm⁻¹. These constants are calculated from a reanalysis of the spectral data of Dressler (1). The corresponding heat of formation of PS(g) is 37.3 ± 25 kcal/mol. The excited state ($C^2\Sigma$) data are used to calculate D^0_0 instead of the ground state(X¹ Π) data because the vibrational constants of the upper level are known more accurately and because the extrapolation is 50 kcal/mol smaller for this level.

Heat Capacity and Entropy

The spectra of PS(g) have been studied by Dressler (1) in the near UV and visible regions. He reported the above electronic levels which correspond to the doublet pi ground state and two of the excited levels ($B^2\Pi$, $C^2\Sigma$). The level of the first excited electronic state ($A^2\Sigma$) is estimated by analogy with NO(g).

Dressler (1) estimated the value of the rotational constant B_e . The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e . The fundamental vibrational frequency ω_e and the anharmonic vibrational term $\omega_e X_e$ are calculated from a reanalysis of the spectral data reported by Dressler (1).

References

1. K. Dressler, *Helv. Phys. Acta* **28**, 563 (1955).

PS

Phosphorus, Diatomic (P₂)

(Ideal Gas) Mol. Wt. = 61.950

P₂PHOSPHORUS, DIATOMIC (P₂) (IDEAL GAS) MOL. WT. = 61.950

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0	0.000	INFINITE	0.000	42.276	42.276	INFINITE
100	0.000	48.747	2.124	42.276	42.276	INFINITE
200	7.195	52.795	0.000	42.637	38.675	97.470
298	7.657	52.110	0.000	42.680	30.393	22.276
300	7.665	52.157	.014	42.676	30.318	22.085
400	6.050	54.418	.801	42.397	26.239	14.335
500	6.311	56.744	1.620	42.074	22.235	9.716
600	6.485	57.776	2.460	41.712	18.299	6.665
700	6.604	58.021	3.315	41.301	14.529	4.505
800	6.690	60.248	4.180	40.840	10.900	3.000
900	6.752	61.275	5.052	40.337	7.429	2.000
1000	6.800	62.200	5.930	39.790	4.000	1.000
1100	6.836	63.041	6.812	39.200	0.000	0.000
1200	6.868	63.811	7.697	38.568	0.000	0.000
1300	6.893	64.522	8.585	37.890	0.000	0.000
1400	6.914	65.182	9.476	37.168	0.000	0.000
1500	6.933	65.797	10.366	36.400	0.000	0.000
1600	6.949	66.374	11.262	35.588	0.000	0.000
1700	6.963	66.917	12.158	34.732	0.000	0.000
1800	6.976	67.430	13.055	33.832	0.000	0.000
1900	6.987	67.916	13.953	32.888	0.000	0.000
2000	6.996	68.377	14.852	31.900	0.000	0.000
2100	7.008	68.816	15.752	30.868	0.000	0.000
2200	7.018	69.235	16.654	29.792	0.000	0.000
2300	7.026	69.636	17.556	28.672	0.000	0.000
2400	7.035	70.021	18.459	27.508	0.000	0.000
2500	7.043	70.390	19.363	26.300	0.000	0.000
2600	7.051	70.745	20.268	25.048	0.000	0.000
2700	7.056	71.086	21.173	23.752	0.000	0.000
2800	7.066	71.416	22.079	22.412	0.000	0.000
2900	7.073	71.734	22.986	21.028	0.000	0.000
3000	7.080	72.042	23.894	19.600	0.000	0.000
3100	7.087	72.340	24.802	18.128	0.000	0.000
3200	7.093	72.628	25.711	16.612	0.000	0.000
3300	7.100	72.908	26.621	15.052	0.000	0.000
3400	7.106	73.180	27.531	13.448	0.000	0.000
3500	7.113	73.444	28.442	11.792	0.000	0.000
3600	7.119	73.701	29.354	10.088	0.000	0.000
3700	7.125	73.951	30.266	8.336	0.000	0.000
3800	7.131	74.194	31.179	6.536	0.000	0.000
3900	7.137	74.431	32.092	4.688	0.000	0.000
4000	7.143	74.663	33.006	2.792	0.000	0.000
4100	7.149	74.889	33.921	0.848	0.000	0.000
4200	7.155	75.109	34.836	-1.148	0.000	0.000
4300	7.161	75.325	35.752	-3.184	0.000	0.000
4400	7.167	75.535	36.668	-5.260	0.000	0.000
4500	7.173	75.741	37.589	-7.376	0.000	0.000
4600	7.178	75.943	38.503	-9.532	0.000	0.000
4700	7.184	76.141	39.421	-11.728	0.000	0.000
4800	7.190	76.334	40.340	-13.964	0.000	0.000
4900	7.196	76.528	41.259	-16.240	0.000	0.000
5000	7.201	76.719	42.179	-18.556	0.000	0.000
5100	7.207	76.907	43.099	-20.912	0.000	0.000
5200	7.213	77.070	44.020	-23.308	0.000	0.000
5300	7.218	77.246	44.942	-25.744	0.000	0.000
5400	7.224	77.418	45.864	-28.220	0.000	0.000
5500	7.229	77.586	46.786	-30.736	0.000	0.000
5600	7.235	77.754	47.710	-33.292	0.000	0.000
5700	7.241	77.916	48.633	-35.888	0.000	0.000
5800	7.246	78.078	49.558	-38.524	0.000	0.000
5900	7.252	78.236	50.483	-41.200	0.000	0.000
6000	7.257	78.392	51.408	-43.916	0.000	0.000

June 30, 1961

D₀^o = 118 ± 1 kcal. mole⁻¹ ΔH_f^o 298.15 = 42.68 ± 0.5 kcal. mole⁻¹Ground State Configuration 1Σ⁺ 3Σ_g⁺ = 52.11 ± 0.1 cal. deg.⁻¹ mole⁻¹Δ₀^o = 780.45 cm.⁻¹ Δ₀^o = 0.21 X 10⁻⁶ cm.⁻¹B₀^o = 0.30327 cm.⁻¹ r₀^o = 1.8943 Å

Heat of Formation

D. P. Stevenson and D. M. Yost, J. Chem. Phys. 9, 403 (1941), have shown that the vapor density measurements of A. Stock, O. E. Gibson and E. Stamm, Ber. 45, 3527 (1912), best fit a vapor composed of P₂ and P₄ molecular species. From these data T. D. Parr, Tennessee Valley Authority, Chemical Engineering Report No. 8, calculated the equilibrium constants which lead to a ΔH_f^o of P₂ for 1. From which ΔH_f^o of P₂ is obtained based upon a ΔH_f^o 298.15 of 30.77 kcal. mole⁻¹ of P₄(g).

(1) P₄(g) 298.15 = P₂(g) 298.15ΔH_r^o = 54.59 ± 0.1 kcal. mole⁻¹

Heat Capacity and Entropy

Molecular and spectroscopic constants are those listed by G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co. Inc., New York, 1945. More recent measurements of K. Dressler, Helv. Phys. Acta 28, 563 (1955) are in agreement with the values selected by Herzberg.

The dissociation energy is given by A. G. Gaydon, "Dissociation Energies", Chapman and Hall, Ltd., London, 1953.

P₂

Phosphorus, Tetratomic (P₄)

(Ideal Gas) Mol. Wt. = 123.90

T, K.	C _p ^o	S ^o - (F°-H ₂₉₈ °)/T	H°-H ₂₉₈ °	ΔH _f ^o	ΔF _f ^o	Log K _p
0	4.000	INFINITE	3.376	30.884	INFINITE	
100	13.294	61.010	1.425	21.821	21.821	12.700
200	16.041	66.893	0.000	30.771	17.337	12.700
298	16.046	66.892	0.000	30.765	17.284	12.562
300	16.046	66.892	0.000	30.765	17.284	12.562
400	16.241	75.835	3.510	29.829	16.478	3.706
600	16.735	79.212	5.363	29.278	4.256	1.550
700	16.922	82.123	7.252	28.635	25.135	0.042
800	17.074	84.676	9.164	27.885	53.785	6.865
900	17.204	86.877	11.093	27.056	21.556	5.234
1000	17.313	88.791	13.033	26.146	10.507	3.735
1100	17.404	90.448	14.981	25.152	5.232	2.876
1200	17.474	91.849	16.936	24.099	53.049	1.997
1300	17.524	92.949	18.895	22.886	7.461	1.254
1400	17.562	93.772	20.859	21.662	3.874	0.620
1500	17.590	94.459	22.826	20.439	2.499	0.073
1600	17.603	94.900	24.795	19.218	1.268	
1700	17.613	95.235	26.766	18.000	0.410	
1800	17.621	95.483	28.739	16.785	0.000	
1900	17.626	95.650	30.724	15.580	1.327	
2000	17.629	95.741	32.729	14.385	1.827	
2100	17.631	95.774	34.666	13.200	2.335	
2200	17.632	95.789	36.644	12.027	2.856	
2300	17.633	95.796	38.663	10.864	3.387	
2400	17.634	95.801	40.662	9.711	3.917	
2500	17.635	95.804	42.652	8.568	4.447	
2600	17.636	95.806	44.633	7.435	4.976	
2700	17.637	95.807	46.606	6.312	5.505	
2800	17.638	95.808	48.571	5.200	6.034	
2900	17.639	95.809	50.528	4.099	6.563	
3000	17.640	95.810	52.477	3.008	7.092	
3100	17.641	95.811	54.419	2.921	7.621	
3200	17.642	95.812	56.354	2.835	8.150	
3300	17.643	95.813	58.281	2.750	8.679	
3400	17.644	95.814	60.201	2.665	9.208	
3500	17.645	95.815	62.115	2.580	9.737	
3600	17.646	95.816	64.024	2.495	10.266	
3700	17.647	95.817	65.928	2.410	10.795	
3800	17.648	95.818	67.827	2.325	11.324	
3900	17.649	95.819	69.721	2.240	11.853	
4000	17.650	95.820	71.610	2.155	12.382	
4100	17.651	95.821	73.494	2.070	12.911	
4200	17.652	95.822	75.373	1.985	13.440	
4300	17.653	95.823	77.247	1.900	13.969	
4400	17.654	95.824	79.116	1.815	14.498	
4500	17.655	95.825	80.980	1.730	15.027	
4600	17.656	95.826	82.839	1.645	15.556	
4700	17.657	95.827	84.693	1.560	16.085	
4800	17.658	95.828	86.542	1.475	16.614	
4900	17.659	95.829	88.386	1.390	17.143	
5000	17.660	95.830	90.225	1.305	17.672	
5100	17.661	95.831	92.059	1.220	18.201	
5200	17.662	95.832	93.888	1.135	18.730	
5300	17.663	95.833	95.712	1.050	19.259	
5400	17.664	95.834	97.531	0.965	19.788	
5500	17.665	95.835	99.345	0.880	20.317	
5600	17.666	95.836	101.154	0.795	20.846	
5700	17.667	95.837	102.958	0.710	21.375	
5800	17.668	95.838	104.757	0.625	21.904	
5900	17.669	95.839	106.551	0.540	22.433	
6000	17.670	95.840	108.340	0.455	22.962	

June 30, 1961

PHOSPHORUS, TETRATOMIC (P₄) (IDEAL GAS)

MOL. WT. = 123.90

ΔH_f^o = 30.84 ± 0.5 kcal. mole⁻¹
 ΔH_f^o = 288.15 = 30.77 ± 0.5 kcal. mole⁻¹
 S_{298.15}^o = 66.89 ± 0.1 cal. deg.⁻¹ mole⁻¹

Point Group T_d

Vibrational Levels and Multiplicities

(ω, cm.⁻¹)

806 (1)
 363 (2)
 464.5 (3)

Bond Lengths and Angles P-P = 2.21 ± 0.2 Å
 Moments of Inertia I_A = I_B = I_C = 25.1 X 10⁻³⁹ g. cm.²
 P-P-P = 109°.28, ϕ = 12

Heat of Formation

Taken as the heat of sublimation of P (red, v).

Heat Capacity and Entropy

The frequency and multiplicities are those assigned by H. S. Gutowsky and G. S. Hoffman, J. Am. Chem. Soc. 72, 5751 (1950). Molecular parameters of the gas were determined from electron diffraction measurements by L. R. Maxwell, S. B. Hendricks and V. M. Moseley, J. Chem. Phys. 23, 699 (1955). C. D. Thomas and N. S. Gingrich, J. Chem. Phys. 23, 659 (1955) obtained a P-P distance of 2.25 Å from x-ray studies on the liquid. On the basis of the selected values for P, White (see sheet) a third law entropy of 66.89 cal. deg.⁻¹ mole⁻¹ is derived for P₄(g) at 298.15°K.

Tetraphosphorus Trisulfide (P_4S_3)
(Solid) Mol. Wt. = 220.098

INTERIM TABLE

T, °K.	C_p°	$S^\circ - (F^\circ - H_{398}^\circ)/T$	$H^\circ - H_{398}^\circ$	ΔH_f°	ΔF_f°	Log K _p
0						
100						
200						
298	35.000	44.000	0.000	37.000	37.986	27.843
300	35.000	44.001	0.045	37.001	37.991	27.875
400	35.000	45.285	3.265	38.930	38.218	20.880
500	35.000	46.092	7.065	40.928	37.858	16.587
600	35.000	47.477	10.565	42.003	37.185	13.544
700	35.000	48.772	14.065	43.435	36.198	11.301
800	35.000	49.946	17.565	45.002	34.411	9.150
900	35.000	51.098	21.065	46.683	32.443	7.453
1000	35.000	52.236	24.565	48.483	30.103	
1100	35.000	53.491	28.065	50.406	27.476	4.175
1200	35.000	54.737	31.565	52.450	24.564	1.450
1300	35.000	56.058	35.065	54.612	21.367	
1400	35.000	57.453	38.565	56.891	17.886	
1500	35.000	58.922	42.065	59.387	14.127	
1600	35.000	60.466	45.565	62.000	10.093	
1700	35.000	62.088	49.065	64.731	5.661	7.310
1800	35.000	63.790	52.565	67.585	0.825	
1900	35.000	65.573	56.065	70.562	-4.429	9.504
2000	35.000	67.438	59.565	73.662	-9.585	10.434

December 31, 1960.

TETRAPHOSPHORUS TRISULFIDE (P_4S_3) (solid)

Mol. Wt. = 220.098

$\Delta H_f^\circ 298.15 = [-37]$ kcal. mole⁻¹

$S_{298.15}^\circ = [48]$ cal. deg.⁻¹ mole⁻¹

$T_m = 440^\circ K.$

$\Delta H_m = [2.2]$ kcal. mole⁻¹

$\Delta H_f^\circ 298.15$ estimated from vapor density reported by D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth- and Sixth- Group Nonmetallic Elements", Prentice-Hall, New York (1944). T_m from Yost and Russell, loc. cit. Other data estimated.

Tetraphosphorus Trisulfide (P_4S_3)
(Liquid) Mol. Wt. = 220.098 INTERIM TABLE

T, °K.	C_p	$S^\circ - (F^\circ - H^\circ_{398})/T$	ΔH°_f	ΔF°_f	Log K_p
0					
100					
200					
298	44.000	49.510	49.510	36.077	37.513
300			.000	36.077	37.513
302	44.000	49.782	49.511	36.062	37.521
304	44.000	49.840	49.511	36.052	37.521
306	44.000	49.898	49.511	36.042	37.521
308	44.000	49.956	49.511	36.032	37.521
310	44.000	50.014	49.511	36.022	37.521
312	44.000	50.072	49.511	36.012	37.521
314	44.000	50.130	49.511	36.002	37.521
316	44.000	50.188	49.511	35.992	37.521
318	44.000	50.246	49.511	35.982	37.521
320	44.000	50.304	49.511	35.972	37.521
322	44.000	50.362	49.511	35.962	37.521
324	44.000	50.420	49.511	35.952	37.521
326	44.000	50.478	49.511	35.942	37.521
328	44.000	50.536	49.511	35.932	37.521
330	44.000	50.594	49.511	35.922	37.521
332	44.000	50.652	49.511	35.912	37.521
334	44.000	50.710	49.511	35.902	37.521
336	44.000	50.768	49.511	35.892	37.521
338	44.000	50.826	49.511	35.882	37.521
340	44.000	50.884	49.511	35.872	37.521
342	44.000	50.942	49.511	35.862	37.521
344	44.000	51.000	49.511	35.852	37.521
346	44.000	51.058	49.511	35.842	37.521
348	44.000	51.116	49.511	35.832	37.521
350	44.000	51.174	49.511	35.822	37.521
352	44.000	51.232	49.511	35.812	37.521
354	44.000	51.290	49.511	35.802	37.521
356	44.000	51.348	49.511	35.792	37.521
358	44.000	51.406	49.511	35.782	37.521
360	44.000	51.464	49.511	35.772	37.521
362	44.000	51.522	49.511	35.762	37.521
364	44.000	51.580	49.511	35.752	37.521
366	44.000	51.638	49.511	35.742	37.521
368	44.000	51.696	49.511	35.732	37.521
370	44.000	51.754	49.511	35.722	37.521
372	44.000	51.812	49.511	35.712	37.521
374	44.000	51.870	49.511	35.702	37.521
376	44.000	51.928	49.511	35.692	37.521
378	44.000	51.986	49.511	35.682	37.521
380	44.000	52.044	49.511	35.672	37.521
382	44.000	52.102	49.511	35.662	37.521
384	44.000	52.160	49.511	35.652	37.521
386	44.000	52.218	49.511	35.642	37.521
388	44.000	52.276	49.511	35.632	37.521
390	44.000	52.334	49.511	35.622	37.521
392	44.000	52.392	49.511	35.612	37.521
394	44.000	52.450	49.511	35.602	37.521
396	44.000	52.508	49.511	35.592	37.521
398	44.000	52.566	49.511	35.582	37.521
400	44.000	52.624	49.511	35.572	37.521
402	44.000	52.682	49.511	35.562	37.521
404	44.000	52.740	49.511	35.552	37.521
406	44.000	52.798	49.511	35.542	37.521
408	44.000	52.856	49.511	35.532	37.521
410	44.000	52.914	49.511	35.522	37.521
412	44.000	52.972	49.511	35.512	37.521
414	44.000	53.030	49.511	35.502	37.521
416	44.000	53.088	49.511	35.492	37.521
418	44.000	53.146	49.511	35.482	37.521
420	44.000	53.204	49.511	35.472	37.521
422	44.000	53.262	49.511	35.462	37.521
424	44.000	53.320	49.511	35.452	37.521
426	44.000	53.378	49.511	35.442	37.521
428	44.000	53.436	49.511	35.432	37.521
430	44.000	53.494	49.511	35.422	37.521
432	44.000	53.552	49.511	35.412	37.521
434	44.000	53.610	49.511	35.402	37.521
436	44.000	53.668	49.511	35.392	37.521
438	44.000	53.726	49.511	35.382	37.521
440	44.000	53.784	49.511	35.372	37.521
442	44.000	53.842	49.511	35.362	37.521
444	44.000	53.900	49.511	35.352	37.521
446	44.000	53.958	49.511	35.342	37.521
448	44.000	54.016	49.511	35.332	37.521
450	44.000	54.074	49.511	35.322	37.521
452	44.000	54.132	49.511	35.312	37.521
454	44.000	54.190	49.511	35.302	37.521
456	44.000	54.248	49.511	35.292	37.521
458	44.000	54.306	49.511	35.282	37.521
460	44.000	54.364	49.511	35.272	37.521
462	44.000	54.422	49.511	35.262	37.521
464	44.000	54.480	49.511	35.252	37.521
466	44.000	54.538	49.511	35.242	37.521
468	44.000	54.596	49.511	35.232	37.521
470	44.000	54.654	49.511	35.222	37.521
472	44.000	54.712	49.511	35.212	37.521
474	44.000	54.770	49.511	35.202	37.521
476	44.000	54.828	49.511	35.192	37.521
478	44.000	54.886	49.511	35.182	37.521
480	44.000	54.944	49.511	35.172	37.521
482	44.000	55.002	49.511	35.162	37.521
484	44.000	55.060	49.511	35.152	37.521
486	44.000	55.118	49.511	35.142	37.521
488	44.000	55.176	49.511	35.132	37.521
490	44.000	55.234	49.511	35.122	37.521
492	44.000	55.292	49.511	35.112	37.521
494	44.000	55.350	49.511	35.102	37.521
496	44.000	55.408	49.511	35.092	37.521
498	44.000	55.466	49.511	35.082	37.521
500	44.000	55.524	49.511	35.072	37.521
502	44.000	55.582	49.511	35.062	37.521
504	44.000	55.640	49.511	35.052	37.521
506	44.000	55.698	49.511	35.042	37.521
508	44.000	55.756	49.511	35.032	37.521
510	44.000	55.814	49.511	35.022	37.521
512	44.000	55.872	49.511	35.012	37.521
514	44.000	55.930	49.511	35.002	37.521
516	44.000	55.988	49.511	34.992	37.521
518	44.000	56.046	49.511	34.982	37.521
520	44.000	56.104	49.511	34.972	37.521
522	44.000	56.162	49.511	34.962	37.521
524	44.000	56.220	49.511	34.952	37.521
526	44.000	56.278	49.511	34.942	37.521
528	44.000	56.336	49.511	34.932	37.521
530	44.000	56.394	49.511	34.922	37.521
532	44.000	56.452	49.511	34.912	37.521
534	44.000	56.510	49.511	34.902	37.521
536	44.000	56.568	49.511	34.892	37.521
538	44.000	56.626	49.511	34.882	37.521
540	44.000	56.684	49.511	34.872	37.521
542	44.000	56.742	49.511	34.862	37.521
544	44.000	56.800	49.511	34.852	37.521
546	44.000	56.858	49.511	34.842	37.521
548	44.000	56.916	49.511	34.832	37.521
550	44.000	56.974	49.511	34.822	37.521
552	44.000	57.032	49.511	34.812	37.521
554	44.000	57.090	49.511	34.802	37.521
556	44.000	57.148	49.511	34.792	37.521
558	44.000	57.206	49.511	34.782	37.521
560	44.000	57.264	49.511	34.772	37.521
562	44.000	57.322	49.511	34.762	37.521
564	44.000	57.380	49.511	34.752	37.521
566	44.000	57.438	49.511	34.742	37.521
568	44.000	57.496	49.511	34.732	37.521
570	44.000	57.554	49.511	34.722	37.521
572	44.000	57.612	49.511	34.712	37.521
574	44.000	57.670	49.511	34.702	37.521
576	44.000	57.728	49.511	34.692	37.521
578	44.000	57.786	49.511	34.682	37.521
580	44.000	57.844	49.511	34.672	37.521
582	44.000	57.902	49.511	34.662	37.521
584	44.000	57.960	49.511	34.652	37.521
586	44.000	58.018	49.511	34.642	37.521
588	44.000	58.076	49.511	34.632	37.521
590	44.000	58.134	49.511	34.622	37.521
592	44.000	58.192	49.511	34.612	37.521
594	44.000	58.250	49.511	34.602	37.521
596	44.000	58.308	49.511	34.592	37.521
598	44.000	58.366	49.511	34.582	37.521
600	44.000	58.424	49.511	34.572	37.521
602	44.000	58.482	49.511	34.562	37.521
604	44.000	58.540	49.511	34.552	37.521
606	44.000	58.598	49.511	34.542	37.521
608	44.000	58.656	49.511	34.532	37.521
610	44.000	58.714	49.511	34.522	37.521
612	44.000	58.772	49.511	34.512	37.521
614	44.000	58.830	49.511	34.502	37.521
616	44.000	58.888	49.511	34.492	37.521
618	44.000	58.946	49.511	34.482	37.521
620	44.000	59.004	49.511	34.472	37.521
622	44.000	59.062	49.511	34.462	37.521
624	44.000	59.120	49.511	34.452	37.521
626	44.000	59.178	49.511	34.442	37.521
628	44.000	59.236	49.511	34.432	37.521
630	44.000	59.294	49.511	34.422	37.521
632	44.000	59.352	49.511	34.412	37.521
634	44.000	59.410	49.511	34.402	37.521
636	44.000	59.468	49.511	34.392	37.521
638	44.000	59.526	49.511	34.382	37.521
640	44.000	59.584	49.511	34.372	37.521
642	44.000	59.642	49.511	34.362	37.521
644	44.000	59.700	49.511	34.352	37.521
646	44.000	59.758	49.511	34.342	37.521
648	44.000				

T, °K.	C _p ^o	S ^o - (F ^o - H ₂₉₈ ^o)/T	H ^o - H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100						
200						
298	37.000	76.280	76.280	.000	- 19.408	- 20.826
300	37.000	76.509	76.281	.068	- 19.406	- 20.883
400	37.000	77.153	77.732	3.768	- 21.935	- 21.040
500	37.000	78.409	80.473	7.468	- 22.553	- 21.766
600	37.000	80.155	83.581	11.168	- 23.108	- 22.508
700	37.000	82.451	88.618	14.868	- 23.620	- 23.402
800	37.000	85.159	95.589	18.568	- 24.097	- 24.411
900	37.000	88.186	104.415	22.268	- 24.540	- 25.504
1000	37.000	91.536	115.087	25.968	- 24.948	- 26.680
1100	37.000	95.202	127.611	29.668	- 25.321	- 27.939
1200	37.000	99.186	142.089	33.368	- 25.660	- 29.280
1300	37.000	103.499	158.524	37.068	- 25.960	- 30.704
1400	37.000	108.141	176.924	40.768	- 26.225	- 32.214
1500	37.000	113.121	197.289	44.468	- 26.458	- 33.804
1600	37.000	118.449	220.629	48.168	- 26.655	- 35.474
1700	37.000	124.127	246.949	51.868	- 26.815	- 37.224
1800	37.000	130.155	276.269	55.568	- 26.940	- 39.054
1900	37.000	136.533	309.589	59.268	- 27.035	- 40.954
2000	37.000	143.261	346.909	62.968	- 27.100	- 42.924
2100	37.000	150.339	388.229	66.668	- 27.135	- 44.964
2200	37.000	157.767	433.549	70.368	- 27.140	- 47.074
2300	37.000	165.545	482.869	74.068	- 27.115	- 49.254
2400	37.000	173.673	536.189	77.768	- 27.060	- 51.504
2500	37.000	182.151	593.509	81.468	- 26.975	- 53.824
2600	37.000	190.979	654.829	85.168	- 26.860	- 56.214
2700	37.000	200.157	720.149	88.868	- 26.715	- 58.674
2800	37.000	209.685	789.469	92.568	- 26.540	- 61.204
2900	37.000	219.563	862.789	96.268	- 26.335	- 63.804
3000	37.000	229.791	940.109	99.968	- 26.100	- 66.474
3100	37.000	240.369	1021.429	103.668	- 25.835	- 69.214
3200	37.000	251.297	1106.749	107.368	- 25.540	- 72.024
3300	37.000	262.575	1196.069	111.068	- 25.215	- 74.904
3400	37.000	274.203	1289.389	114.768	- 24.860	- 77.854
3500	37.000	286.181	1386.709	118.468	- 24.475	- 80.874
3600	37.000	298.509	1488.029	122.168	- 24.060	- 83.964
3700	37.000	311.187	1593.349	125.868	- 23.615	- 87.124
3800	37.000	324.215	1702.669	129.568	- 23.140	- 90.354
3900	37.000	337.593	1815.989	133.268	- 22.635	- 93.654
4000	37.000	351.321	1933.309	136.968	- 22.100	- 97.024
4100	37.000	365.399	2054.629	140.668	- 21.535	- 100.464
4200	37.000	379.827	2180.949	144.368	- 20.940	- 103.974
4300	37.000	394.605	2312.269	148.068	- 20.315	- 107.554
4400	37.000	409.733	2448.589	151.768	- 19.660	- 111.204
4500	37.000	425.211	2589.909	155.468	- 18.975	- 114.924
4600	37.000	441.039	2736.229	159.168	- 18.260	- 118.714
4700	37.000	457.217	2887.549	162.868	- 17.515	- 122.574
4800	37.000	473.745	3043.869	166.568	- 16.740	- 126.504
4900	37.000	490.623	3205.189	170.268	- 15.935	- 130.504
5000	37.000	507.851	3371.509	173.968	- 15.100	- 134.574
5100	37.000	525.429	3542.829	177.668	- 14.235	- 138.714
5200	37.000	543.357	3719.149	181.368	- 13.340	- 142.924
5300	37.000	561.635	3900.469	185.068	- 12.415	- 147.204
5400	37.000	580.263	4086.789	188.768	- 11.460	- 151.554
5500	37.000	599.241	4278.109	192.468	- 10.475	- 155.974
5600	37.000	618.569	4474.429	196.168	- 9.460	- 160.464
5700	37.000	638.247	4675.749	199.868	- 8.415	- 165.024
5800	37.000	658.275	4882.069	203.568	- 7.340	- 169.654
5900	37.000	678.653	5093.389	207.268	- 6.235	- 174.354
6000	37.000	699.381	5309.709	210.968	- 5.100	- 179.124

December 31, 1960.

TETRAPHOSPHORUS TRISULFIDE (P₄S₃) (Ideal Gas)

Mol. Wt. = 220.098

ΔH_f^o 298.15 = [-19.408] kcal. mole⁻¹S_{298.15}^o = [76.280] cal. deg.⁻¹ mole⁻¹C_p = [37] cal. deg.⁻¹ mole⁻¹

All data estimated.

Lead (Pb)

(Reference State) At. Wt. = 207.21

T, °K.	C _p	S° - (F°-H° ₂₉₈)/T	cal. mole ⁻¹ deg ⁻¹	cal. mole ⁻¹	ΔF [‡]	Log K _F
0	.000	INFINITE	-	1.644	.000	.000
100	5.816	8.403	21.013	1.221	.000	.000
200	6.183	12.972	16.062	.618	.000	.000
298	6.414	15.484	15.484	.000	.000	.000
300	6.418	15.524	15.484	.012	.000	.000
400	6.626	17.399	15.738	.664	.000	.000
500	6.823	18.698	16.225	1.337	.000	.000
600	7.006	20.157	16.778	2.037	.000	.000
700	7.174	21.450	17.413	2.757	.000	.000
800	7.326	22.413	18.013	3.497	.000	.000
900	7.468	23.143	18.571	4.258	.000	.000
1000	7.606	24.684	19.060	5.032	.000	.000
1100	7.742	26.394	20.270	6.737	.000	.000
1200	7.876	28.145	21.003	8.118	.000	.000
1300	8.008	29.565	21.369	9.168	.000	.000
1400	8.141	30.552	21.767	9.999	.000	.000
1500	8.283	31.225	22.202	10.633	.000	.000
1600	8.440	31.668	22.612	11.179	.000	.000
1700	8.597	32.082	23.004	11.653	.000	.000
1800	8.757	32.479	23.364	12.061	.000	.000
1900	8.902	32.859	23.712	12.421	.000	.000
2000	9.050	33.220	24.043	12.754	.000	.000
2100	9.194	33.569	24.359	13.069	.000	.000
2200	9.336	33.907	24.662	13.367	.000	.000
2300	9.476	34.232	24.953	13.649	.000	.000
2400	9.614	34.546	25.232	13.916	.000	.000
2500	9.751	34.849	25.500	14.169	.000	.000
2600	9.887	35.142	25.758	14.409	.000	.000
2700	10.022	35.426	26.006	14.636	.000	.000
2800	10.156	35.700	26.244	14.851	.000	.000
2900	10.289	35.965	26.472	15.054	.000	.000
3000	10.421	36.222	26.691	15.246	.000	.000
3100	10.553	36.471	26.901	15.428	.000	.000
3200	10.685	36.712	27.102	15.601	.000	.000
3300	10.816	36.946	27.294	15.765	.000	.000
3400	10.947	37.172	27.478	15.920	.000	.000
3500	11.078	37.391	27.654	16.067	.000	.000
3600	11.208	37.602	27.822	16.206	.000	.000
3700	11.338	37.806	27.982	16.338	.000	.000
3800	11.467	38.003	28.135	16.463	.000	.000
3900	11.596	38.193	28.282	16.581	.000	.000
4000	11.724	38.376	28.422	16.693	.000	.000
4100	11.852	38.552	28.556	16.799	.000	.000
4200	11.979	38.721	28.684	16.900	.000	.000
4300	12.106	38.883	28.807	17.000	.000	.000
4400	12.232	39.039	28.924	17.095	.000	.000
4500	12.358	39.189	29.036	17.186	.000	.000
4600	12.483	39.333	29.142	17.272	.000	.000
4700	12.608	39.472	29.243	17.354	.000	.000
4800	12.732	39.606	29.339	17.431	.000	.000
4900	12.856	39.735	29.431	17.504	.000	.000
5000	12.979	39.859	29.519	17.572	.000	.000
5100	13.102	39.978	29.603	17.636	.000	.000
5200	13.225	40.093	29.683	17.695	.000	.000
5300	13.348	40.204	29.759	17.750	.000	.000
5400	13.470	40.311	29.832	17.801	.000	.000
5500	13.592	40.414	29.901	17.848	.000	.000
5600	13.714	40.513	29.966	17.891	.000	.000
5700	13.836	40.609	30.027	17.930	.000	.000
5800	13.958	40.702	30.084	17.965	.000	.000
5900	14.079	40.792	30.137	17.997	.000	.000
6000	14.199	40.879	30.186	18.026	.000	.000

See crystal, liquid, and ideal monatomic gas for details.

AT. WT. = 207.21

(REFERENCE STATE)

LEAD (Pb)

0° to 600.58°K Crystal
600.58° to 2026°K Liquid
2026° to 5000°K Ideal Monatomic Gas

March 31, 1962

Pb

T, °K.	C _p	S°	cal. mole ⁻¹ deg. ⁻¹	-(F°-H ₂₉₈)/T	H°-H ₂₉₈	keal. mole ⁻¹	ΔH _f ⁰	ΔF _f ⁰	Log K _p
100	5.000	8.000	INFINITE	INFINITE	1.664	.000	.000	INFINITE	
200	6.885	12.972	16.062	16.062	.618	.000	.000	.000	
298	8.418	15.484	15.484	15.484	.012	.000	.000	.000	
300	8.416	15.524	15.484	15.484	.012	.000	.000	.000	
400	8.626	17.399	15.738	15.738	.664	.000	.000	.000	
500	8.821	18.898	16.225	16.225	1.337	.000	.000	.000	
600	8.998	20.157	16.778	16.778	2.027	.000	.000	.000	
700	9.158	21.257	17.341	17.341	2.741	1.156	.190	.059	
800	9.291	22.242	17.893	17.893	3.479	1.139	.382	.104	
900	9.403	23.137	18.427	18.427	4.239	1.093	.569	.136	
1000	9.506	23.963	18.940	18.940	5.023	1.015	.750	.164	
1100	9.589	24.732	19.432	19.432	5.831	.906	.921	.183	
1200	9.652	25.455	19.904	19.904	6.661	.767	1.083	.197	
1300	9.694	26.138	20.357	20.357	7.515	.599	1.230	.207	
1400	9.723	26.788	20.794	20.794	8.392	.407	1.363	.213	
1500	9.740	27.409	21.218	21.218	9.292	.191	1.483	.216	

March 31, 1962

LEAD (Pb)

(CRYSTAL)

AT. WT. = 207.21

$$\Delta H_{f0}^0 = 0$$

$$\Delta H_{f0}^0 \text{ 298.15} = 0$$

$$\Delta H_{f0}^0 \text{ 298.15} = 46.75 \pm 0.13 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 15.484 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_{f0}^0 = 1.141 \text{ kcal. mole}^{-1}$$

$$T_m = 800.58 \pm 0.00^\circ \text{K}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Heat capacity measurements have been reported by M. Horowitz, A. A. Silvini, S. P. Malaker and J. G. Daunt, (1° to 4°, 14° to 21°, and 64° to 77°K.), Phys. Rev. **88**, 1182 (1952); P. F. Meade, W. R. Forsythe and W. F. Giauque, (15° to 300°K.), J. Am. Chem. Soc. **55**, 1902 (1941); T. B. Douglas and J. L. Dever, (298.16° to 1200°K.), J. Am. Chem. Soc. **76**, 4824 (1954), and many others whose work is listed by K. K. Kelley, U. S. Bur. Mines Bull. 584 (1960).

Heat capacities from 15° to 300° and 1° to 4°K. (in superconducting state) were taken from Meade, Forsythe, and Giauque, and Horowitz, Silvini, Malaker, and Daunt, respectively. The missing data below the melting point were obtained by graphical extrapolation and joined smoothly to data of Douglas and Dever on approaching the melting point.

Melting.

The melting point of pure Pb(c) was found by E. H. McLaren and E. G. Mardock, Can. J. Phys. **38**, 577 (1960) to be $327.426 \pm 0.002^\circ \text{C}$. ΔH_m given by Douglas and Dever, loc. cit.

Heat of Sublimation.

ΔH_g^0 298.15 was derived from third law analysis of the vapor pressure data of W. H. Rodebush and A. L. Dixon, J. Am. Chem. Soc. **47**, 1038 (1925) and Phys. Rev. **26**, 851 (1925); A. C. G. Egerton, Proc. Roy. Soc. (London) **A103**, 469 (1923); P. Hartack, Z. physik. Chem. **134**, 1 (1928); A. T. Aldred and J. N. Pratt, Trans. Faraday Soc. **57**, 611 (1961); E. Baur and R. Brunner, Helv. Chim. Acta. **27**, 558 (1934), and J. Fischer, Z. anorg. Chem. **219**, 1, 367 (1934), which are in good agreement. Most weight was given to the results of Rodebush and Dixon. Older vapor pressure data of lower accuracy have not been used.

Lead (Pb)

(Liquid) At. Wt. = 207.21

Pb

T, °K.	C_p^o	$S^o - (F^o - H_{298}^o)/T$	ΔH_f^o	ΔF_f^o	Log K_p
0					
100					
200					
298	6.414	17.141	0.000	0.531	0.389
300					
400	6.818	17.181	0.012	0.528	0.385
500	7.270	19.056	1.395	0.362	0.198
600	7.396	20.715	1.407	0.187	0.082
700	7.322	22.056	1.484	0.022	0.001
800	7.250	23.179	1.557	0.000	0.000
900	7.098	24.082	1.592	0.000	0.000
1000	7.026	25.126	1.612	0.000	0.000
1100	6.953	26.393	1.611	0.000	0.000
1200	6.880	27.884	1.591	0.000	0.000
1300	6.807	29.601	1.558	0.000	0.000
1400	6.734	31.551	1.513	0.000	0.000
1500	6.661	33.743	1.458	0.000	0.000
1600	6.588	36.166	1.394	0.000	0.000
1700	6.515	38.831	1.321	0.000	0.000
1800	6.442	41.748	1.239	0.000	0.000
1900	6.369	44.925	1.152	0.000	0.000
2000	6.296	48.374	1.061	0.000	0.000
2100	6.223	52.103	0.966	0.000	0.000
2200	6.150	56.118	0.868	0.000	0.000
2300	6.077	60.423	0.768	0.000	0.000
2400	6.004	65.021	0.666	0.000	0.000
2500	5.931	69.915	0.562	0.000	0.000
2600	5.858	75.107	0.455	0.000	0.000
2700	5.785	80.600	0.348	0.000	0.000
2800	5.712	86.406	0.242	0.000	0.000
2900	5.639	92.527	0.137	0.000	0.000
3000	5.566	98.966	0.032	0.000	0.000

LEAD (Pb)

(LIQUID)

At. Wt. = 207.21

$$\Delta H_f^o 298.15 = [1.025] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^o = [17.141] \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta H_m^o = 1.141 \text{ kcal. mole}^{-1}$$

$$\Delta H_v^o = 42.53 \pm 0.13 \text{ kcal. mole}^{-1}$$

$$T_m = 600.58 \pm 0.00^\circ \text{K}$$

$$T_b = 2026^\circ \text{K}$$

Heat of Formation.

Obtained from ΔH_m^o .

Heat Capacity and Extrapolation.

Heat capacity from T_m to 1200°K taken from T. B. Douglas and J. I. Dever, J. Am. Chem. Soc. 76, 4824 (1954).
 C_p values below T_m and above 1200°K were extrapolated, a glass transition being assumed at 400°K.

Entropy.

Calculated from that of crystal.

Vaporization Phenomena.

 T_b and ΔH_v^o calculated from $\Delta H_f^o 298.15$ and functions for condensed and gaseous states.

From the vapor pressure, the free energy functions of Pb(g) and Pb₂(g), and the dissociation energy of Pb₂(g), it appears that below the boiling point the amount of Pb₂(g) in the vapor is negligible.

AT. WT. = 207.21

(IDEAL GAS)

LEAD (Pb)

T, °K.	C_p	$\int_{0}^T C_p dT$	$\int_{0}^T C_p dT / T$	$H^\circ - H_{298}^\circ$	ΔF°	Log K _p
0	0.000	INFINITE	INFINITE	46,910	46,910	INFINITE
100	4.968	39,307	42,335	46,910	46,910	INFINITE
200	4.968	39,307	42,335	46,910	46,910	INFINITE
298	4.968	41,890	44,890	46,910	46,910	INFINITE
300	4.968	41,921	44,921	46,910	46,910	INFINITE
400	4.968	43,359	46,359	46,910	46,910	INFINITE
500	4.968	44,459	47,459	46,910	46,910	INFINITE
600	4.968	45,365	48,365	46,910	46,910	INFINITE
700	4.968	46,130	49,130	46,910	46,910	INFINITE
800	4.968	46,794	49,794	46,910	46,910	INFINITE
900	4.968	47,380	50,380	46,910	46,910	INFINITE
1000	4.968	47,903	50,903	46,910	46,910	INFINITE
1100	4.992	48,379	51,379	46,910	46,910	INFINITE
1200	5.017	48,814	51,814	46,910	46,910	INFINITE
1300	5.042	49,217	52,217	46,910	46,910	INFINITE
1400	5.067	49,594	52,594	46,910	46,910	INFINITE
1500	5.092	49,949	52,949	46,910	46,910	INFINITE
1600	5.117	50,287	53,287	46,910	46,910	INFINITE
1700	5.141	50,611	53,611	46,910	46,910	INFINITE
1800	5.165	50,924	53,924	46,910	46,910	INFINITE
1900	5.189	51,227	54,227	46,910	46,910	INFINITE
2000	5.213	51,521	54,521	46,910	46,910	INFINITE
2100	5.237	51,815	54,815	46,910	46,910	INFINITE
2200	5.261	52,109	55,109	46,910	46,910	INFINITE
2300	5.285	52,403	55,403	46,910	46,910	INFINITE
2400	5.309	52,697	55,697	46,910	46,910	INFINITE
2500	5.333	52,991	55,991	46,910	46,910	INFINITE
2600	5.357	53,285	56,285	46,910	46,910	INFINITE
2700	5.381	53,579	56,579	46,910	46,910	INFINITE
2800	5.405	53,873	56,873	46,910	46,910	INFINITE
2900	5.429	54,167	57,167	46,910	46,910	INFINITE
3000	5.453	54,461	57,461	46,910	46,910	INFINITE
3100	5.477	54,755	57,755	46,910	46,910	INFINITE
3200	5.501	55,049	58,049	46,910	46,910	INFINITE
3300	5.525	55,343	58,343	46,910	46,910	INFINITE
3400	5.549	55,637	58,637	46,910	46,910	INFINITE
3500	5.573	55,931	58,931	46,910	46,910	INFINITE
3600	5.597	56,225	59,225	46,910	46,910	INFINITE
3700	5.621	56,519	59,519	46,910	46,910	INFINITE
3800	5.645	56,813	59,813	46,910	46,910	INFINITE
3900	5.669	57,107	60,107	46,910	46,910	INFINITE
4000	5.693	57,401	60,401	46,910	46,910	INFINITE
4100	5.717	57,695	60,695	46,910	46,910	INFINITE
4200	5.741	57,989	60,989	46,910	46,910	INFINITE
4300	5.765	58,283	61,283	46,910	46,910	INFINITE
4400	5.789	58,577	61,577	46,910	46,910	INFINITE
4500	5.813	58,871	61,871	46,910	46,910	INFINITE
4600	5.837	59,165	62,165	46,910	46,910	INFINITE
4700	5.861	59,459	62,459	46,910	46,910	INFINITE
4800	5.885	59,753	62,753	46,910	46,910	INFINITE
4900	5.909	60,047	63,047	46,910	46,910	INFINITE
5000	5.933	60,341	63,341	46,910	46,910	INFINITE
5100	5.957	60,635	63,635	46,910	46,910	INFINITE
5200	5.981	60,929	63,929	46,910	46,910	INFINITE
5300	5.999	61,223	64,223	46,910	46,910	INFINITE
5400	6.017	61,517	64,517	46,910	46,910	INFINITE
5500	6.035	61,811	64,811	46,910	46,910	INFINITE
5600	6.053	62,105	65,105	46,910	46,910	INFINITE
5700	6.071	62,399	65,399	46,910	46,910	INFINITE
5800	6.089	62,693	65,693	46,910	46,910	INFINITE
5900	6.107	62,987	65,987	46,910	46,910	INFINITE
6000	6.125	63,281	66,281	46,910	46,910	INFINITE

March 31, 1962

$\Delta H_f^\circ = 46.91 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 46.75 \pm 0.13 \text{ kcal. mole}^{-1}$
 $\Delta G_f^\circ = 41.890 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

Ground State Configuration 3P_0

Electronic Levels and Multiplicities

$E^\circ, \text{cm.}^{-1}$	g_1	$E_1^\circ, \text{cm.}^{-1}$	g_1
0.00	1	46,152.76	15
7,819.35	3	46,760.32	12
10,650.47	5	51,741.79	12
21,457.90	5	52,505.53	48
29,466.61	1	53,493.33	4
34,959.90	1	54,895.15	4
35,287.24	3	55,343.74	60
42,918.68	3	56,716.24	52
44,400.92	1	57,520.36	68
44,675.00	3	58,403.73	139
44,809.41	5	59,321.54	51
45,443.26	5		

Heat of Formation.

The same as ΔH_f° 298.15

Heat Capacity and Entropy.

Electronic levels and multiplicities from C. E. Moore, Natl. Bur. Standards (U. S.) Circ. 467, Vol. III (1958).

Lead, Diatomic (Pb₂)
(Ideal Gas) Mol. Wt. = 414.42

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔF° ₂₉₈	Log K _p
0	∞	∞	∞	∞	∞
100	58.087	58.087	2.391	80.397	INFINITE
200	7.712	63.744	1.675	76.219	- 156.568
300	8.545	67.216	0.854	72.322	- 79.026
400	8.825	69.216	0.000	68.693	- 50.351
500	8.928	70.216	0.016	65.492	- 49.991
600	9.000	71.184	0.046	62.546	- 49.546
700	9.050	72.115	1.807	59.633	- 49.029
800	9.115	73.006	2.716	56.812	- 48.437
900	9.169	73.855	3.630	54.054	- 47.782
1000	9.219	74.666	4.549	51.356	- 47.066
1100	9.265	75.442	5.472	48.720	- 46.298
1200	9.309	76.188	6.402	46.142	- 45.478
1300	9.351	76.909	7.335	43.616	- 44.607
1400	9.393	77.601	8.273	41.142	- 43.687
1500	9.434	78.268	9.214	38.717	- 42.716
1600	9.475	78.914	10.160	36.342	- 41.695
1700	9.515	79.535	11.109	34.017	- 40.624
1800	9.555	80.135	12.063	31.743	- 39.503
1900	9.595	80.714	13.020	29.519	- 38.332
2000	9.635	81.274	13.982	27.345	- 37.111
2100	9.674	81.819	14.947	25.219	- 35.840
2200	9.714	82.350	15.916	23.143	- 34.519
2300	9.753	82.867	16.890	21.117	- 33.148
2400	9.793	83.371	17.867	19.143	- 31.717
2500	9.832	83.862	18.848	17.219	- 30.226
2600	9.871	84.340	19.834	15.345	- 28.675
2700	9.909	84.807	20.823	13.519	- 27.064
2800	9.948	85.262	21.816	11.743	- 25.393
2900	9.987	85.707	22.812	10.017	- 23.662
3000	10.026	86.144	23.812	8.341	- 21.871
3100	10.064	86.571	24.816	6.715	- 20.020
3200	10.103	86.989	25.823	5.139	- 18.119
3300	10.141	87.398	26.833	3.613	- 16.168
3400	10.179	87.798	27.846	2.137	- 14.167
3500	10.217	88.189	28.862	0.711	- 12.116
3600	10.255	88.571	29.880	- 0.764	- 10.015
3700	10.293	88.944	30.900	- 2.213	- 7.864
3800	10.331	89.308	31.922	- 3.652	- 5.663
3900	10.369	89.663	32.946	- 5.081	- 3.412
4000	10.407	90.009	33.972	- 6.500	- 1.111
4100	10.445	90.346	34.999	- 7.909	1.240
4200	10.483	90.674	36.027	- 9.308	3.539
4300	10.521	90.993	37.056	- 10.697	5.788
4400	10.559	91.303	38.086	- 12.076	7.987
4500	10.597	91.604	39.116	- 13.445	10.136
4600	10.635	91.896	40.146	- 14.804	12.235
4700	10.673	92.179	41.176	- 16.153	14.284
4800	10.711	92.453	42.206	- 17.492	16.283
4900	10.749	92.719	43.236	- 18.821	18.232
5000	10.787	92.976	44.266	- 20.140	20.131
5100	10.825	93.224	45.296	- 21.459	21.980
5200	10.863	93.463	46.326	- 22.768	23.779
5300	10.901	93.693	47.356	- 24.067	25.528
5400	10.939	93.914	48.386	- 25.356	27.227
5500	10.977	94.126	49.416	- 26.635	28.876
5600	11.015	94.329	50.446	- 27.904	30.475
5700	11.053	94.523	51.476	- 29.163	32.024
5800	11.091	94.708	52.506	- 30.412	33.523
5900	11.129	94.884	53.536	- 31.651	34.972
6000	11.167	95.059	54.566	- 32.880	36.371
6100	11.205	95.225	55.596	- 34.109	37.720
6200	11.243	95.382	56.626	- 35.328	39.019
6300	11.281	95.539	57.656	- 36.537	40.268
6400	11.319	95.696	58.686	- 37.736	41.467
6500	11.357	95.853	59.716	- 38.925	42.616
6600	11.395	96.009	60.746	- 40.104	43.715
6700	11.433	96.166	61.776	- 41.273	44.764
6800	11.471	96.323	62.806	- 42.432	45.763
6900	11.509	96.479	63.836	- 43.581	46.712
7000	11.547	96.636	64.866	- 44.720	47.611
7100	11.585	96.793	65.896	- 45.859	48.460
7200	11.623	96.949	66.926	- 46.998	49.259
7300	11.661	97.106	67.956	- 48.137	50.008
7400	11.699	97.263	68.986	- 49.276	50.707
7500	11.737	97.419	70.016	- 50.415	51.356
7600	11.775	97.576	71.046	- 51.554	51.955
7700	11.813	97.733	72.076	- 52.693	52.504
7800	11.851	97.889	73.106	- 53.832	53.003
7900	11.889	98.046	74.136	- 54.971	53.452
8000	11.927	98.203	75.166	- 56.110	53.851
8100	11.965	98.359	76.196	- 57.249	54.200
8200	12.003	98.516	77.226	- 58.388	54.509
8300	12.041	98.673	78.256	- 59.527	54.768
8400	12.079	98.829	79.286	- 60.666	54.977
8500	12.117	98.986	80.316	- 61.805	55.136
8600	12.155	99.143	81.346	- 62.944	55.245
8700	12.193	99.299	82.376	- 64.083	55.304
8800	12.231	99.456	83.406	- 65.222	55.353
8900	12.269	99.613	84.436	- 66.361	55.352
9000	12.307	99.769	85.466	- 67.500	55.301
9100	12.345	99.926	86.496	- 68.639	55.200
9200	12.383	100.083	87.526	- 69.778	55.049
9300	12.421	100.239	88.556	- 70.917	54.848
9400	12.459	100.396	89.586	- 72.056	54.597
9500	12.497	100.553	90.616	- 73.195	54.296
9600	12.535	100.709	91.646	- 74.334	53.945
9700	12.573	100.866	92.676	- 75.473	53.544
9800	12.611	101.023	93.706	- 76.612	53.093
9900	12.649	101.179	94.736	- 77.751	52.592
10000	12.687	101.336	95.766	- 78.890	52.041

Mar. 31, 1962; June 30, 1963; Sept. 30, 1963.

MOL. WT. = 414.42

(IDEAL GAS)

LEAD, DIATOMIC (Pb₂)

Ground State Configuration [5s²5p²]
 $\Delta H_f^\circ = 80.4 \pm 4.6 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ = 79.5 \pm 4.6 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$$\frac{\epsilon_i}{\epsilon_0} = \frac{g_i}{\sum g_i}$$

$$\omega_e x_e = 2.95 \text{ cm}^{-1}$$

$$\omega_e = [0.01727] \text{ cm}^{-1}$$

$$\sigma = 2$$

$$r_e = [3.08] \text{ \AA}$$

Heat of Formation.

$H_f^\circ = 256.5 \text{ cm}^{-1}$
 $B_e = [0.01727] \text{ cm}^{-1}$
 Heat of formation was calculated from the dissociation energy of Pb₂(g) reported by A. G. Daydon, "Dissociation Energies," Chapman and Hall Ltd., London, 1953.

Heat Capacity and Entropy.

The values of ω_e and $\omega_e x_e$ were obtained from G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, 1950. Those for B_e and ω_e were estimated according to the method suggested by G. Herzberg, loc. cit. The bond distance (r_e) was calculated from the moment of inertia, $I = 1630 \times 10^{-40} \text{ g. cm}^2$, estimated by K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 1961. The ground state configuration was assumed to be 5s² by comparison to that for Si₂(g) reported by A. E. Douglas, Can. J. Phys. 33, 801 (1955).

Sulfur (S)

(Reference State) At. Wt. = 32.064

SULFUR (S)

(REFERENCE STATE)

AT. WT. = 32.064

0° to 368.54°K. Crystal, Rhombic
 368.54° to 388.36°K. Crystal, Monoclinic
 388.36° to 717.75°K. Liquid
 717.75° to 8000°K. Ideal Gas, Diatomic

See crystal, liquid and diatomic gas for details.

T, °K.	C _p	S° - (F° - H° ₂₉₈)/T	cal. mole ⁻¹ deg. ⁻¹	cal. mole ⁻¹	ΔH° _f	ΔF° _f	Log K _p
0	∞	∞	∞	∞	∞	∞	∞
100	3.050	11.855	∞	∞	∞	∞	∞
200	4.462	7.631	∞	∞	∞	∞	∞
298	5.401	7.631	∞	∞	∞	∞	∞
300	5.412	7.665	7.632	∞	∞	∞	∞
400	7.734	10.574	7.801	1.109	∞	∞	∞
500	9.081	12.768	8.673	2.047	∞	∞	∞
600	8.200	14.333	9.492	2.904	∞	∞	∞
700	7.799	15.601	10.309	3.704	∞	∞	∞
800	4.368	31.363	9.452	17.529	∞	∞	∞
900	4.396	31.879	11.916	17.967	∞	∞	∞
1000	4.418	32.384	13.636	18.408	∞	∞	∞
1100	4.435	32.765	15.628	18.851	∞	∞	∞
1200	4.450	33.152	17.073	19.295	∞	∞	∞
1300	4.461	33.509	18.324	19.740	∞	∞	∞
1400	4.471	33.840	19.420	20.187	∞	∞	∞
1500	4.480	34.148	20.392	20.635	∞	∞	∞
1600	4.488	34.438	21.261	21.083	∞	∞	∞
1700	4.495	34.710	22.044	21.532	∞	∞	∞
1800	4.501	34.967	22.755	21.982	∞	∞	∞
1900	4.507	35.211	23.404	22.432	∞	∞	∞
2000	4.513	35.442	24.000	22.883	∞	∞	∞
2100	4.518	35.662	24.550	23.335	∞	∞	∞
2200	4.523	35.873	25.060	23.787	∞	∞	∞
2300	4.528	36.074	25.535	24.240	∞	∞	∞
2400	4.532	36.267	25.978	24.693	∞	∞	∞
2500	4.537	36.452	26.393	25.146	∞	∞	∞
2600	4.541	36.630	26.784	25.600	∞	∞	∞
2700	4.545	36.801	27.151	26.054	∞	∞	∞
2800	4.549	36.966	27.499	26.509	∞	∞	∞
2900	4.553	37.126	27.828	26.964	∞	∞	∞
3000	4.557	37.281	28.141	27.420	∞	∞	∞
3100	4.561	37.430	28.438	27.875	∞	∞	∞
3200	4.565	37.575	28.721	28.332	∞	∞	∞
3300	4.568	37.715	28.992	28.788	∞	∞	∞
3400	4.572	37.852	29.250	29.245	∞	∞	∞
3500	4.575	37.984	29.498	29.703	∞	∞	∞
3600	4.579	38.113	29.735	30.160	∞	∞	∞
3700	4.583	38.239	29.964	30.619	∞	∞	∞
3800	4.586	38.361	30.183	31.077	∞	∞	∞
3900	4.590	38.480	30.394	31.536	∞	∞	∞
4000	4.593	38.597	30.598	31.995	∞	∞	∞
4100	4.596	38.710	30.794	32.454	∞	∞	∞
4200	4.600	38.821	30.984	32.914	∞	∞	∞
4300	4.603	38.929	31.168	33.374	∞	∞	∞
4400	4.607	39.035	31.345	33.835	∞	∞	∞
4500	4.610	39.139	31.517	34.296	∞	∞	∞
4600	4.613	39.240	31.684	34.757	∞	∞	∞
4700	4.617	39.339	31.846	35.218	∞	∞	∞
4800	4.620	39.436	32.003	35.680	∞	∞	∞
4900	4.624	39.532	32.156	36.142	∞	∞	∞
5000	4.627	39.625	32.304	36.605	∞	∞	∞
5100	4.630	39.717	32.449	37.068	∞	∞	∞
5200	4.633	39.807	32.589	37.531	∞	∞	∞
5300	4.637	39.895	32.726	37.994	∞	∞	∞
5400	4.640	39.982	32.860	38.458	∞	∞	∞
5500	4.643	40.067	32.990	38.922	∞	∞	∞
5600	4.647	40.151	33.117	39.387	∞	∞	∞
5700	4.650	40.233	33.241	39.852	∞	∞	∞
5800	4.653	40.314	33.363	40.317	∞	∞	∞
5900	4.656	40.393	33.481	40.782	∞	∞	∞
6000	4.660	40.472	33.597	41.248	∞	∞	∞

Dec. 31, 1960; Mar. 31, 1961; Dec. 31, 1965

Sulfur (S)

(Crystal) At. Wt. = 32.064

T, °K.	C _p	S°	-(F°-H° ₃₉₈)/T	H°-H° ₃₉₈	ΔH _f ⁰	ΔF _f ⁰	Log K _p
0	0.000	0.000	INFINITE	1.0653	0.000	0.000	0.000
100	3.050	2.965	11.855	0.889	0.000	0.000	0.000
200	4.638	5.622	8.104	0.469	0.000	0.000	0.000
298	5.401	7.631	7.631	0.000	0.000	0.000	0.000
300	5.412	7.665	7.432	-0.10	0.000	0.000	0.000
400	6.133	9.251	6.871	-1.680	-0.011	-0.009	-0.009
500	6.819	11.013	6.358	-3.327	-0.720	-0.158	-0.069
600	7.504	12.317	6.011	-4.044	-0.860	-0.349	-0.127
700	8.190	13.525	5.485	-5.268	-1.006	-0.488	-0.180
800	8.876	14.644	4.804	-6.463	-1.154	-0.628	-0.233
900	9.561	15.769	4.034	-7.694	-1.281	-0.768	-0.286
1000	10.247	16.792	3.198	-8.964	-1.406	-0.906	-0.339
1100	10.933	17.800	2.297	-10.241	-1.525	-1.043	-0.392
1200	11.619	18.781	1.297	-11.515	-1.640	-1.179	-0.445
1300	12.305	19.738	0.297	-12.787	-1.752	-1.313	-0.498
1400	12.990	20.675	0.297	-14.059	-1.860	-1.445	-0.551
1500	13.676	21.595	0.297	-15.331	-1.964	-1.576	-0.604
1600	14.361	22.499	0.297	-16.603	-2.064	-1.706	-0.657
1700	15.047	23.390	0.297	-17.875	-2.160	-1.835	-0.710
1800	15.733	24.270	0.297	-19.147	-2.252	-1.963	-0.763
1900	16.418	25.139	0.297	-20.419	-2.340	-2.090	-0.816
2000	17.104	25.998	0.297	-21.691	-2.424	-2.216	-0.869

SULFUR (S)

(CRYSTAL)

AT. WT. = 32.064

$$\Delta H_f^0 = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = 0 \text{ kcal. mole}^{-1}$$

$$\Delta H_f^0 = 96.01 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_f^0 = 0.38 \pm 0.2 \text{ cal. mole}^{-1}$$

$$\Delta H_f^0 = 410.52 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_f^0 \text{ 298.15} = 66.68 \pm 0.5 \text{ kcal. mole}^{-1}$$

$$S_{298.15}^0 = 7.63 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 368.5^\circ \text{K.}$$

$$T_{t_2} = 374^\circ \text{K.}$$

$$T_m = 368.5^\circ \text{K.}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

E. D. Eastman and W. C. McDoveck, J. Am. Chem. Soc. 59, 145 (1937), have measured the low temperature heat capacities of sulfur from 15° to 375°K. E. D. West, J. Am. Chem. Soc. 81, 29 (1959), has measured the high temperature heat capacities from 298° to 678°K. These two sets of data were joined smoothly at 298.15 K. by a graphical method.

The values of entropy at 110°C and above in E. D. West's paper (table VIII) have been lowered by 0.5841 joule. deg.⁻¹ mole⁻¹ because of a calculational error which was pointed out by J. P. McCullough and D. W. Scott, private communication, Sept. 27, 1960.

The entropy of rhombic sulfur at 298.15°K. was taken from E. D. Eastman and W. C. McDoveck, loc. cit., based on an extrapolation of $S_{15}^0 = 0.12 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Transition Data.

The enthalpies of transition at 368.5°K. and 374°K. were obtained from E. D. West, loc. cit. The first transition at 368.5°K. was the known rhombic-monoclinic transition, but the second one near 374°K. was a previously unreported transition.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Heat of Sublimation.

The heat of sublimation of sulfur (c) is the heat of formation of monatomic sulfur (g). See S(g) table for details. Since S_g and lower polymers are major vapor species at room temperature, the heat of sublimation to the equilibrium gas is much smaller. See $S_g(g)$ table for details.

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T cal. mole ⁻¹	H°-H° ₂₉₈ ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0					
100	7.579	8.444	0.000	0.000	0.068
200	7.579	8.444	0.000	0.000	0.068
298	7.579	8.444	0.000	0.000	0.068
300	7.579	8.444	0.000	0.000	0.068
400	7.579	8.444	0.000	0.000	0.068
500	7.579	8.444	0.000	0.000	0.068
600	8.200	10.053	2.568	0.000	0.000
700	7.790	10.790	3.368	0.000	0.000
800	7.694	11.457	4.218	0.000	0.000
900	7.694	12.121	5.049	0.000	0.000
1000	7.694	12.781	5.860	0.000	0.000
1100	7.694	13.441	6.649	0.000	0.000
1200	7.694	14.101	7.418	0.000	0.000
1300	7.694	14.761	8.167	0.000	0.000
1400	7.694	15.421	8.897	0.000	0.000
1500	7.694	16.081	9.607	0.000	0.000
1600	7.694	16.741	10.296	0.000	0.000
1700	7.694	17.401	10.965	0.000	0.000
1800	7.694	18.061	11.615	0.000	0.000
1900	7.694	18.721	12.245	0.000	0.000
2000	7.694	19.381	12.855	0.000	0.000

Dec. 31, 1960; Dec. 31, 1965

$$\Delta H_f^{298.15} = 0.34 \pm 0.01 \text{ kcal. mole}^{-1}$$

$$\Delta H_m^{298.15} = 410.52 \pm 0.5 \text{ cal. mole}^{-1}$$

$$\Delta H_v^{298.15} = [2.30] \text{ kcal. mole}^{-1}$$

$$S_{298.15}^{298.15} = 8.44 \pm 0.5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$T_m = 368.36^\circ \text{K.}$$

$$T_b = 717.75^\circ \text{K.}$$

Heat of Formation.

The $\Delta H_f^{298.15} (S, l)$ was obtained from that of the crystal by adding $\Delta H_m^{298.15}$ and the difference between $H_{298.15}^{298.15}$ for crystal and liquid.

Heat Capacity and Entropy.

The heat capacity of the liquid phase was obtained from E. D. West, J. Am. Chem. Soc. **81**, 29 (1959). No simple equation fits the curve of C_p against T which shows a peak.

The value of $S_{298.15}^{298.15} (S, l)$ was obtained in a manner analogous to that of the heat of formation. The heat capacity of sulfur (liquid) below the melting point was assumed to be constant as $7.579 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, and above the boiling point, it was assumed as $7.694 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.

Melting Data.

The heat of melting and the temperature were obtained from E. D. West, loc. cit.

Vaporization Data.

According to the international practical temperature scale, the boiling point is 717.75°K. The heat of vaporization to the equilibrium vapor mixture was estimated by D. R. Stull and G. C. Sink, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., 1956. The equilibrium vapor involves monomeric and several polymeric species; S_2 and S_8 predominate above 1000°K. While S_8 , S_6 and possible S_4 and S_3 are favored at lower temperatures.

Sulfur, Monatomic (S)

(Ideal Gas) At. Wt. = 32.064

T, °K.	C _p	S°	-(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	Log K _p
0	0.000	0.000	INFINITE	1.591	66.142	INFINITE
100	5.103	34.127	4.046	1.092	66.477	138.468
200	5.589	37.831	4.004	0.955	66.621	65.758
298	5.659	40.086	4.000	0.900	66.680	41.783
300	5.658	40.121	4.000	0.900	66.680	41.783
400	5.654	41.736	4.007	0.912	66.718	33.941
500	5.636	42.962	4.020	0.921	66.754	22.141
600	5.630	43.944	4.178	1.659	67.363	17.363
700	5.666	44.762	4.634	2.190	67.753	13.972
800	5.689	45.464	5.000	2.666	68.044	11.512
900	5.699	46.072	5.232	3.000	68.250	9.825
1000	5.713	46.615	5.426	3.277	68.378	8.425
1100	5.721	47.103	5.581	3.500	68.431	7.215
1200	5.725	47.547	5.712	3.677	68.481	6.152
1300	5.727	47.954	5.823	3.812	68.529	5.212
1400	5.729	48.331	5.918	3.919	68.576	4.392
1500	5.730	48.680	6.000	4.000	68.621	3.686
1600	5.730	49.007	6.068	4.068	68.663	3.073
1700	5.729	49.314	6.125	4.125	68.702	2.535
1800	5.727	49.597	6.172	4.172	68.738	2.061
1900	5.724	49.857	6.210	4.210	68.771	1.641
2000	5.720	50.138	6.239	4.239	68.801	1.265
2100	5.715	50.436	6.261	4.261	68.828	0.932
2200	5.709	50.744	6.276	4.276	68.852	0.641
2300	5.702	51.061	6.284	4.284	68.873	0.391
2400	5.694	51.387	6.287	4.287	68.891	0.181
2500	5.685	51.722	6.284	4.284	68.906	0.011
2600	5.675	52.066	6.276	4.276	68.918	-0.119
2700	5.664	52.419	6.263	4.263	68.927	-0.249
2800	5.652	52.780	6.245	4.245	68.933	-0.379
2900	5.639	53.150	6.213	4.213	68.936	-0.509
3000	5.625	53.529	6.168	4.168	68.936	-0.639
3100	5.610	53.917	6.112	4.112	68.932	-0.769
3200	5.594	54.314	6.047	4.047	68.925	-0.899
3300	5.577	54.721	5.972	3.972	68.915	-1.029
3400	5.559	55.137	5.888	3.888	68.902	-1.159
3500	5.540	55.562	5.795	3.795	68.886	-1.289
3600	5.520	56.000	5.693	3.693	68.867	-1.419
3700	5.499	56.449	5.581	3.581	68.845	-1.549
3800	5.477	56.909	5.459	3.459	68.820	-1.679
3900	5.454	57.380	5.328	3.328	68.793	-1.809
4000	5.430	57.861	5.188	3.188	68.763	-1.939
4100	5.405	58.352	5.039	3.039	68.730	-2.069
4200	5.379	58.853	4.881	2.881	68.694	-2.199
4300	5.352	59.364	4.714	2.714	68.655	-2.329
4400	5.324	59.885	4.538	2.538	68.613	-2.459
4500	5.295	60.416	4.353	2.353	68.568	-2.589
4600	5.265	60.957	4.159	2.159	68.520	-2.719
4700	5.234	61.508	3.956	1.956	68.469	-2.849
4800	5.202	62.069	3.744	1.744	68.415	-2.979
4900	5.169	62.640	3.522	1.522	68.358	-3.109
5000	5.135	63.221	3.291	1.291	68.298	-3.239
5100	5.100	63.812	3.050	1.050	68.235	-3.369
5200	5.064	64.413	2.799	0.799	68.169	-3.499
5300	5.027	65.024	2.538	0.538	68.100	-3.629
5400	4.989	65.645	2.267	0.267	68.028	-3.759
5500	4.950	66.276	1.986	0.000	67.953	-3.889
5600	4.910	66.917	1.695	-0.267	67.875	-4.019
5700	4.869	67.568	1.394	-0.534	67.795	-4.149
5800	4.827	68.229	1.083	-0.803	67.712	-4.279
5900	4.784	68.900	0.762	-1.072	67.627	-4.409
6000	4.740	69.581	0.431	-1.341	67.540	-4.539

Dec. 31, 1960; June 30, 1961; Dec. 31, 1965

AT. WT. = 32.064

(IDEAL GAS)

SULFUR, MONATOMIC (S)

Ground State Configuration $3p_4^2$
 $S_{298.15}^\circ = 40.1 \pm 0.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$
 $\Delta H_f^\circ 0 = 66.14 \pm 0.5 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 66.68 \pm 0.5 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

E_i , cm. ⁻¹	E_i , cm. ⁻¹	E_i , cm. ⁻¹	E_i , cm. ⁻¹
0.0	5	67,878.03	9
396.8	3	67,890.45	7
573.6	1	67,888.25	5
9,239.0	5	67,885.97	3
22,181.4	1	67,884.67	1
52,823.88	5	69,238.7	5
55,331.15	3	70,168.9	3
63,446.36	3	70,166.8	5
63,457.33	5	70,170.7	7
63,475.26	7	[70,706.0]	5
64,891.71	1	71,352.5	3
64,893.23	3	72,025.5	5
64,892.89	5	72,382.5	3
67,816.87	3	72,572.4	1
67,825.72	5	73,911.53	3
67,843.38	7	73,915.16	5

Heat of Formation.

L. Brewer, J. Chem. Phys. 21, 1143 (1953), has reviewed the three possible values of $D_0^\circ(S_2)$, i.e. 4.4 e.v., 3.6 e.v. and 3.3 e.v., which were due to the ambiguity of defining the excitation state of the atomic products resulting from predissociation in the spectroscopic measurements. The value of 4.4 e.v. (101.5 kcal. mole⁻¹) was shown to be the most probable one. Since this review, further support for his value have been given by the following investigators. J. R. Marquart, Dissertation Abstract 24, 5027 (1964), has found that the value of $D_0^\circ(S_2)$ to be consistent with the value of 4.4 e.v. in mass spectroscopic studies. R. Colin, P. Goldfinger and M. Jeunhomme, Trans. Faraday Soc. 60, 306 (1964), have found $D_0^\circ(S_2) = 97 \pm 5 \text{ kcal. mole}^{-1}$ in their mass-spectroscopic studies of the vaporization of CS_2 , CS_2 and CS_2 , but they reported a revised value, i.e. $D_0^\circ(S_2) = 101 \pm 1 \text{ kcal. mole}^{-1}$, which was given in the note in proof. A. N. Singh and D. K. Rai, J. Chem. Phys. 43, 2151 (1965), have selected the best value of $D_0^\circ(S_2) = 4.4 \text{ e.v.}$ in theoretical comparisons of the potential-energy curve. As pointed out by L. Brewer, loc. cit., and A. O. Gaydon, "Dissociation Energies", Chapman and Hall Ltd., 2nd. Ed., London, 1953, the old vapor pressure measurements which are not consistent with $D_0(S_2) = 4.4 \text{ e.v.}$ (101.5 kcal. mole⁻¹) are probably not reliable.

The value $D_0(S_2, g) = 4.4 \text{ e.v.}$ (101.5 kcal. mole⁻¹) was selected as the dissociation energy of diatomic sulfur, and combination of this value with heat of formation of diatomic sulfur gives the heat of formation of monatomic sulfur, $\Delta H_f^\circ 298(S, g) = 66.68 \text{ kcal. mole}^{-1}$.

Heat Capacity and Entropy.

The ground state configuration, electronic levels and quantum weight were obtained from C. E. Moore, "Atomic Energy Levels", Vol. 1, National Bureau of Standards Circular 467, June, 1949.

INTERIM TABLE

Mol. Wt. = 60.156

(Ideal Gas)

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T kcal. mole ⁻¹	H°-H° ₂₉₈ ΔH° _f kcal. mole ⁻¹	ΔF° _f	Log K _p
0	6.962	∞	14.600	16.600	INFINITE
100	6.962	45.567	17.068	12.999	-28.189
200	7.231	50.449	17.106	8.991	-9.496
298	7.711	53.427	16.926	4.596	-3.366
300	7.720	53.474	16.921	4.516	-3.290
400	8.100	55.751	16.921	4.443	-3.242
500	8.352	57.587	16.921	4.443	-3.242
600	8.516	59.126	16.921	4.443	-3.242
700	8.604	60.446	16.921	4.443	-3.242
800	8.672	61.608	16.921	4.443	-3.242
900	8.721	62.636	16.921	4.443	-3.242
1000	8.751	63.562	16.921	4.443	-3.242
1100	8.772	64.405	16.921	4.443	-3.242
1200	8.786	65.168	16.921	4.443	-3.242
1300	8.794	65.860	16.921	4.443	-3.242
1400	8.798	66.500	16.921	4.443	-3.242
1500	8.799	67.100	16.921	4.443	-3.242
1600	8.799	67.660	16.921	4.443	-3.242
1700	8.799	68.190	16.921	4.443	-3.242
1800	8.799	68.690	16.921	4.443	-3.242
1900	8.799	69.160	16.921	4.443	-3.242
2000	8.799	69.600	16.921	4.443	-3.242
2100	8.799	70.010	16.921	4.443	-3.242
2200	8.799	70.390	16.921	4.443	-3.242
2300	8.799	70.740	16.921	4.443	-3.242
2400	8.799	71.060	16.921	4.443	-3.242
2500	8.799	71.350	16.921	4.443	-3.242
2600	8.799	71.610	16.921	4.443	-3.242
2700	8.799	71.840	16.921	4.443	-3.242
2800	8.799	72.040	16.921	4.443	-3.242
2900	8.799	72.210	16.921	4.443	-3.242
3000	8.799	72.350	16.921	4.443	-3.242
3100	8.799	72.460	16.921	4.443	-3.242
3200	8.799	72.540	16.921	4.443	-3.242
3300	8.799	72.600	16.921	4.443	-3.242
3400	8.799	72.640	16.921	4.443	-3.242
3500	8.799	72.660	16.921	4.443	-3.242
3600	8.799	72.670	16.921	4.443	-3.242
3700	8.799	72.670	16.921	4.443	-3.242
3800	8.799	72.660	16.921	4.443	-3.242
3900	8.799	72.640	16.921	4.443	-3.242
4000	8.799	72.610	16.921	4.443	-3.242
4100	8.799	72.570	16.921	4.443	-3.242
4200	8.799	72.520	16.921	4.443	-3.242
4300	8.799	72.460	16.921	4.443	-3.242
4400	8.799	72.390	16.921	4.443	-3.242
4500	8.799	72.310	16.921	4.443	-3.242
4600	8.799	72.220	16.921	4.443	-3.242
4700	8.799	72.120	16.921	4.443	-3.242
4800	8.799	72.010	16.921	4.443	-3.242
4900	8.799	71.890	16.921	4.443	-3.242
5000	8.799	71.760	16.921	4.443	-3.242
5100	8.799	71.620	16.921	4.443	-3.242
5200	8.799	71.470	16.921	4.443	-3.242
5300	8.799	71.310	16.921	4.443	-3.242
5400	8.799	71.140	16.921	4.443	-3.242
5500	8.799	70.960	16.921	4.443	-3.242
5600	8.799	70.770	16.921	4.443	-3.242
5700	8.799	70.570	16.921	4.443	-3.242
5800	8.799	70.360	16.921	4.443	-3.242
5900	8.799	70.140	16.921	4.443	-3.242
6000	8.799	69.910	16.921	4.443	-3.242

December 31, 1960.

Silicon Monosulfide (SiS)

(Ideal Gas)

Mol. Wt. = 60.156

 $\Delta H_f^\circ = 16.926 \text{ kcal. mole}^{-1}$ $\Delta S_f^\circ = 53.427 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ Ground State Configuration $1\Sigma^+$

Electronic Level and Multiplicity

 $\epsilon \text{ cm.}^{-1}$ $\frac{g_i}{l}$ $\omega_e x_e = 2.55 \text{ cm.}^{-1}$ $\omega_e = 0.30363 \text{ cm.}^{-1}$ $\epsilon = 1$ $r_e = 1.9288 \text{ \AA}$ Heat of Formation. $\Delta H_f^\circ = 298.15$ was found in J. S. Gordon, Thiokol

Chemical Corp., Reaction Motors Division, Denville, N. J., "Thermo-

dynamic Data for Combustion Products", January, 1960.

Heat Capacity and Entropy. Molecular constants were taken from

J. S. Gordon, op. cit.

Sulfur, Diatomic (S_2)

(Ideal Gas) Mol. Wt. = 64.128

T, K.	C _p	S°	(F°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH° _f	ΔF° _f	Log K _p
0	.000	INFINITE	-	2.441	30.805	INFINITE	INFINITE
100	6.964	46.623	61.075	-1.445	27.104	-59.232	-
200	7.265	51.515	55.204	-.738	23.040	-25.176	-
298	7.479	54.510	50.840	.000	19.138	-14.028	-
300	7.468	54.558	50.834	.014	19.066	-13.889	-
400	8.144	56.848	46.819	.811	29.433	-8.323	-
500	8.389	58.693	45.416	1.639	28.385	-5.160	-
600	8.549	60.238	44.094	2.486	27.518	-3.123	-
700	8.725	61.726	42.875	3.317	26.800	-1.200	-
800	8.795	63.175	41.755	4.127	26.200	.000	.000
900	8.792	63.758	40.709	5.093	.000	.000	.000
1000	8.836	64.687	39.712	5.975	.000	.000	.000
1100	8.870	65.531	38.794	6.860	.000	.000	.000
1200	8.902	66.294	37.944	7.746	.000	.000	.000
1300	8.922	67.017	37.171	8.640	.000	.000	.000
1400	8.942	67.679	36.470	9.533	.000	.000	.000
1500	8.960	68.296	35.834	10.428	.000	.000	.000
1600	8.976	68.875	35.255	11.325	.000	.000	.000
1700	8.990	69.416	34.728	12.223	.000	.000	.000
1800	9.002	69.934	34.253	13.123	.000	.000	.000
1900	9.014	70.421	33.824	14.024	.000	.000	.000
2000	9.025	70.884	33.442	14.926	.000	.000	.000
2100	9.036	71.324	33.107	15.829	.000	.000	.000
2200	9.045	71.742	32.814	16.734	.000	.000	.000
2300	9.052	72.147	32.560	17.638	.000	.000	.000
2400	9.058	72.539	32.343	18.544	.000	.000	.000
2500	9.064	72.913	32.161	19.451	.000	.000	.000
2600	9.068	73.259	32.012	20.359	.000	.000	.000
2700	9.071	73.582	31.894	21.267	.000	.000	.000
2800	9.073	73.892	31.802	22.176	.000	.000	.000
2900	9.074	74.186	31.731	23.086	.000	.000	.000
3000	9.074	74.461	31.677	23.997	.000	.000	.000
3100	9.073	74.716	31.636	24.909	.000	.000	.000
3200	9.071	74.951	31.605	25.822	.000	.000	.000
3300	9.068	75.166	31.582	26.736	.000	.000	.000
3400	9.064	75.360	31.565	27.649	.000	.000	.000
3500	9.059	75.534	31.553	28.563	.000	.000	.000
3600	9.053	75.688	31.545	29.479	.000	.000	.000
3700	9.046	75.822	31.541	30.395	.000	.000	.000
3800	9.038	75.936	31.540	31.312	.000	.000	.000
3900	9.029	76.030	31.541	32.229	.000	.000	.000
4000	9.018	76.103	31.544	33.148	.000	.000	.000
4100	9.002	76.149	31.549	34.066	.000	.000	.000
4200	8.981	76.168	31.556	34.984	.000	.000	.000
4300	8.956	76.159	31.564	35.902	.000	.000	.000
4400	8.926	76.113	31.571	36.820	.000	.000	.000
4500	8.891	76.029	31.577	37.749	.000	.000	.000
4600	8.850	75.906	31.582	38.678	.000	.000	.000
4700	8.804	75.746	31.585	39.607	.000	.000	.000
4800	8.753	75.550	31.586	40.536	.000	.000	.000
4900	8.697	75.319	31.585	41.465	.000	.000	.000
5000	8.636	75.054	31.582	42.394	.000	.000	.000
5100	8.570	74.756	31.576	43.323	.000	.000	.000
5200	8.499	74.426	31.566	44.252	.000	.000	.000
5300	8.423	74.066	31.552	45.181	.000	.000	.000
5400	8.342	73.677	31.534	46.110	.000	.000	.000
5500	8.256	73.260	31.512	47.039	.000	.000	.000
5600	8.165	72.817	31.486	47.968	.000	.000	.000
5700	8.069	72.348	31.457	48.897	.000	.000	.000
5800	7.968	71.854	31.424	49.826	.000	.000	.000
5900	7.862	71.336	31.387	50.755	.000	.000	.000
6000	7.751	70.794	31.346	51.684	.000	.000	.000

Dec. 31, 1960; Dec. 31, 1965

SULFUR, DIATOMIC (S_2)

(IDEAL GAS)

MOL. WT. = 64.128

Ground State Configuration $3\Sigma_g^-$
 $S_{298.15}^\circ = 54.51 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$

$\Delta H_f^\circ 0 = 30.80 \pm 0.2 \text{ kcal. mole}^{-1}$
 $\Delta H_f^\circ 298.15 = 30.84 \pm 0.2 \text{ kcal. mole}^{-1}$

Electronic Levels and Quantum Weight

$\epsilon, \text{ cm.}^{-1}$ g_i

0	3
---	---

$\omega_e = 724.68 \text{ cm.}^{-1}$
 $x_e = 2.852 \text{ cm.}^{-1}$
 $\alpha_e = 0.0018 \text{ cm.}^{-1}$

$\sigma^+ = 2$
 $r_e = 1.889 \text{ \AA}$

Heat of Formation.

The standard enthalpy of formation of gaseous diatomic sulfur, $\Delta H_f^\circ 298 = 30.84 \text{ kcal. mole}^{-1}$, was calculated from $\Delta H_f^\circ 298 = -20.30 \text{ kcal. mole}^{-1}$ for the reaction $H_2(g) + 0.5 S_2(g) \rightarrow H_2S(g)$ with JANAP value $\Delta H_f^\circ 298(H_2S, g) = -4.88 \pm 0.15 \text{ kcal. mole}^{-1}$. The $\Delta H_f^\circ 298$ was obtained by the second and third law analyses of equilibrium constants which have been determined by G. Freuner and W. Schupp (ref. 1) and M. Randall and P. R. Bichowsky (ref. 2). The results obtained are presented as follows:

Ref.	Temp. Range	Points	2nd law $\Delta H_f^\circ 298 \text{ kcal. mole}^{-1}$	3rd law $\Delta H_f^\circ 298 \text{ kcal. mole}^{-1}$	Drift cal. mole ⁻¹ deg. ⁻¹
1	1023-1405°K	5	-19.92 ± 0.13	-20.295	-0.282 ± 0.097
2	1362-1667°K	4	-20.74 ± 0.40	-20.307	$+0.281 \pm 0.269$
3	1023-1667°K	9	-20.13 ± 0.12	-20.300	-0.066 ± 0.083

References

1. G. Freuner and W. Schupp, Z. physik. Chem. **69**, 157 (1910).
2. M. Randall and P. R. Bichowsky, J. Am. Chem. Soc. **40**, 368 (1918).
3. Combination of above references.

The third law value of the combination set was selected to calculate the heat of formation of diatomic sulfur.

The dissociation energy of gaseous diatomic sulfur, $D_0^\circ(S_2) = 101.5 \text{ kcal. mole}^{-1}$, was chosen. For discussions see JANAP monatomic sulfur (g) and sulfur monoxide (g) tables.

Heat Capacity and Entropy.

The molecular constants which were taken from G. Herzberg, "Spectra of Diatomic Molecules", 2nd Ed., D. Van Nostrand Company, New York, have been modified for the natural isotopic abundances reported by D. Strominger, J. M. Hollander and G. T. Seaborg, Rev. Mod. Phys. **30**, 585 (1958).

INTERIM TABLE

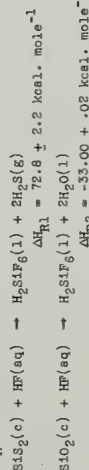
T, °K.	C _p ^o	S ^o - (F ^o - H _{298^o)/T}	H ^o - H _{298^o}	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100	14.990	16.000	.000	- 43.000	- 41.899	30.711
200						
298						
300	15.000	16.093	.093	- 43.001	- 41.892	30.517
400	15.600	17.594	1.594	- 43.176	- 41.867	22.656
500	16.600	17.795	3.165	- 44.996	- 40.693	17.786
600	17.100	19.060	4.840	- 45.608	- 39.772	14.486
700	17.600	20.408	6.595	- 46.053	- 38.714	12.087
800	18.500	21.738	8.400	- 47.090	- 37.162	10.781
900	19.500	23.047	10.400	- 47.890	- 36.142	9.769
1000	19.500	24.276	12.240	- 47.847	- 35.192	7.035
1100	20.600	25.478	14.265	- 47.140	- 28.274	5.617
1200	21.300	26.635	16.360	- 47.571	- 24.400	4.444
1300	22.000	27.751	18.225	- 48.525	- 20.276	3.453
1400	22.700	28.828	20.065	- 49.483	- 16.483	2.633
1500	23.400	29.870	21.065	- 49.483	- 13.089	1.907
1600	24.100	30.879	25.440	- 47.655	- 9.419	1.287
1700	24.800	31.859	27.885	- 47.866	- 5.699	.733
1800	25.500	32.810	30.900	- 47.866	- 1.762	.321
1900	26.200	33.736	32.485	- 47.866	- 1.762	.321

December 31, 1960.

Silicon Disulfide (SiS₂) (Crystal)

Mol. Wt. = 92.222
ΔH_f^o 298.15 = -50.7 kcal. mole⁻¹
S_{298.15} = [16.0] cal. deg.⁻¹ mole⁻¹
T_m = 1363°K.
ΔH_m = [5.0] kcal. mole⁻¹

Heat of Formation. ΔH_f^o 298.15 was calculated from the measured ΔH_f^os of the following reactions:



ΔH_{R1} was taken from R. Rocquet, M. T. Ancey-Maret, Bull. Soc. Chim. France 1954, 1059 (1954); ΔH_{R2} was from D. Torgeson and Th. G. Samaha, J. Am. Chem. Soc. 76, 2156 (1954). ΔH_f^o 298.15 of SiS₂ was recalculated using the corrected value for ΔH_f^o 298.15 of SiO₂.

Heat Capacity and Entropy. C_p and S_{298.15} values are estimated.

Melting Data. T_m was from National Bureau of Standards Circular 500, "Selected Values of Chemical Thermodynamic Properties", 1952. ΔH_m was estimated.

S₂Si

Silicon Disulfide (SiS₂)
(Liquid) Mol. Wt. = 92.222

INTERIM TABLE

T. °K.	C _p ^o	S ^o - (F°-H ₂₉₈ °)/T	H°-H ₂₉₈ ^o	ΔH _f ^o	ΔF _f ^o	Log K _p
0						
100		21.621	0.000	- 37.303	- 37.878	27.764
200	11.040	21.621		- 37.312	- 37.881	27.595
300	11.070	21.622	+0.00	- 37.310	- 37.882	20.740
400	12.700	22.065		- 37.310	- 37.882	16.442
500	14.300	22.506	2.561	- 39.903	- 37.617	
600	15.600	30.835	4.059	- 40.692	- 37.061	13.506
700	16.900	33.339	5.665	- 41.258	- 36.184	10.434
800	18.100	35.675	7.435	- 41.584	- 35.184	8.383
900	19.200	37.671	9.401	- 42.382	- 34.521	6.752
1000	20.200	39.347	11.272	- 46.918	- 30.894	
1100	21.200	41.920	13.343	- 66.365	- 27.320	5.828
1200	22.150	43.605	15.510	- 65.624	- 26.190	3.318
1300	23.000	45.611	17.767	- 65.624	- 25.190	2.648
1400	23.600	47.286	20.102	- 65.704	- 24.264	1.979
1500	24.000	48.686	22.485	- 63.366	- 13.580	
1600	24.000	50.637	24.889	- 62.509	- 10.285	1.405
1700	24.000	51.992	27.289	- 73.763	- 6.335	.866
1800	24.000	53.364	29.689	- 71.491	- 3.025	.595
1900	24.000	54.861	32.089	- 71.491	- 4.632	
2000	24.000	55.892	34.489	- 71.106		

Silicon Disulfide (SiS₂) (liquid)

Mol. Wt. = 92.222

ΔH_f^o 298.15 = [45.0] kcal. mole⁻¹

S_{298.15}^o = [21.621] cal. deg.⁻¹ mole⁻¹

T_m = 1363°K.

ΔH_m^o = [5.0] kcal. mole⁻¹

Heat of Formation. ΔH_f^o 298.15 was calculated from the ΔH_f^o 298.15 of the crystal and the heat of melting.

Heat Capacity and Entropy. C_p and S_{298.15} were estimated.

Melting Data. T_m was from National Bureau of Standards Circ. 500, 1952. ΔH_m^o was estimated.

S₂Si

S₂Si

T, °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ ΔH° _f	ΔH° _f kcal. mole ⁻¹	Log K _p
0	∞	INFINITE	-7.487	25.137	INFINITE
100	20.431	70.514	132.035	20.481	44.798
200	32.066	88.909	106.096	24.731	17.422
298	37.296	102.823	102.823	24.200	8.609
300	37.361	103.054	102.824	24.189	8.500
400	39.641	114.183	104.324	19.272	4.237
500	41.137	123.227	107.229	15.823	2.308
600	41.887	130.709	110.944	13.121	1.253
700	42.355	137.293	115.012	10.935	0.685
800	42.682	143.066	118.587	8.941	0.347
900	42.882	148.000	121.667	7.247	0.168
1000	43.038	152.536	123.342	5.931	2.698
1100	43.154	156.643	124.186	5.003	4.553
1200	43.244	160.402	124.883	4.357	6.000
1300	43.313	163.852	125.462	3.920	7.280
1400	43.369	167.072	125.951	3.631	8.340
1500	43.414	170.073	126.363	3.441	9.216
1600	43.450	172.875	126.708	3.316	10.232
1700	43.481	175.510	126.984	3.231	10.946
1800	43.508	177.999	127.200	3.178	11.479
1900	43.528	180.346	127.366	3.146	12.135
2000	43.547	182.582	127.498	3.126	12.633
2100	43.563	184.707	127.598	3.114	13.079
2200	43.577	186.734	127.666	3.108	13.483
2300	43.589	188.678	127.706	3.104	13.853
2400	43.599	190.552	127.722	3.101	14.197
2500	43.609	192.367	127.728	3.099	14.522
2600	43.617	194.118	127.724	3.097	14.830
2700	43.625	195.806	127.711	3.095	15.121
2800	43.631	197.437	127.689	3.093	15.395
2900	43.637	199.018	127.658	3.091	15.654
3000	43.643	200.551	127.619	3.089	15.898
3100	43.648	202.042	127.573	3.087	16.128
3200	43.652	203.496	127.521	3.085	16.345
3300	43.656	204.918	127.464	3.083	16.550
3400	43.660	206.305	127.402	3.081	16.744
3500	43.663	207.656	127.336	3.079	16.928
3600	43.666	208.978	127.266	3.077	17.102
3700	43.669	210.270	127.192	3.075	17.267
3800	43.672	211.531	127.115	3.073	17.423
3900	43.674	212.762	127.036	3.071	17.571
4000	43.676	213.973	126.953	3.069	17.711
4100	43.678	215.163	126.867	3.067	17.843
4200	43.680	216.333	126.778	3.065	17.968
4300	43.682	217.483	126.685	3.063	18.086
4400	43.684	218.613	126.589	3.061	18.198
4500	43.685	219.724	126.490	3.059	18.304
4600	43.687	220.816	126.388	3.057	18.405
4700	43.688	221.890	126.283	3.055	18.501
4800	43.690	222.946	126.175	3.053	18.593
4900	43.692	223.984	126.064	3.051	18.681
5000	43.693	225.004	125.950	3.049	18.765
5100	43.694	226.006	125.833	3.047	18.846
5200	43.695	227.000	125.713	3.045	18.923
5300	43.696	228.000	125.590	3.043	19.000
5400	43.697	229.000	125.464	3.041	19.075
5500	43.697	230.000	125.336	3.039	19.148
5600	43.698	231.000	125.206	3.037	19.219
5700	43.698	232.000	125.073	3.035	19.288
5800	43.699	233.000	124.938	3.033	19.355
5900	43.700	234.000	124.801	3.031	19.420
6000	43.700	235.000	124.662	3.029	19.483

Dec. 31, 1960; June 30, 1964

Point group D_{4d}S_{298.15}° = 102.823 cal. deg.⁻¹ mole⁻¹

Ground State Quantum Weight = [1]

Vibrational Frequencies and Degeneracies		
(W), cm. ⁻¹	(W), cm. ⁻¹	(W), cm. ⁻¹
475 (1)	475 (2)	243 (1)
218 (1)	152 (2)	437 (2)
471 (2)	56 (2)	248 (2)
191 (2)	411 (1)	

Bond Distance: S-S = 2.059 ± 0.002 Å

Bond Angle: S-S-S = 107.9 ± 0.6°

Product of the Moments of Inertia: I_AI_BI_C = 3.90328 × 10⁻¹¹¹ g.³ cm.⁶

σ = 8

Heat of Formation.

The vapor pressure of S(g) has been measured by many investigators. Using the seven more recent vapor pressure data, the respective heat of sublimation (ΔH_g^{298.15}) was calculated by both the third and second law methods. The values obtained are tabulated as follows:

Investigator	Temperature Range, °K.	ΔH _g ^{298.15} , kcal. mole ⁻¹
West-Menzies ¹	376.6 - 446.8	24.29
Neumann ²	352.6 - 362.1	24.35
Fourtner ³	304.1 - 351.6	24.36
Tallade ⁴	303.6 - 352.5	24.29
Bradley ⁵	288.3 - 305.7	24.29
Magee ⁶	331.9 - 368.0	24.11
Briske ⁷	332.7 - 367.4	23.88
	275.2 - 313.2	24.28
		24.00

¹ W. A. West and A. W. Menzies, J. Phys. Chem. **53**, 1880 (1959).² K. Neumann, Z. physik. Chem. **117**, 416 (1954).³ G. Fourtner, Compt. rend. **218**, 194 (1944).⁴ M. Tallade, Compt. rend. **218**, 836 (1944).⁵ R. S. Bradley, Proc. Roy. Soc. (London) **A 205**, 553 (1951).⁶ D. W. Magee, Ph. D. Thesis, The Ohio State University, 1955.⁷ C. Briske, N. H. Hartshorne and D. R. Stranks, J. Chem. Soc. (London), 1200 (1960).

Due to the presence of S₈(g) in S₈(g), the measured total pressures were corrected to give the partial pressures of S₈(g) for the first five sets of vapor pressure data, according to D. W. Scott, U. S. Bureau of Mines, Bartlesville, Oklahoma, private communication, May 22, 1964. However, the magnitude of the correction is only 0.1 - 0.2 kcal. mole⁻¹. The adopted value is the weighted average of both the third and second law values.

Heat Capacity and Entropy.

The vibrational frequencies were taken from D. W. Scott, J. P. McCullough and F. H. Krue, "Vibrational Assignment and Force Constants of S₈ (condensed States) from a Normal-Coordinate Treatment", Prepublication Report 64, U. S. Bureau of Mines, May 20, 1963. Four of the eighteen frequencies, i.e. 86(2) and 218(2) cm.⁻¹, were changed to 56(2) and 248(2) cm.⁻¹, respectively, suggested by D. W. Scott, loc. cit., private communication, April 23, 1964. The molecular structure and bond distance and angle were reported by J. Donohue, A. Caron and E. Goldstein, J. Am. Chem. Soc. **83**, 3748 (1961). The three principle moments of inertia are: I_A = I_B = 1.28594 × 10⁻⁵⁷ and I_C = 2.36042 × 10⁻⁵⁷ g. cm.².

Silicon (Si)

(Reference State) GFW = 28.086

T, °K	Cp	gibbs/mol S° - (G° - H° ₂₉₈)/T	kcal/mol H° - H° ₂₉₈	ΔHf°	ΔGf°	Log Kp
0	1.000	0.000	0.000	0.000	0.000	0.000
100	1.797	0.000	0.000	0.000	0.000	0.000
200	3.737	2.768	0.000	0.000	0.000	0.000
298	4.740	4.498	0.000	0.000	0.000	0.000
300	4.782	4.528	0.000	0.000	0.000	0.000
400	5.292	5.983	0.516	0.000	0.000	0.000
500	5.576	7.197	1.050	0.000	0.000	0.000
600	5.773	8.231	1.628	0.000	0.000	0.000
700	5.928	9.133	2.213	0.000	0.000	0.000
800	6.061	9.933	2.813	0.000	0.000	0.000
900	6.184	10.655	3.425	0.000	0.000	0.000
1000	6.295	11.312	4.049	0.000	0.000	0.000
1100	6.400	11.917	4.684	0.000	0.000	0.000
1200	6.500	12.478	5.329	0.000	0.000	0.000
1300	6.600	13.002	5.984	0.000	0.000	0.000
1400	6.700	13.495	6.649	0.000	0.000	0.000
1500	6.800	13.961	7.324	0.000	0.000	0.000
1600	6.900	14.403	8.009	0.000	0.000	0.000
1700	6.500	21.941	9.767	20.597	0.000	0.000
1800	6.500	22.313	10.454	21.347	0.000	0.000
1900	6.500	22.664	11.097	21.997	0.000	0.000
2000	6.500	22.998	11.694	22.597	0.000	0.000
2100	6.500	23.315	12.221	23.297	0.000	0.000
2200	6.500	23.617	12.732	23.947	0.000	0.000
2300	6.500	23.906	13.212	24.597	0.000	0.000
2400	6.500	24.183	13.663	25.247	0.000	0.000
2500	6.500	24.448	14.099	25.897	0.000	0.000
2600	6.500	24.703	14.493	26.547	0.000	0.000
2700	6.500	24.948	14.876	27.197	0.000	0.000
2800	6.500	25.185	15.240	27.847	0.000	0.000
2900	6.500	25.413	15.586	28.497	0.000	0.000
3000	6.500	25.633	15.918	29.147	0.000	0.000
3100	6.500	25.846	16.235	29.797	0.000	0.000
3200	6.500	26.053	16.538	30.447	0.000	0.000
3300	6.500	26.253	16.830	31.097	0.000	0.000
3400	6.500	26.447	17.110	31.747	0.000	0.000
3500	6.500	26.635	17.379	32.397	0.000	0.000
3600	5.508	52.990	18.265	125.004	0.000	0.000
3700	5.513	53.141	19.206	125.559	0.000	0.000
3800	5.516	53.288	20.101	126.110	0.000	0.000
3900	5.519	53.431	20.954	126.662	0.000	0.000
4000	5.521	53.571	21.767	127.214	0.000	0.000
4100	5.523	53.707	22.545	127.767	0.000	0.000
4200	5.524	53.840	23.288	128.319	0.000	0.000
4300	5.524	53.970	24.000	128.871	0.000	0.000
4400	5.524	54.097	24.693	129.424	0.000	0.000
4500	5.524	54.222	25.358	129.976	0.000	0.000
4600	5.523	54.343	25.967	130.528	0.000	0.000
4700	5.522	54.462	26.572	131.081	0.000	0.000
4800	5.521	54.578	27.155	131.633	0.000	0.000
4900	5.520	54.692	27.715	132.185	0.000	0.000
5000	5.519	54.803	28.258	132.737	0.000	0.000
5100	5.519	54.913	28.778	133.289	0.000	0.000
5200	5.518	55.020	29.281	133.841	0.000	0.000
5300	5.518	55.125	29.768	134.392	0.000	0.000
5400	5.518	55.228	30.238	134.944	0.000	0.000
5500	5.520	55.328	30.694	135.496	0.000	0.000
5600	5.521	55.429	31.134	136.048	0.000	0.000
5700	5.524	55.527	31.562	136.600	0.000	0.000
5800	5.527	55.623	31.976	137.153	0.000	0.000
5900	5.530	55.717	32.377	137.705	0.000	0.000
6000	5.536	55.810	32.767	138.256	0.000	0.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966; Mar. 31, 1967

SILICON (Si)

0 to 1685°K Crystal

1685 to 3513.8°K Liquid

3513.8 to 6000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

OPW = 28.086

Si

Si

SILICON (Si)

OFW = 28.086

(CRYSTAL)

GFW = 28.086

Silicon (Si)
(Crystal)

T, °K	Cp°	S°	gibbs/mol	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol	ΔHf°	ΔGf°	Log Kp
0	0.000	0.000	INFINITE	-	7.69	0.000	0.000	0.000	INFINITE
100	1.737	0.016	7.066	-	7.05	0.000	0.000	0.000	0.000
200	3.737	2.788	6.908	-	4.24	0.000	0.000	0.000	0.000
298	4.780	4.498	6.498	0.000	0.000	0.000	0.000	0.000	0.000
300	4.792	4.528	6.498	0.009	0.009	0.000	0.000	0.000	0.000
400	5.292	5.967	6.498	0.009	0.009	0.000	0.000	0.000	0.000
500	5.576	7.197	5.076	0.000	1.060	0.000	0.000	0.000	0.000
600	5.773	8.231	5.518	0.000	1.628	0.000	0.000	0.000	0.000
700	5.928	9.133	5.071	0.000	2.213	0.000	0.000	0.000	0.000
800	6.054	9.905	6.419	0.000	2.813	0.000	0.000	0.000	0.000
900	6.164	11.655	6.419	0.000	3.425	0.000	0.000	0.000	0.000
1000	6.295	11.312	7.263	0.000	4.049	0.000	0.000	0.000	0.000
1100	6.400	11.917	7.659	0.000	4.684	0.000	0.000	0.000	0.000
1200	6.500	12.478	8.037	0.000	5.329	0.000	0.000	0.000	0.000
1300	6.600	13.000	8.400	0.000	5.984	0.000	0.000	0.000	0.000
1400	6.700	13.495	8.746	0.000	6.649	0.000	0.000	0.000	0.000
1500	6.800	13.961	9.078	0.000	7.324	0.000	0.000	0.000	0.000
1600	6.900	14.403	9.397	0.000	8.009	0.000	0.000	0.000	0.000
1700	7.000	14.824	9.704	0.000	8.704	0.000	0.000	0.000	0.000
1800	7.100	15.224	10.000	0.000	9.400	0.000	0.000	0.000	0.000
1900	7.200	15.614	10.296	0.000	10.104	0.000	0.000	0.000	0.000
2000	7.300	15.985	10.561	0.000	10.849	0.000	0.000	0.000	0.000
2100	7.400	16.344	10.828	0.000	11.584	0.000	0.000	0.000	0.000
2200	7.500	16.691	11.086	0.000	12.329	0.000	0.000	0.000	0.000
2300	7.600	17.028	11.334	0.000	13.084	0.000	0.000	0.000	0.000
2400	7.700	17.352	11.581	0.000	13.849	0.000	0.000	0.000	0.000
2500	7.800	17.668	11.818	0.000	14.624	0.000	0.000	0.000	0.000

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1966

$$\Delta H_f^\circ = 0 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 0 \text{ kcal/mol}$$

$$\Delta H_m^\circ = 12.0 \pm 0.1 \text{ kcal/mol}$$

$$\Delta H_f^\circ_{298.15} = 107.7 \pm 1 \text{ kcal/mol}$$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

Low temperature heat capacities are based on the precise data (8-300°K) of Flubacher, Leadbetter and Morrison. The entropy is obtained from the heat capacity using $S_g^\circ = 0.0003$ eu. The selected values are consistent with recent data of Keesom and Seidel (1.2 - 4.2°K) and Kailishevich et al. (60-300°K). Earlier data have been reviewed by R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965.

High temperature studies are summarized below, along with the pertinent low temperature studies. The selected heat capacities above 300°K are obtained from a Shomate plot of the adopted low temperature heat capacities and the enthalpies reported or derived from the work of Dennison (1963), Kantor et al. (1960), Olette (1956), Serebrennikov and Gel'd (1952), and Magnus (1952). Discrepancies are apparent in the enthalpy data, particularly in the range of 370 to 1100°K, where only the recent study of Dennison made use of a high purity sample. Enthalpies from Dennison join most smoothly with the low temperature C_p° but deviate increasingly at higher temperatures, being 1-2% lower than the other measurements above 1000°K. The selected functions agree with Dennison below 600°K, with Magnus from 600 to 1200°K, and with Kantor et al. above 1200°K. The resulting heat capacities are slightly different from those selected by Hultgren et al., loc. cit.; the latter are 0.07 gibbs/mol higher at 800°K and 0.21 gibbs/mol lower at the melting point.

Investigators	Method	Quantity Reported	T Range, °K	Sample
1. Flubacher et al. (1959)	Calorimetry	C_p°	7.7 - 300	Single crystal, annealed, resistance (300°K) 0.027 ohm cm, Carrier Concentration $\leq 10^{15} \text{ cm}^{-3}$
2. Keesom et al. (1959)	Calorimetry	Specific Heat	1.2 - 4.2	
3. Kailishevich et al. (1965)	Calorimetry	C_p°	60 - 300	99.99%
4. Gerlich et al. (1965)	Temperature Modulation	C_p°	300 - 900	Resistance (300°K) = 0.027 ohm cm, Carrier Concentration = 10^{19} cm^{-3}
5. Dennison (1963)	Drop Calorimetry	Specific Heat	273 - 1373	Resistance (300°K) = 107 ohm cm
6. Kantor et al. (1960)	Drop Calorimetry	Enthalpy Equation	1148 - 1695	"Highly purified"
7. Olette (1956)	Drop Calorimetry	Specific Enthalpy	1467 - 1695	99.99%
8. Serebrennikov et al.	Drop Calorimetry	Specific Enthalpy	302 - 1556	99.3%
9. Magnus (1952)	Drop Calorimetry	Specific Enthalpy	372 - 1175	99.2%

Reference:

1. P. Flubacher, A. J. Leadbetter and J. A. Morrison, *Phil. Mag.* **4**, 273 (1959).
2. F. H. Keesom and G. Seidel, *Phys. Rev.* **113**, 53 (1959).
3. G. I. Kailishevich, P. V. Gel'd and R. F. Krentsis, *Russ. J. Phys. Chem.* **39**, 1802 (1965).
4. D. Gerlich, B. Abeles and R. E. Miller, *J. Appl. Phys.* **36**, 76 (1965).
5. D. H. Dennison quoted by H. R. Shanks et al., *Phys. Rev.* **130**, 1743 (1963).
6. P. B. Kantor, A. M. Kiehl and E. M. Romachev, *Ukrain. Fiz. Zhur.* **5**, 358 (1960).
7. M. Olette, *Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1956*, 18-26 (Pub. 1958).
8. N. N. Serebrennikov and P. V. Gel'd, *Doklady Akad. Nauk SSSR* **87**, 1021 (1952).
9. A. Magnus, *Ann. Physik* **70**, 303 (1923).

Melting Data.

See the Si(l) table for details.

Heat of Sublimation.

 $\Delta H_f^\circ_{298.15}$ is calculated as the difference between $\Delta H_f^\circ_{298.15}$ for Si(g) and Si(c).

Silicon (Si)
(Liquid)

GFW = 28.086

T, °K	C _p ^o	S ^o - (C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H _T ^o	ΔH _T ^o	ΔG ^o	Log K _p
100						
200						
298	6.500	10.426	0.00	11.585	9.758	7.153
300	6.500	10.466	0.12	11.588	9.747	7.100
400	6.500	12.536	0.62	11.731	9.110	4.977
500	6.500	13.987	1.312	11.837	8.442	3.690
600	6.500	15.172	1.942	11.919	7.758	2.825
700	6.500	17.042	2.652	11.984	7.058	2.203
800	6.500	17.807	3.262	12.034	6.337	1.734
900	6.500	18.492	3.912	12.072	5.635	1.368
1000	6.500	19.128	4.562	12.098	4.918	1.075
1100	6.500	19.712	5.212	12.113	4.199	0.836
1200	6.500	20.247	5.862	12.118	3.479	0.638
1300	6.500	20.739	6.512	12.113	2.760	0.464
1400	6.500	21.188	7.162	12.098	2.040	0.319
1500	6.500	21.597	7.812	12.073	1.323	0.193
1600	6.500	21.967	8.462	12.038	0.608	0.083
1700	6.500	22.303	9.112	11.993	0.000	0.000
1800	6.500	22.603	9.762	11.938	0.000	0.000
1900	6.500	22.869	10.412	11.873	0.000	0.000
2000	6.500	23.097	11.062	11.798	0.000	0.000
2100	6.500	23.287	11.712	11.713	0.000	0.000
2200	6.500	23.437	12.362	11.618	0.000	0.000
2300	6.500	23.556	13.012	11.513	0.000	0.000
2400	6.500	23.643	13.662	11.398	0.000	0.000
2500	6.500	23.698	14.312	11.273	0.000	0.000
2600	6.500	23.723	14.962	11.138	0.000	0.000
2700	6.500	23.717	15.612	10.993	0.000	0.000
2800	6.500	23.681	16.262	10.838	0.000	0.000
2900	6.500	23.613	16.912	10.673	0.000	0.000
3000	6.500	23.533	17.562	10.498	0.000	0.000
3100	6.500	23.443	18.212	10.313	0.000	0.000
3200	6.500	23.343	18.862	10.118	0.000	0.000
3300	6.500	23.233	19.512	9.913	0.000	0.000
3400	6.500	23.113	20.162	9.698	0.000	0.000
3500	6.500	22.983	20.812	9.473	0.000	0.000
3600	6.500	22.843	21.462	9.238	2.258	0.137
3700	6.500	22.693	22.112	8.993	1.543	0.289
3800	6.500	22.533	22.762	8.738	0.828	0.431
3900	6.500	22.363	23.412	8.473	0.113	0.566
4000	6.500	22.193	24.062	8.198	0.000	0.694
4100	6.500	22.013	24.712	7.913	0.000	0.816
4200	6.500	21.823	25.362	7.618	0.000	0.932
4300	6.500	21.623	26.012	7.313	0.000	1.043
4400	6.500	21.413	26.662	6.998	0.000	1.148
4500	6.500	21.193	27.312	6.673	0.000	1.249

SILICON (Si) (LIQUID) GFW = 28.086

$S_{298.15}^{\circ} = 10.426$ gibbs/mol
 $\Delta H_f^{\circ} = 11.585$ kcal/mol
 $\Delta H_m^{\circ} = 12.0 \pm 0.1$ kcal/mol
 $\Delta H_v^{\circ} = [92.047]$ kcal/mol
 $\Delta H_v^{\circ} = [85.8]$ kcal/mol

T_m = 1685 ± 3°K

T_b = [3513.8] °K (to monomer only)

T_b = [3492] °K (to equilibrium mixture)

Heat of Formation.

The heat of formation is obtained from that of the crystal by adding ΔH_m° and the difference between $H_{298.15}^{\circ}$ - $H_{298.15}^{\circ}$ for crystal and liquid.

Heat Capacity and Entropy.

Enthalpy data for high purity samples in quartz or vitreous silica capsules have been reported for the range 1698-1915°K by P. B. Kantor, A. M. Kisil and E. M. Fomichev, Ukrain. Fiz. Zhur. 5, 358 (1960), and for the range 1686-1825°K by M. Olette, Phys. Chem. Steelmaking, Proc. Dedham, Mass. 1955, 18-28 (Pub. 1958). Due to the limited temperature range and the experimental uncertainty, the data do not appear to justify more than a constant heat capacity. A value of 6.5 gibbs/mol is selected, intermediate between the values of 6.75 and 6.15 obtained from the separate experiments. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data.

Modern determinations of the melting point range from 1683 ± 1 to 1690 ± 4°K, the former from the specific volume study of L. D. Lucas and G. Urbain, Compt. Rend. 255, 2414 (1962), and the latter from the enthalpy study of Kantor et al. The selected value of T_m = 1685°K is taken from R. Hultgren, R. L. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, who have reviewed the melting data. The heat of melting is calculated from the selected enthalpy of the crystal and the liquid enthalpy measurements of Kantor et al. and Olette, who reported comparable values of $\Delta H_m^{\circ} = 11.95 \pm 0.18$ and 12.085 ± 0.1 kcal/mol, respectively.

Vaporization Data.

T_b is calculated as the temperature for which the $\Delta G_r^{\circ} = 0$ for Si(l) = Si(g). ΔH_v° is calculated as the difference between $\Delta H_f^{\circ}(g)$ and $\Delta H_f^{\circ}(l)$ at T_b. The normal boiling for the equilibrium vapor is calculated as the temperature at which Si₁, Si₂ and Si₃ attain a total pressure of one atm. ΔH_v° at this temperature is calculated as the enthalpy of vaporization of one GFW of liquid to vapor containing 92.1, 7.0 and 0.9 mole percent of monomer, dimer and trimer, respectively. Tetramer and higher polymers, which are ignored in the equilibrium calculation, are probably negligible at this temperature.

T, °K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	∞	∞	∞	∞	∞	∞	∞
100	4.697	33.446	45.140	106.644	106.644	106.644	∞
200	5.687	37.931	40.617	107.256	103.983	227.585	∞
298	5.318	40.121	40.121	107.587	100.558	109.485	∞
300	5.318	40.121	40.121	107.700	97.079	71.161	∞
400	5.318	40.121	40.121	107.701	97.079	71.161	∞
500	5.095	42.404	40.713	107.717	93.466	39.287	∞
600	5.056	44.729	41.441	107.625	86.326	31.444	∞
700	5.033	46.506	41.568	107.584	82.783	25.846	∞
800	5.012	48.168	42.367	107.536	75.734	16.990	∞
900	5.011	49.696	42.734	107.483	72.229	15.786	∞
1000	5.016	50.777	43.080	107.400	68.737	13.657	∞
1100	5.027	51.421	43.406	107.327	65.287	11.885	∞
1200	5.043	51.790	43.709	107.256	61.790	10.309	∞
1300	5.067	51.983	43.984	107.183	58.246	8.916	∞
1400	5.097	52.103	44.234	107.108	54.653	7.698	∞
1500	5.113	52.156	44.458	107.033	51.013	6.629	∞
1600	5.142	52.156	44.657	106.958	47.328	5.709	∞
1700	5.142	52.156	44.830	106.883	43.598	4.929	∞
1800	5.142	52.156	44.979	106.808	39.828	4.278	∞
1900	5.142	52.156	45.103	106.733	36.018	3.738	∞
2000	5.142	52.156	45.203	106.658	32.168	3.298	∞
2100	5.142	52.156	45.283	106.583	28.278	2.948	∞
2200	5.142	52.156	45.343	106.508	24.348	2.668	∞
2300	5.142	52.156	45.383	106.433	20.378	2.438	∞
2400	5.142	52.156	45.413	106.358	16.368	2.248	∞
2500	5.142	52.156	45.433	106.283	12.318	2.098	∞
2600	5.142	52.156	45.453	106.208	8.228	1.978	∞
2700	5.142	52.156	45.473	106.133	4.098	1.878	∞
2800	5.142	52.156	45.493	106.058	0.000	1.798	∞
2900	5.142	52.156	45.513	105.983	-4.098	1.738	∞
3000	5.142	52.156	45.533	105.908	-8.228	1.698	∞
3100	5.142	52.156	45.553	105.833	-12.318	1.668	∞
3200	5.142	52.156	45.573	105.758	-16.368	1.648	∞
3300	5.142	52.156	45.593	105.683	-20.378	1.628	∞
3400	5.142	52.156	45.613	105.608	-24.348	1.608	∞
3500	5.142	52.156	45.633	105.533	-28.278	1.588	∞
3600	5.142	52.156	45.653	105.458	-32.168	1.568	∞
3700	5.142	52.156	45.673	105.383	-36.018	1.548	∞
3800	5.142	52.156	45.693	105.308	-39.828	1.528	∞
3900	5.142	52.156	45.713	105.233	-43.598	1.508	∞
4000	5.142	52.156	45.733	105.158	-47.328	1.488	∞
4100	5.142	52.156	45.753	105.083	-51.013	1.468	∞
4200	5.142	52.156	45.773	105.008	-54.653	1.448	∞
4300	5.142	52.156	45.793	104.933	-58.246	1.428	∞
4400	5.142	52.156	45.813	104.858	-61.790	1.408	∞
4500	5.142	52.156	45.833	104.783	-65.287	1.388	∞
4600	5.142	52.156	45.853	104.708	-68.737	1.368	∞
4700	5.142	52.156	45.873	104.633	-72.168	1.348	∞
4800	5.142	52.156	45.893	104.558	-75.568	1.328	∞
4900	5.142	52.156	45.913	104.483	-78.928	1.308	∞
5000	5.142	52.156	45.933	104.408	-82.248	1.288	∞
5100	5.142	52.156	45.953	104.333	-85.528	1.268	∞
5200	5.142	52.156	45.973	104.258	-88.768	1.248	∞
5300	5.142	52.156	45.993	104.183	-91.968	1.228	∞
5400	5.142	52.156	46.013	104.108	-95.128	1.208	∞
5500	5.142	52.156	46.033	104.033	-98.248	1.188	∞
5600	5.142	52.156	46.053	103.958	-101.328	1.168	∞
5700	5.142	52.156	46.073	103.883	-104.368	1.148	∞
5800	5.142	52.156	46.093	103.808	-107.368	1.128	∞
5900	5.142	52.156	46.113	103.733	-110.328	1.108	∞
6000	5.142	52.156	46.133	103.658	-113.248	1.088	∞

Dec. 31, 1960; Dec. 31, 1962; Dec. 31, 1965; Mar. 31, 1967

Ground State Configuration $3p_0$ $\Delta H_f^\circ = 106.66 \pm 1$ kcal/mol
 $S_{298.15}^\circ = 40.121$ gibbs/mol $\Delta H_f^\circ = 107.7 \pm 1$ kcal/mol

Electronic Levels and Quantum Weights

e_1, cm^{-1}	g_1	e_2, cm^{-1}	g_2	e_3, cm^{-1}	g_3	e_4, cm^{-1}	g_4	e_5, cm^{-1}	g_5
0	1	45,303	15	50,533	9	56,699	9	56,782	28
77.12	3	47,284	3	51,612	1	56,780	3	58,802	3
223.16	5	47,352	5	53,362	7	57,094	15	58,893	7
6,298.66	5	48,161	15	53,387	3	57,402	9	59,077	15
15,394.37	1	49,128	9	54,226	15	57,489	21	59,108	56
33,326	5	49,400	3	54,425	9	57,542	3	59,674	21
39,860	9	49,966	21	54,871	3	57,798	5	60,706	36
40,592	3	50,169	5	56,503	5	59,311	1	61,278	72

Heat of Formation

The heat of formation is the heat of sublimation, $\Delta H_{298.15}^\circ = 107.7$ kcal/mol, selected from third law analyses of the vapor pressure data reviewed below. Langmuir, Knudsen and transport studies are all in satisfactory agreement throughout the range of 1400 - 2000°K. In addition, O. C. Trueman and P. O. Schlassel, Condensation Evaporation Solids Proc. Symp., Dayton, Ohio 1962, 313-17 (Pub. 1964), have experimentally verified that the vaporization coefficient is about 0.8 at 1300°K. This was accomplished by mass spectrometric determination of the Langmuir and Knudsen rates of sublimation from a single crystal sample in a cell designed to give Knudsen effusion from one end and free evaporation from the other end.

The recent studies confirm the mass spectrometric data of R. E. Honig, J. Chem. Phys. 22, 1610 (1954), and substantiate the author's postulate that vapor pressures obtained in early boiling point experiments are too large due to reaction or decomposition of the alumina and silicon carbide containers. In their review of the earlier experiments, R. Hultgren, R. I. Orr and K. K. Kelley, "Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys," Univ. of California, Berkeley, November, 1965, calculated apparent heats of sublimation of less than 90 kcal/mol from the data. Neither these values nor the value of 92 kcal/mol, obtained from the Knudsen data (1485 - 1593°K) of A. V. Tselyayeva, Yu. A. Priselkov and V. V. Karelin, Vestnik Moskov. Univ., Ser. 2 Khim. 15, No. 5, 36 (1960), were considered in the JANAF selection. It is not clear why Tselyayeva et al. obtain pressures larger by a factor of 200 from their molybdenum cell.

Source	Method	Container or Support	T Range (°K)	No. of Points	ΔH_{298}° (kcal/mol)	Drift eu
1. Guldbransen (1966)	Langmuir	Quartz fiber	1373-1623	10	104.9 ± 4.1	107.15
2. Nannichi (1963)	Langmuir	Tantalum	1599-1527	4	95.3 ± 6.0	107.99
3. Batdorf (1959)	Langmuir	Tantalum	1473-1600	12	108.8 ± 5.7	109.02
4. Davis (1961)	Knudsen	SIC-lined graphite	1848-2003*	11	112.6 ± 12	108.50
5. Oriveson (1959)	Knudsen	SIC-lined graphite	1640-1684	3	97.5 ± 0.2	107.72
Oriveson (1959)	Knudsen	SIC-lined graphite	1701-1900*	9	109.7 ± 0.1	107.74
Oriveson (1959)	Transport	SIC-lined graphite and MoSi ₂	1853*	14	-	107.73
6. Drowart (1960)	Mass Spec.	SIC-lined graphite	1703-2160*	12	108 ± 1.0	107.00

*Data for liquid phase.

- E. A. Guldbransen, K. F. Andrew and P. A. Bressart, J. Electrochem. Soc. 113, 834 (1966).
- Y. Nannichi, Japan J. Appl. Phys. 2, 566 (1963), data given graphically.
- R. L. Batdorf and P. M. Smith, J. Appl. Phys. 30, 259 (1959), data given graphically.
- S. G. Davis, D. P. Anthony and A. W. Searcy, J. Chem. Phys. 34, 659 (1961).
- P. Oriveson and C. B. Alcock, Special Ceramics, Proc. Symposium Brit. Ceram. Research Assoc., Stoke-on-Trent 1959, 183-208 (Pub. 1960). Points above 1900°K are omitted.
- J. Drowart and G. De Maris, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, London, 1960.

Heat Capacity and Entropy

Electronic levels and quantum weights are from L. J. Radziemski and K. L. Andrew, J. Opt. Soc. Am. 55, 474 (1965), and V. Kaufman, L. J. Radziemski and K. L. Andrew, ibid. 55, 911 (1966). An additional level with quantum weight of 200 is estimated above the observed levels and below the dissociation limit; however, the effect of this level on the entropy at 6000°K is negligible. Levels above 39000 cm^{-1} are averaged.

T, °K	Cp ^a	S ^b	-(G°-H°-TS°)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	∞	∞	∞	2.214	140.324	140.324	INFINITE
100	7.029	46.055	61.829	1.517	140.893	136.410	-298.124
200	7.692	51.715	55.632	.783	141.064	131.637	-144.064
298	8.234	56.695	51.895	.000	141.000	127.315	-93.125
300	8.242	56.946	51.895	.015	140.997	127.230	-92.687
400	8.658	57.375	51.828	.861	140.827	122.665	-67.021
500	9.079	59.352	51.857	1.747	140.627	118.148	-51.643
600	9.499	61.085	56.584	2.676	140.420	113.671	-41.604
700	9.917	62.537	57.330	3.645	140.219	109.230	-34.103
800	10.331	63.875	58.066	4.647	140.021	104.814	-28.634
900	10.743	65.082	58.779	5.672	139.822	100.428	-24.397
1000	10.853	66.178	59.465	6.713	139.615	96.061	-20.994
1100	10.502	67.177	60.122	7.761	139.393	91.716	-18.222
1200	10.201	68.091	60.748	8.812	139.154	87.392	-15.916
1300	10.085	68.932	61.348	9.861	138.893	83.087	-13.968
1400	10.047	69.707	61.916	10.908	138.610	78.806	-12.302
1500	10.001	70.427	62.460	11.951	138.303	74.545	-10.861
1600	10.354	71.094	62.970	12.988	137.970	70.306	-9.603
1700	10.309	71.723	63.475	14.022	137.628	66.099	-8.523
1800	10.268	72.311	63.950	15.050	137.276	61.923	-7.713
1900	10.232	72.865	64.404	16.075	136.913	57.781	-7.169
2000	10.200	73.389	64.841	17.097	136.538	53.671	-6.340
2100	10.174	73.884	65.260	18.116	136.154	49.583	-5.753
2200	10.153	74.359	65.663	19.132	135.761	45.524	-5.222
2300	10.135	74.810	66.050	20.146	135.358	41.495	-4.737
2400	10.122	75.241	66.425	21.159	134.945	37.495	-4.295
2500	10.112	75.654	66.785	22.171	134.522	33.522	-3.889
2600	10.104	76.050	67.134	23.182	134.088	29.575	-3.515
2700	10.101	76.432	67.472	24.192	133.645	25.651	-3.169
2800	10.099	76.799	67.798	25.202	133.193	21.745	-2.849
2900	10.099	77.153	68.115	26.212	132.732	17.858	-2.552
3000	10.100	77.496	68.422	27.222	132.262	13.990	-2.276
3100	10.103	77.827	68.720	28.232	131.783	10.143	-2.018
3200	10.107	78.146	69.009	29.242	131.295	6.316	-1.777
3300	10.111	78.459	69.291	30.253	130.798	2.500	-1.551
3400	10.117	78.761	69.565	31.265	130.292	-1.308	-1.338
3500	10.124	79.054	69.832	32.277	129.777	-5.149	-1.139
3600	10.131	79.339	70.092	33.289	129.252	-9.014	-1.295
3700	10.137	79.617	70.364	34.303	128.717	-12.895	-1.349
3800	10.147	79.887	70.594	35.317	128.172	-16.790	-1.467
3900	10.156	80.151	70.835	36.332	127.617	-20.699	-1.579
4000	10.165	80.408	71.071	37.344	127.052	-24.622	-1.686
4100	10.175	80.660	71.302	38.365	126.477	-28.560	-1.787
4200	10.185	80.905	71.528	39.383	125.892	-32.513	-1.884
4300	10.195	81.145	71.749	40.402	125.297	-36.480	-1.976
4400	10.206	81.379	71.965	41.422	124.692	-40.462	-2.064
4500	10.218	81.609	72.177	42.444	124.077	-44.459	-2.149
4600	10.229	81.833	72.384	43.466	123.452	-48.474	-2.230
4700	10.241	82.053	72.588	44.489	122.817	-52.507	-2.307
4800	10.254	82.269	72.787	45.514	122.172	-56.558	-2.382
4900	10.266	82.481	72.983	46.540	121.517	-60.626	-2.453
5000	10.279	82.688	73.175	47.567	120.852	-64.711	-2.521
5100	10.293	82.892	73.363	48.596	120.177	-68.813	-2.586
5200	10.306	83.092	73.548	49.626	119.492	-72.932	-2.651
5300	10.320	83.288	73.730	50.657	118.797	-77.067	-2.712
5400	10.335	83.481	73.909	51.690	118.092	-81.226	-2.771
5500	10.349	83.671	74.085	52.724	117.377	-85.409	-2.828
5600	10.364	83.856	74.258	53.760	116.652	-89.616	-2.883
5700	10.379	84.041	74.428	54.797	115.917	-93.847	-2.936
5800	10.395	84.222	74.595	55.836	115.172	-98.102	-2.987
5900	10.410	84.400	74.760	56.876	114.417	-102.381	-3.036
6000	10.426	84.575	74.922	57.914	113.652	-106.684	-3.084

Dec. 31, 1960; Dec. 31, 1962; Mar. 31, 1967

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 54.895 \text{ gibbs/mol}$$

$$\Delta H_f^\circ = 140.3 \pm 3 \text{ kcal/mol}$$

$$\Delta H_f^\circ = 141 \pm 3 \text{ kcal/mol}$$

Silicon, Triatomic (Si₃)

(Ideal Gas) GFW = 84.258

OFW = 84.258

'SILICON, TRIATOMIC (Si₃)

(IDEAL GAS)

OFW = 84.258

Point Group [D_{3h}]
 $\Delta H_f^\circ = 151.2 \pm 10$ kcal/mol
 $\Delta H_f^\circ = 152 \pm 10$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_1, \text{ cm}^{-1}$ $\frac{g_1}{3}$

(10000) [6]
 (18000) [2]
 21460 3

Vibrational Frequencies and Degeneracies

$\omega, \text{ cm}^{-1}$

[360] (1)
 [200] (2)
 [630] (1)

Bond Distance: Si-Si = [2.25] Å

Bond Angle: Si-Si-Si = [180]°

Rotational Constant: $B_0 = [0.05928] \text{ cm}^{-1}$

$\sigma = [2]$

Heat of Formation.

The selected value is an average based on the equilibrium data summarized below. Drowart and co-workers have used the Knudsen effusion-mass spectrometric technique to determine the vapor species over the systems SiC-graphite¹ and SiC-silicon². Third law analysis of the partial pressures of Si₃ and Si yields the values 154.0 and 149.9 kcal/mol. Both drifts suggest that the entropy may be lower than the tabulated values. It is unlikely that the entropy is in error by more than 5 eu so that most of the drift is inherent in the data. The adopted value of $\Delta H_f^\circ = 152 \pm 10$ kcal/mol includes allowance for an error of up to 5 eu.

Source	Method	Range, °K	No. of Points	ΔH_f° (kcal/mol)*
Drowart (1958)	Mass Spec.	2230-2316	2	209
Drowart (1960)	"	1703-1890	4	204±3
	"	"	"	169.1
	"	"	"	173.2
	"	"	"	149.9

*For reaction $\text{Si}_3(\text{g}) = 3 \text{ Si}(\text{g})$

Heat Capacity and Entropy.

Wetmore and McLeod³ observed an absorption band near 4660 Å in matrix isolation studies. Their tentative assignment of this band as the $\Sigma_u^- \leftarrow \Sigma_g^-$ transition of Si₃ is adopted here. A $1W_u$ state is assumed at 18000 cm⁻¹, which is 7000 and 2000 cm⁻¹ below the analogous levels³ for C₃ and C₂Si. Also a $3W_u$ level is assumed at 10000 cm⁻¹, presumably arising from the same molecular orbital configuration as the $1W_u$ state. The molecule is assumed to be linear with a bond distance equal to that in Si₂. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 2.16 \times 10^5$ and $k_2/k_1 = 0.11 \times 10^5 \text{ dyn/cm}$. The stretching force constant is obtained from Si₂, while the bending force constant is based on C₂Si and the $1W_u$ excited state³ of C₃. The moment of inertia is $47.22 \times 10^{-39} \text{ g cm}^2$.

References.

1. J. Drowart, G. DeMaria and M. G. Inghram, *J. Chem. Phys.* **29**, 1015 (1958).
2. J. Drowart and G. DeMaria, pp. 16-23 in "Silicon Carbide," Edited by J. R. O'Connor and J. Smiltens, Pergamon Press, New York, 1960.
3. W. Wetmore, Jr. and D. McLeod, Jr., *J. Chem. Phys.* **41**, 235 (1964); **40**, 1305 (1964); **45**, 3096 (1966).

Dec. 31, 1960; Dec. 31, 1961; Mar. 31, 1967

T, °K	Cp*	$-\left(G^\circ - H^\circ_{298.15}\right)/T$	H° - H° _{298.15}	kcal/mol ΔH_f°	ΔG_f°	Log Kp
0	0.000	INFINITE	-3.084	151.219	151.219	INFINITE
100	9.357	74.779	-2.318	151.997	146.912	-371.076
200	11.927	58.983	-1.512	152.034	141.810	-155.072
298	13.156	44.002	-0.000	152.000	135.941	-100.360
300	13.174	44.084	0.024	151.997	136.947	-99.693
400	13.411	37.971	1.377	151.829	131.420	-72.023
500	14.162	31.084	2.777	151.597	126.846	-55.444
600	14.371	26.688	4.205	151.321	121.919	-44.409
700	14.524	23.865	5.695	150.985	117.212	-36.553
800	14.638	21.865	7.265	150.592	112.812	-30.655
900	14.656	20.587	8.567	150.292	107.432	-26.088
1000	14.702	19.134	10.035	149.888	102.590	-22.443
1100	14.738	17.527	11.507	149.355	97.900	-19.469
1200	14.761	15.821	12.982	148.695	93.331	-16.998
1300	14.770	14.084	14.460	147.908	88.711	-14.914
1400	14.814	12.315	15.940	147.993	84.131	-13.133
1500	14.838	10.513	17.423	147.451	79.591	-11.596
1600	14.863	8.682	18.904	146.881	75.084	-10.254
1700	14.881	6.836	20.394	146.501	70.591	-9.119
1800	14.926	4.986	21.886	145.845	66.031	-8.133
1900	14.964	3.138	23.381	145.390	61.511	-7.632
2000	15.007	1.413	24.879	145.038	56.931	-7.005
2100	15.055	0.214	26.383	144.89	52.399	-6.439
2200	15.097	0.007	27.892	144.84	47.869	-5.926
2300	15.144	0.000	29.404	144.81	43.339	-5.461
2400	15.224	0.000	30.923	144.81	38.809	-5.036
2500	15.288	0.000	32.449	144.81	34.279	-4.666
2600	15.354	0.000	33.981	144.81	29.749	-4.287
2700	15.421	0.000	35.513	144.81	25.219	-3.907
2800	15.483	0.000	37.045	144.81	20.689	-3.527
2900	15.544	0.000	38.577	144.81	16.159	-3.147
3000	15.636	0.000	40.114	144.81	11.629	-2.767
3100	15.707	0.000	41.655	144.81	7.099	-2.387
3200	15.777	0.000	43.197	144.81	2.569	-2.007
3300	15.847	0.000	44.739	144.81	-2.000	-1.627
3400	15.915	0.000	46.281	144.81	-2.430	-1.247
3500	15.981	0.000	47.823	144.81	-2.860	-0.867
3600	16.046	0.000	49.365	144.81	-3.290	-0.487
3700	16.111	0.000	50.907	144.81	-3.720	-0.107
3800	16.168	0.000	52.449	144.81	-4.150	0.273
3900	16.225	0.000	53.991	144.81	-4.580	0.653
4000	16.279	0.000	55.533	144.81	-5.010	1.033
4100	16.331	0.000	57.075	144.81	-5.440	1.413
4200	16.380	0.000	58.617	144.81	-5.870	1.793
4300	16.426	0.000	60.159	144.81	-6.300	2.173
4400	16.469	0.000	61.701	144.81	-6.730	2.553
4500	16.509	0.000	63.243	144.81	-7.160	2.933
4600	16.547	0.000	64.785	144.81	-7.590	3.313
4700	16.582	0.000	66.327	144.81	-8.020	3.693
4800	16.614	0.000	67.869	144.81	-8.450	4.073
4900	16.643	0.000	69.411	144.81	-8.880	4.453
5000	16.670	0.000	70.953	144.81	-9.310	4.833
5100	16.694	0.000	72.495	144.81	-9.740	5.213
5200	16.715	0.000	74.037	144.81	-10.170	5.593
5300	16.732	0.000	75.579	144.81	-10.600	5.973
5400	16.752	0.000	77.121	144.81	-11.030	6.353
5500	16.767	0.000	78.663	144.81	-11.460	6.733
5600	16.780	0.000	80.205	144.81	-11.890	7.113
5700	16.791	0.000	81.747	144.81	-12.320	7.493
5800	16.800	0.000	83.289	144.81	-12.750	7.873
5900	16.807	0.000	84.831	144.81	-13.180	8.253
6000	16.813	0.000	86.373	144.81	-13.610	8.633

Titanium (Ti)

(Reference State) GFW = 47.90

T, °K	Cp ^a	gibbs/mol S ^b - (C ^a - H ²⁹⁸)/T	H ^a - H ²⁹⁸	kcal/mol ΔH ^c	ΔG ^d	Log Kp
0	0.000	0.000 INFINITE	- 1.152	0.000	0.000	0.000
100	3.412	1.969	12.152	0.000	0.000	0.000
200	5.333	5.069	7.870	0.000	0.000	0.000
298	5.987	7.325	7.325	0.000	0.000	0.000
300	5.996	7.362	7.325	0.011	0.000	0.000
400	6.258	10.278	8.028	0.000	0.000	0.000
500	6.556	10.278	8.028	1.275	0.000	0.000
600	6.755	11.791	8.557	1.941	0.000	0.000
700	6.976	12.848	9.096	2.627	0.000	0.000
800	7.229	13.796	9.625	3.337	0.000	0.000
900	7.499	14.663	10.137	4.071	0.000	0.000
1000	7.767	15.467	10.631	4.837	0.000	0.000
1100	8.025	16.220	11.105	5.626	0.000	0.000
1200	8.268	16.941	11.592	6.438	0.000	0.000
1300	8.500	17.632	12.087	7.273	0.000	0.000
1400	8.721	18.297	12.592	8.131	0.000	0.000
1500	8.934	18.936	13.066	9.014	0.000	0.000
1600	9.140	19.550	13.509	9.922	0.000	0.000
1700	9.340	20.140	13.929	10.854	0.000	0.000
1800	9.534	20.707	14.324	11.811	0.000	0.000
1900	9.721	21.252	14.695	12.792	0.000	0.000
2000	9.899	21.777	15.042	13.797	0.000	0.000
2100	10.068	22.287	15.366	14.826	0.000	0.000
2200	10.228	22.781	15.676	15.878	0.000	0.000
2300	10.379	23.259	15.972	16.952	0.000	0.000
2400	10.521	23.722	16.254	18.047	0.000	0.000
2500	10.654	24.171	16.521	19.162	0.000	0.000
2600	10.779	24.605	16.774	20.297	0.000	0.000
2700	10.895	25.025	17.014	21.452	0.000	0.000
2800	11.002	25.431	17.240	22.626	0.000	0.000
2900	11.100	25.823	17.453	23.818	0.000	0.000
3000	11.189	26.202	17.652	25.028	0.000	0.000
3100	11.269	26.568	17.837	26.256	0.000	0.000
3200	11.340	26.921	18.008	27.502	0.000	0.000
3300	11.402	27.261	18.165	28.766	0.000	0.000
3400	11.455	27.588	18.308	30.048	0.000	0.000
3500	11.500	27.902	18.437	31.348	0.000	0.000
3600	11.536	28.203	18.552	32.666	0.000	0.000
3700	11.564	28.491	18.654	33.992	0.000	0.000
3800	11.583	28.766	18.743	35.326	0.000	0.000
3900	11.594	29.028	18.819	36.666	0.000	0.000
4000	11.597	29.277	18.882	38.012	0.000	0.000
4100	11.592	29.513	18.931	39.364	0.000	0.000
4200	11.579	29.736	18.967	40.722	0.000	0.000
4300	11.558	29.947	18.990	42.086	0.000	0.000
4400	11.529	30.146	19.000	43.456	0.000	0.000
4500	11.492	30.333	19.097	44.832	0.000	0.000
4600	11.447	30.508	19.181	46.214	0.000	0.000
4700	11.394	30.671	19.252	47.602	0.000	0.000
4800	11.333	30.822	19.308	49.000	0.000	0.000
4900	11.264	30.961	19.350	50.408	0.000	0.000
5000	11.187	31.088	19.378	51.826	0.000	0.000
5100	11.102	31.203	19.392	53.254	0.000	0.000
5200	11.009	31.306	19.392	54.692	0.000	0.000
5300	10.908	31.397	19.378	56.140	0.000	0.000
5400	10.799	31.476	19.350	57.598	0.000	0.000
5500	10.682	31.543	19.308	59.066	0.000	0.000
5600	10.557	31.597	19.252	60.544	0.000	0.000
5700	10.424	31.639	19.181	62.032	0.000	0.000
5800	10.283	31.668	19.097	63.530	0.000	0.000
5900	10.134	31.684	19.000	65.038	0.000	0.000
6000	9.977	31.687	18.882	66.556	0.000	0.000
6100	9.812	31.672	18.743	68.084	0.000	0.000
6200	9.639	31.640	18.582	69.622	0.000	0.000
6300	9.458	31.583	18.400	71.170	0.000	0.000
6400	9.269	31.501	18.197	72.728	0.000	0.000
6500	9.072	31.394	17.972	74.296	0.000	0.000
6600	8.867	31.261	17.724	75.874	0.000	0.000
6700	8.654	31.103	17.453	77.462	0.000	0.000
6800	8.433	30.920	17.159	79.060	0.000	0.000
6900	8.204	30.712	16.842	80.668	0.000	0.000
7000	7.967	30.479	16.495	82.286	0.000	0.000
7100	7.721	30.222	16.117	83.914	0.000	0.000
7200	7.467	29.941	15.708	85.552	0.000	0.000
7300	7.204	29.636	15.269	87.200	0.000	0.000
7400	6.932	29.308	14.800	88.858	0.000	0.000
7500	6.651	28.957	14.299	90.526	0.000	0.000
7600	6.361	28.583	13.766	92.204	0.000	0.000
7700	6.062	28.186	13.200	93.892	0.000	0.000
7800	5.754	27.767	12.600	95.590	0.000	0.000
7900	5.437	27.325	11.966	97.298	0.000	0.000
8000	5.111	26.860	11.297	99.016	0.000	0.000
8100	4.776	26.372	10.592	100.744	0.000	0.000
8200	4.432	25.861	9.850	102.482	0.000	0.000
8300	4.079	25.327	9.072	104.230	0.000	0.000
8400	3.716	24.771	8.258	105.988	0.000	0.000
8500	3.344	24.192	7.408	107.756	0.000	0.000
8600	2.962	23.590	6.522	109.534	0.000	0.000
8700	2.570	22.965	5.599	111.322	0.000	0.000
8800	2.168	22.317	4.639	113.120	0.000	0.000
8900	1.755	21.646	3.642	114.928	0.000	0.000
9000	1.331	20.952	2.608	116.746	0.000	0.000
9100	0.896	20.235	1.536	118.574	0.000	0.000
9200	0.459	19.496	0.428	120.412	0.000	0.000
9300	0.020	18.735	- 0.716	122.260	0.000	0.000
9400	- 0.421	17.952	- 1.882	124.118	0.000	0.000
9500	- 0.852	17.147	- 3.076	125.986	0.000	0.000
9600	- 1.273	16.320	- 4.296	127.864	0.000	0.000
9700	- 1.684	15.471	- 5.540	129.752	0.000	0.000
9800	- 2.085	14.599	- 6.808	131.650	0.000	0.000
9900	- 2.476	13.704	- 8.099	133.558	0.000	0.000
10000	- 2.857	12.787	- 9.412	135.476	0.000	0.000

Dec. 31, 1960; Sept. 30, 1966

(REFERENCE STATE)

0 to 1155°K Crystal alpha
1155 to 1933°K Crystal beta
1933 to 3591°K Liquid
3591 to 8000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas for details.

TITANIUM (Ti)

OPW = 47.90

Ti

Ti

T, K	Cp°	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	+0.00	+0.00	INFINITE	-1.152	+0.00	+0.00	+0.00
100	3.412	1.969	12.152	-1.018	+0.00	+0.00	+0.00
200	5.333	5.069	7.870	-0.960	+0.00	+0.00	+0.00
298	5.987	7.325	7.325	-0.960	+0.00	+0.00	+0.00
300	5.996	7.362	7.325	-0.911	+0.00	+0.00	+0.00
400	6.361	9.139	7.565	-0.629	+0.00	+0.00	+0.00
500	6.559	10.578	8.028	-1.275	+0.00	+0.00	+0.00
600	6.755	11.791	8.537	-1.941	+0.00	+0.00	+0.00
800	7.229	12.998	9.096	-3.537	+0.00	+0.00	+0.00
900	7.499	14.663	10.137	-4.073	+0.00	+0.00	+0.00
1000	7.767	15.467	10.631	-4.837	+0.00	+0.00	+0.00
1100	8.025	16.220	11.105	-5.626	+0.00	+0.00	+0.00
1200	8.256	16.956	11.561	-6.435	+0.00	+0.00	+0.00
1300	8.461	17.673	12.003	-7.242	+0.00	+0.00	+0.00
1400	8.616	18.267	12.423	-8.153	+0.00	+0.00	+0.00
1500	8.767	18.864	12.832	-9.048	+0.00	+0.00	+0.00
1600	8.936	19.456	13.228	-9.968	+0.00	+0.00	+0.00
1700	9.086	20.056	13.611	-10.885	+0.00	+0.00	+0.00
1800	9.256	20.656	13.985	-11.845	+0.00	+0.00	+0.00
1900	10.116	21.128	14.346	-12.866	+0.00	+0.00	+0.00
2000	10.376	21.653	14.698	-13.910	+0.00	+0.00	+0.00

Dec. 31, 1960; Sept. 30, 1966

$\Delta H^\circ_{298.15} = 7.325 \pm 0.02$ gibbs/mol
 $\Delta H^\circ_{298.15} = 0$ kcal/mol
 $\Delta H^\circ = 0.99$ kcal/mol
 $\Delta H^\circ_{298.15} = 113.0 \pm 1.0$ kcal/mol

Heat of Formation.
Zero by definition.
Heat Capacity and Entropy.

The low temperature heat capacities, 1.1 - 305.51°K, have been measured by many investigators. Their measured temperature range, specimen purity and value of $S^\circ_{298.15}$ reported are listed in the following table. The Cp values, below 298°K, adopted were mainly derived from the data obtained from references 3, 5 and 6, which are in good agreement with other sets of Cp data.

Investigator	Temperature, °K	Purity, %	$S^\circ_{298.15}$, eu
1. K. K. Kelley (1944)	53.5 - 295.1	98.75	7.24 ± 0.07
2. Estermann et al. (1952)	1.8 - 4.2	99	-
3. Kothen and Johnston (1953)	15.44 - 305.51	99.98	7.33 ± 0.02
4. Aven et al. (1956)	3.95 - 15.78	99.95	-
5. Wolcott (1957)	1.17 - 20.95	99.98	-
6. Clusius and Franzosini (1958)	13.72 - 271.92	99.98	-
7. Burk et al. (1958)	22.5 - 200.0	99	-
8. Kneip et al. (1963)	1.1 - 4.5	99.66	-
9. Hake and Cape (1964)	1.2 - 4.5	99.92	-
1. K. K. Kelley, Ind. Eng. Chem. 36, 865 (1944). $S^\circ_{50.12} = 0.401$ eu.			
2. I. Estermann, S. A. Friedberg and J. E. Goldman, Phys. Rev. 87, 582 (1952).			
3. C. W. Kothen and H. L. Johnston, J. Am. Chem. Soc. 75, 3101 (1953). $S^\circ_{15} = 0.013$ eu.			
4. M. H. Aven, R. S. Craig, T. R. Waite and W. E. Wallace, Phys. Rev. 102, 1263 (1956).			
5. N. M. Wolcott, Phil. Mag. 2, 1246 (1957).			
6. K. Clusius and P. Franzosini, Z. Physik. Chem. 16, 194 (1958).			
7. D. L. Burk, I. Estermann and S. A. Friedberg, Z. Physik. Chem. 16, 183 (1958).			
8. O. D. Kneip, Jr., J. O. Betterton, Jr. and J. O. Scarbrough, Phys. Rev. 130, 1687 (1963).			
9. R. P. Hake and J. A. Cape, Phys. Rev. 135, A1151 (1964).			

The high temperature heat capacities, 320-1856°K, have also been determined by many investigators. The values above 1155°K are not in good agreement. The measured temperature range, method used, and kind of data reported by these investigators are presented in the table below.

Investigator	Temperature, °K	Method	Property Measured
1. Jaeger et al. (1936)	492.9 - 1475.6	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
2. Kothen (1952)	1067.0 - 1856.0	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
3. Scott (1957)	333.2 - 1233.2	adiabatic calorimetry	Cp
4. Backhurst (1958)	873.2 - 1353.2	adiabatic calorimetry	Cp
5. Golutvin (1959)	388.0 - 1401.9	drop calorimetry	$H^\circ_T - H^\circ_{298.15}$
6. Holland (1963)	595.0 - 1345.0	resistance measurement	Cp
7. Kohlhaas et al. (1965)	320.0 - 1800.0	adiabatic calorimetry	Cp
1. F. M. Jaeger, E. Rosenbohm and R. Fonteyne, Rec. trav. chim. 55, 615 (1936).			
2. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952. Sample purity 99.96%.			
3. J. L. Scott, ORNL-2328, Oak Ridge National Laboratory, July 1957.			
4. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1958).			
5. Y. M. Golutvin, Russ. J. Phys. Chem. 33, 164 (1959).			
6. L. R. Holland, J. Appl. Phys. 34, 2350 (1963).			
7. R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20a, 1077 (1965). Sample purity 99.96%.			

The adopted Cp values, 298.15 - 1155°K, were mainly derived from the Cp data reported by reference 7. The low temperature and high temperature Cp data were joined smoothly at 298°K. The Cp values above 1155°K were estimated by graphical extrapolation. $S^\circ_{298.15}$ was derived from the adopted Cp, based on $S^\circ_{13} = 0.015$ eu.

Transition Data.

See the Ti (β, c) table for details.

Heat of Sublimation.

 $\Delta H^\circ_{298.15}$ is calculated as the difference between $\Delta H^\circ_{298.15}$ for Ti(g) and Ti (α, c).

T, °K	Cp ^a	$\frac{\text{gibbs/mol}}{S^{\circ}} - (G^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	$\frac{\text{kcal/mol}}{\Delta H^{\circ}}$	ΔG°	Log Kp
0						
100						
200						
298	6.205	8.691	8.691	0.000	1.026	- .752
300	6.206	8.729	8.691	0.011	1.023	- .746
400	6.280	10.525	8.935	0.596	0.885	- .484
500	6.358	11.934	9.959	1.268	0.748	- .327
600	6.439	13.101	9.922	1.907	0.613	- .223
700	6.525	14.100	10.449	2.556	0.485	- .151
800	6.618	14.977	10.961	3.213	0.364	- .099
900	6.728	15.762	11.452	3.879	0.250	- .061
1000	6.825	16.475	11.919	4.536	0.144	- .032
1100	6.940	17.131	12.363	5.245	0.050	- .010
1200	7.068	17.741	12.786	5.945	0.000	0.000
1300	7.210	18.312	13.190	6.659	0.000	0.000
1400	7.360	18.847	13.575	7.387	0.000	0.000
1500	7.540	19.366	13.944	8.133	0.000	0.000
1600	7.730	19.858	14.298	8.896	0.000	0.000
1700	7.940	20.333	14.639	9.679	0.000	0.000
1800	8.160	20.793	14.969	10.484	0.000	0.000
1900	8.390	21.240	15.287	11.311	0.000	0.009
2000	8.630	21.677	15.596	12.162	0.000	0.017
2100	8.860	22.103	15.895	13.037	0.000	0.040
2200	9.090	22.521	16.187	13.934	0.000	0.061
2300	9.312	22.930	16.471	14.855	0.000	0.079
2400	9.530	23.331	16.749	15.797	0.000	0.096
2500	9.750	23.724	17.020	16.761	0.000	0.112

Sept. 30, 1956

ΔH°_0 = Unknown
 $\Delta H^{\circ}_{298.15} = 1.433$ kcal/mol
 $\Delta H^{\circ} = 0.99$ kcal/mol
 $\Delta H^{\circ} = [4.45]$ kcal/mol
 $\Delta H^{\circ}_{298.15} = [111.57]$ kcal/mol

Heat of Formation.

The heat of formation ($\Delta H^{\circ}_{298.15}$) was obtained from $\Delta H^{\circ}_{298.15}$ (α , c) by adding ΔH° and the difference $H^{\circ}_{Ti} - H^{\circ}_{298.15}$ for Ti (α , c) and Ti (β , c).

Heat Capacity and Entropy.

The heat capacities, 1155 - 1856°K, have been determined by many investigators. See the Ti (α , c) table for details. The selected Cp values were evaluated based on the data reported by C. W. Kothen, Ph. D. dissertation, The Ohio State University, 1952, and R. Kohlhaas, M. Braun and O. Vollmer, Z. Naturforsch. 20A, 1077 (1965). The heat capacities below 1155°K and above 1800°K were estimated by graphical extrapolation. The entropy was obtained in a manner analogous to that of the heat of formation.

Transition Data.

Titanium has two crystal forms, i.e., the hexagonal close-packed low-temperature form and the body-centered cubic high-temperature form. The $\alpha \rightarrow \beta$ transition temperature has been determined and reported over a range of temperatures, 1154-1167°K, by many investigators. The value of Tt is affected by the impurities in the specimen or adsorbed by the specimen during the measurement and the method used for the determination. The following table indicates the values of Tt reported by different investigators. Also included are the heats of transition (ΔH°_t), purity of specimen and property measured. The value of Tt adopted is 1155 \pm 3°K, and the value of ΔH°_t is selected as 0.99 kcal/mol.

Investigator	Tt, °K	ΔH°_t , kcal/mol	Purity, %	Method or Property Measured
1. Fast (1939)	1159 \pm 10	-	Iodide	electrical resistance
2. Greiner and Ellis (1949)	1158 \pm 2	-	99.9	electrical resistance
3. McQuillen (1950)	1155.7 \pm 1	-	99.93	hydrogen solubility
4. Dwez (1951)	1155 \pm 4	-	Iodide	cooling curve
5. Wornor (1951)	1158 \pm 2	-	99.93	thermoelectric power
6. Kothen (1952)	1154	0.943	99.96	dropping calorimetry
7. Edwards et al. (1953)	1157 \pm 3.5	-	99.88	cooling curve
8. Schofield (1956)	1158	0.814	-	rate of heating
9. Scott (1957)	1156 \pm 2	0.978 \pm 0.025	Iodide	adiabatic calorimetry
10. Backhurst (1958)	-	0.880	Commercial	adiabatic calorimetry
11. Golutvin (1959)	1155	0.820 \pm 0.020	Iodide	dropping calorimetry
12. Kohlhaas, et al. (1965)	1167	0.992	99.8	adiabatic calorimetry

1. J. D. Fast, Rec. trav. chim. 58, 973 (1939).
2. E. S. Greiner and W. C. Ellis, Trans. Am. Inst. Min. Met. Eng. 180, 657 (1949).

3. A. D. McQuillen, J. Inst. Metals, 76, 249 (1950).

4. P. Dwez, J. Metals, 3, 765 (1951).

5. H. W. Wornor, Australian J. Sci. Res. 4, 62 (1951).

6. C. W. Kothen, Ph. D. Dissertation, The Ohio State University, 1952.

7. J. W. Edwards, H. L. Johnston and W. E. Dittmars, J. Am. Chem. Soc. 75, 2467 (1953).

8. T. H. Schofield, J. Inst. Metals, 85, 68 (1956).

9. J. L. Scott, ORNL - 2328, Oak Ridge National Laboratory, July 1957.

10. I. Backhurst, J. Iron Steel Inst. (London) 189, 124 (1956).

11. Y. M. Golutvin, Russ. J. Phys. Chem. 33, 164 (1959).

12. R. Kohlhaas, M. Braun and D. Vollmer, Z. Naturforsch. 20A, 1077 (1965).

Melting Data.

See the Ti(l) table for details.

Heat of Sublimation.

$\Delta H^{\circ}_{298.15}$ is calculated as the difference between $\Delta H^{\circ}_{298.15}$ for Ti(g) and Ti (β , c).

Titanium (Ti)

(Liquid) GFW = 47.90

T, °K	Cp ^a	$S^{\circ} - (C^{\circ} - H^{\circ})/T$	$H^{\circ} - H_{298}^{\circ}$	kcal/mol ΔH°	ΔG°	Log Kp
0						
100	6.205	10.695	10.695	5.433	4.428	-3.246
200						
298						
300	6.206	10.733	10.695	5.433	4.422	-3.222
400	6.280	12.529	10.939	5.436	4.084	-2.231
500	6.358	13.938	11.403	5.426	3.746	-1.637
600	6.439	15.105	11.926	5.399	3.411	-1.242
700	6.525	16.104	12.556	5.362	3.082	-0.862
800	6.618	16.981	13.213	5.309	2.761	-0.754
900	6.718	17.766	13.879	5.239	2.447	-0.594
1000	6.825	18.479	14.566	5.152	2.140	-0.468
1100	6.940	19.135	15.267	5.045	1.845	-0.367
1200	7.068	19.745	15.990	4.900	1.595	-0.291
1300	7.200	20.316	16.734	4.700	1.395	-0.234
1400	7.330	20.846	17.492	4.450	1.189	-0.186
1500	7.460	21.332	18.260	4.150	0.977	-0.142
1600	7.590	21.775	19.039	3.750	0.758	-0.103
1700	7.720	22.179	19.829	3.250	0.533	-0.068
1800	7.850	22.544	20.629	2.650	0.305	-0.037
1900	7.980	22.871	21.439	1.950	0.076	-0.009
2000	8.100	23.167	22.260	1.150	0.000	0.000
2100	8.200	23.432	23.090	0.250	0.000	0.000
2200	8.280	23.667	23.829	-0.700	0.000	0.000
2300	8.350	23.871	24.479	-1.550	0.000	0.000
2400	8.400	24.044	25.039	-2.300	0.000	0.000
2500	8.430	24.187	25.509	-2.950	0.000	0.000
2600	8.450	24.300	25.889	-3.500	0.000	0.000
2700	8.460	24.383	26.179	-3.950	0.000	0.000
2800	8.460	24.437	26.379	-4.300	0.000	0.000
2900	8.450	24.462	26.489	-4.550	0.000	0.000
3000	8.430	24.457	26.509	-4.700	0.000	0.000
3100	8.400	24.422	26.439	-4.750	0.000	0.000
3200	8.350	24.357	26.269	-4.650	0.000	0.000
3300	8.300	24.272	26.009	-4.400	0.000	0.000
3400	8.250	24.167	25.659	-4.000	0.000	0.000
3500	8.200	24.042	25.229	-3.450	0.000	0.000
3600	8.150	23.897	24.729	-2.750	0.000	0.000
3700	8.100	23.732	24.159	-1.900	0.000	0.000
3800	8.050	23.547	23.509	-0.900	0.000	0.000
3900	8.000	23.342	22.759	0.100	0.000	0.000
4000	7.950	23.117	21.909	1.050	0.000	0.000
4100	7.900	22.872	20.959	1.900	0.000	0.000
4200	7.850	22.607	19.909	2.550	0.000	0.000
4300	7.800	22.322	18.759	3.000	0.000	0.000
4400	7.750	22.017	17.509	3.250	0.000	0.000
4500	7.700	21.692	16.159	3.300	0.000	0.000

Dec. 31, 1960; Sept. 30, 1966

Titanium (Ti)

(Ideal Gas) GFW = 47.90

T, °K	Cp°	gibbs/mol S° - (C° - H° ₂₉₈)/T	H° - H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	INFINITE	-1.602	112.350	112.350	INFINITE
100	6.447	36.123	48.594	-1.246	109.357	-236.998
200	6.330	40.635	43.615	.596	105.851	-115.660
298	5.339	43.066	43.066	.000	102.344	-75.020
300	5.331	43.102	43.066	.011	113.000	-74.509
400	5.322	44.733	43.291	.577	112.948	-53.933
500	5.344	45.945	43.706	1.120	112.845	-41.595
600	5.337	46.009	44.162	1.658	112.707	-31.379
700	5.170	46.711	44.911	2.198	112.541	-23.518
800	5.128	46.998	45.044	2.683	112.346	-17.129
900	5.104	46.901	45.451	3.194	112.121	-11.722
1000	5.096	46.838	45.833	3.704	111.867	-7.002
1100	5.106	50.024	46.493	4.214	111.588	-14.783
1200	5.176	50.481	46.950	4.724	111.288	-12.944
1300	5.237	51.267	47.152	5.241	110.949	-11.400
1400	5.297	51.267	47.152	5.762	109.941	-10.078
1500	5.313	51.631	47.438	6.289	109.723	-8.935
1600	5.303	51.977	47.711	6.825	109.494	-7.937
1700	5.304	52.307	47.977	7.370	109.258	-7.058
1800	5.316	52.625	48.222	7.926	109.009	-6.279
1900	5.337	52.932	48.461	8.494	108.750	-5.583
2000	5.364	53.229	48.692	9.074	108.432	-4.975
2100	5.396	53.518	48.915	9.666	108.078	-4.434
2200	5.432	53.801	49.131	10.270	107.690	-3.944
2300	5.471	54.076	49.340	10.893	107.270	-3.497
2400	5.513	54.346	49.543	11.527	106.820	-3.089
2500	5.557	54.611	49.740	12.176	106.344	-2.714
2600	5.601	54.871	49.933	12.839	105.847	-2.368
2700	5.647	55.121	50.121	13.516	105.324	-2.049
2800	5.693	55.378	50.304	14.208	104.778	-1.752
2900	5.740	55.626	50.483	14.915	104.223	-1.477
3000	5.786	55.871	50.659	15.636	103.649	-1.220
3100	5.832	56.112	50.831	16.372	103.056	-.981
3200	5.876	56.350	50.999	17.122	102.444	-.756
3300	5.922	56.585	51.165	17.887	101.810	-.546
3400	5.966	56.818	51.328	18.667	101.155	-.347
3500	6.007	57.048	51.488	19.461	100.480	-.160
3600	6.045	57.270	51.644	20.269	99.784	.000
3700	6.080	57.486	51.796	21.090	99.068	.000
3800	6.117	57.723	51.954	21.925	98.332	.000
3900	6.156	57.944	52.105	22.773	97.576	.000
4000	6.196	58.162	52.253	23.634	96.800	.000
4100	6.239	58.378	52.400	24.508	96.004	.000
4200	6.281	58.591	52.545	25.394	95.188	.000
4300	6.325	58.802	52.688	26.292	94.352	.000
4400	6.369	59.011	52.829	27.201	93.496	.000
4500	6.414	59.218	52.969	28.121	92.620	.000
4600	6.459	59.423	53.107	29.051	91.734	.000
4700	6.501	59.625	53.244	29.991	90.838	.000
4800	6.544	59.825	53.379	30.941	89.932	.000
4900	6.587	60.022	53.512	31.900	89.016	.000
5000	6.631	60.218	53.644	32.867	88.090	.000
5100	6.674	60.411	53.775	33.842	87.154	.000
5200	6.717	60.602	53.905	34.825	86.208	.000
5300	6.760	60.790	54.033	35.815	85.262	.000
5400	6.803	60.977	54.160	36.812	84.306	.000
5500	6.846	61.161	54.285	37.814	83.340	.000
5600	6.889	61.342	54.410	38.824	82.364	.000
5700	6.931	61.522	54.533	39.834	81.378	.000
5800	6.974	61.699	54.655	40.855	80.382	.000
5900	7.017	61.874	54.776	41.876	79.376	.000
6000	7.059	62.046	54.895	42.905	78.360	.000

Dec. 31, 1960; Sept. 30, 1967; June 30, 1967

TITANIUM (Ti)

(IDEAL GAS)

GFW = 47.90

Ground State Configuration $3p^2$ $\Delta H_f^\circ = 112.4 \pm 1.0$ kcal/mol $\Delta H_f^\circ = 113.0 \pm 1.0$ kcal/mol $S^\circ_{298.15} = 43.066$ gibbs/mol

Electronic Levels and Quantum Weights

ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i	ϵ_i , cm ⁻¹	g_i
0.00	5	11639.82	7	17467.00	15
170.13	7	11776.82	9	18101.00	9
386.87	9	[12000.00]	[1]	18392.00	76
6556.86	3	12118.46	9	19789.00	44
6598.83	5	13981.75	3	21381.00	38
6661.00	7	14028.47	5	22270.00	12
6742.79	9	14105.68	7	25405.00	87
6843.00	11	15108.15	7	27178.00	123
7255.23	5	15156.80	9	28745.00	65
8436.63	1	15220.40	11	30144.00	89
8492.44	3	16008.00	21	31849.00	76
8602.35	5	16971.00	24	33751.00	54
11531.81	5	17046.00	35	34698.00	28

Heat of Formation

The vapor pressure of Ti (β), 1510-1822°K, has been measured in three separate investigations. Based on the reported vapor pressures, the enthalpies of sublimation (ΔH_{sub}°) are evaluated by both the second and third law methods. The results obtained are presented in the following table. The adopted value of ΔH_f° for Ti(g) is 113.0 ± 1.0 kcal/mol.

Reference	Temperature, °K	ΔH_f° , kcal/mol	Drift, eu
1	1510 - 1822	Second Law Value	
2	1658 - 1808	112.23 \pm 1.91	110.26 \pm 0.81
3	1587 - 1764	112.41 \pm 6.30	110.71 \pm 1.10
		112.26 \pm 1.12	111.79 \pm 0.18
		112.26 \pm 0.18	111.79 \pm 0.18
		ΔH_f° (3rd law)	111.69
		ΔH_f° (2nd law)	113.22
1.	J. M. Blocher, Jr., and I. E. Campbell, J. Am. Chem. Soc. 71, 4040 (1949).		
2.	L. G. Carpenter and W. N. Mair, Proc. Phys. Soc. 54, 57 (1951). The preliminary results were reported by L. G. Carpenter and F. R. Reavell, Nature, 163, 527 (1949).		
3.	J. W. Edwards, H. L. Johnston and W. E. Dittmars, J. Am. Chem. Soc. 75, 2467 (1953).		

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from C. E. Moore, National Bureau of Standards Circular 467 (1949). However, above the level $\epsilon_i = 15877.17$ cm⁻¹, the values of ϵ_i and g_i listed in the above table are average values calculated from those given by Moore. The $S^\circ_{298.15}$ level of the ground multiplet which has not been observed is estimated to lie at 12000 cm⁻¹ by comparison with the corresponding levels for Ti²⁺ ion, Zr and Zr²⁺ ion reported by C. E. Moore, loc. cit.

Titanium Unipositive Ion (Ti⁺)

GEW = 47.89945

(Ideal Gas)

T, °K	Cp ^a	$\frac{\text{kcal/mol}}{S^{\circ}} - (G^{\circ} - H^{\circ}_{298})/T$	$H^{\circ} - H^{\circ}_{298}$	ΔH°	Log Kp
0					
100	6.257	43.854	0.000	271.840	-190.190
200	6.257	43.893	-0.012	271.850	-198.961
300	6.245	43.692	48.100	259.385	-136.409
400	6.177	47.079	48.562	272.354	-109.623
500	6.160	48.194	45.078	272.826	-95.733
600	6.131	48.904	46.043	273.270	-85.402
700	6.102	49.204	46.043	273.679	-75.502
800	6.073	49.504	46.043	274.057	-66.814
900	6.044	49.804	46.043	274.390	-58.491
1000	6.015	50.104	46.043	274.680	-50.482
1100	5.986	50.404	46.043	274.928	-42.834
1200	5.957	50.704	46.043	275.135	-35.487
1300	5.928	51.004	46.043	275.302	-28.402
1400	5.899	51.304	46.043	275.430	-21.527
1500	5.870	51.604	46.043	275.528	-14.912
1600	5.841	51.904	46.043	275.597	-8.517
1700	5.812	52.204	46.043	275.637	-2.302
1800	5.783	52.504	46.043	275.648	3.733
1900	5.754	52.804	46.043	275.630	9.810
2000	5.725	53.104	46.043	275.593	15.887
2100	5.696	53.404	46.043	275.528	21.912
2200	5.667	53.704	46.043	275.435	27.847
2300	5.638	54.004	46.043	275.315	33.652
2400	5.609	54.304	46.043	275.168	39.287
2500	5.580	54.604	46.043	275.000	44.712
2600	5.551	54.904	46.043	274.813	49.887
2700	5.522	55.204	46.043	274.600	54.772
2800	5.493	55.504	46.043	274.365	59.327
2900	5.464	55.804	46.043	274.110	63.512
3000	5.435	56.104	46.043	273.835	67.287
3100	5.406	56.404	46.043	273.540	70.612
3200	5.377	56.704	46.043	273.225	73.447
3300	5.348	57.004	46.043	272.890	75.752
3400	5.319	57.304	46.043	272.535	77.507
3500	5.290	57.604	46.043	272.160	78.682
3600	5.261	57.904	46.043	271.765	79.227
3700	5.232	58.204	46.043	271.350	79.192
3800	5.203	58.504	46.043	270.915	78.527
3900	5.174	58.804	46.043	270.460	77.192
4000	5.145	59.104	46.043	270.000	75.147
4100	5.116	59.404	46.043	269.535	72.352
4200	5.087	59.704	46.043	269.065	68.787
4300	5.058	60.004	46.043	268.590	64.432
4400	5.029	60.304	46.043	268.110	59.257
4500	5.000	60.604	46.043	267.625	53.242
4600	4.971	60.904	46.043	267.135	46.357
4700	4.942	61.204	46.043	266.640	38.572
4800	4.913	61.504	46.043	266.140	29.857
4900	4.884	61.804	46.043	265.635	20.272
5000	4.855	62.104	46.043	265.125	10.787
5100	4.826	62.404	46.043	264.610	1.372
5200	4.797	62.704	46.043	264.090	-9.013
5300	4.768	63.004	46.043	263.565	-19.298
5400	4.739	63.304	46.043	263.035	-29.553
5500	4.710	63.604	46.043	262.500	-39.668
5600	4.681	63.904	46.043	261.960	-49.533
5700	4.652	64.204	46.043	261.415	-59.148
5800	4.623	64.504	46.043	260.865	-68.513
5900	4.594	64.804	46.043	260.310	-77.628
6000	4.565	65.104	46.043	259.750	-86.493

Dec. 31, 1967

(IDEAL GAS)

Ground State Configuration "F_{3/2}S_{298.15} = 43.854 ± 0.01 gibbs/mol $\Delta H^{\circ}_{298.15} = 269.62 \pm 1.0$ kcal/mol $\Delta H^{\circ}_{298.15} = 271.84 \pm 1.0$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i	$\frac{\epsilon_i, \text{cm}^{-1}}{g_i}$	$\frac{\epsilon_i, \text{cm}^{-1}}{g_i}$	$\frac{\epsilon_i, \text{cm}^{-1}}{g_i}$
0	4	9508.611	14	46339.691
93.94	6	9970.051	16	52658.791
225.47	8	12722.863	32	56744.104
393.22	10	15593.028	24	62717.485
907.96	4	22558.664	26	65139.311
983.80	6	30448.862	64	65650.954
1087.21	8	32094.291	44	67896.381
1215.58	10	36951.357	36	69610.661
4782.319	14	40329.131	38	
8945.376	28	43558.293	40	

Heat of Formation

The heat of formation is calculated from the reaction $\text{Ti(g)} = \text{Ti}^+(\text{g}) + e^-(\text{g})$ with the JANAF auxiliary value for Ti(g) and an ionization potential = 6.82 eV or 157,276 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. III, 1958.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. I, 1949. The electronic levels above 4700 cm^{-1} are averaged. The $H^{\circ} - H^{\circ}_{298}$ value at 0°K is -1.888 kcal/mol.

GEW = 47.89945

Ti⁺Ti⁺

Tungsten (W)

(Reference State) GFW = 183.85

T, °K	Cp ^o	$\frac{\text{gibbs/mol}}{T}$	$-(G^o - H^o_{298})/T$	$H^o - H^o_{298}$	$\frac{\text{kcal/mol}}{\Delta H^o}$	ΔG^o	Log Kp
0	.000	.000	INFINITE	- 1.189	.000	.000	.000
100	3.832	2.297	12.624	- 1.033	.000	.000	.000
200	5.375	5.562	8.327	.553	.000	.000	.000
298	5.807	7.806	7.806	.000	.000	.000	.000
300	5.811	7.842	7.806	.011	.000	.000	.000
400	5.958	9.535	8.036	1.201	.000	.000	.000
500	6.061	10.875	8.474	1.201	.000	.000	.000
600	6.164	11.989	8.970	1.812	.000	.000	.000
700	6.279	12.977	9.457	2.523	.000	.000	.000
800	6.394	13.940	9.951	3.079	.000	.000	.000
900	6.480	14.848	10.428	3.709	.000	.000	.000
1000	6.598	15.737	10.875	4.362	.000	.000	.000
1100	6.696	15.869	11.301	5.026	.000	.000	.000
1200	6.812	17.006	12.095	6.387	.000	.000	.000
1300	6.914	17.522	12.662	7.084	.000	.000	.000
1400	7.025	18.011	12.816	7.792	.000	.000	.000
1500	7.137	18.475	13.155	8.511	.000	.000	.000
1600	7.250	18.912	13.482	9.242	.000	.000	.000
1700	7.377	19.342	13.795	9.984	.000	.000	.000
1800	7.509	19.749	14.098	10.737	.000	.000	.000
1900	7.642	20.142	14.391	11.502	.000	.000	.000
2000	7.786	20.521	14.673	12.279	.000	.000	.000
2100	7.933	20.884	14.946	13.068	.000	.000	.000
2200	8.083	21.243	15.216	13.868	.000	.000	.000
2300	8.182	21.589	15.472	14.680	.000	.000	.000
2400	8.302	21.925	15.726	15.504	.000	.000	.000
2500	8.424	22.253	15.968	16.340	.000	.000	.000
2600	8.550	22.579	16.200	17.186	.000	.000	.000
2700	8.680	22.903	16.422	18.042	.000	.000	.000
2800	8.812	23.225	16.638	18.907	.000	.000	.000
2900	8.950	23.545	16.849	19.783	.000	.000	.000
3000	9.080	23.864	17.056	20.669	.000	.000	.000
3100	9.210	24.182	17.259	21.564	.000	.000	.000
3200	9.340	24.499	17.458	22.468	.000	.000	.000
3300	9.470	24.815	17.654	23.381	.000	.000	.000
3400	9.600	25.130	17.846	24.302	.000	.000	.000
3500	9.730	25.444	18.034	25.230	.000	.000	.000
3600	9.860	25.757	18.218	26.164	.000	.000	.000
3700	9.990	26.069	18.400	27.104	.000	.000	.000
3800	10.120	26.380	18.578	28.049	.000	.000	.000
3900	10.250	26.690	18.754	29.000	.000	.000	.000
4000	10.380	26.999	18.927	29.956	.000	.000	.000
4100	10.510	27.307	19.100	30.917	.000	.000	.000
4200	10.640	27.614	19.270	31.882	.000	.000	.000
4300	10.770	27.920	19.438	32.851	.000	.000	.000
4400	10.900	28.226	19.604	33.824	.000	.000	.000
4500	11.030	28.531	19.768	34.801	.000	.000	.000
4600	11.160	28.836	19.930	35.782	.000	.000	.000
4700	11.290	29.140	20.091	36.766	.000	.000	.000
4800	11.420	29.444	20.251	37.753	.000	.000	.000
4900	11.550	29.748	20.410	38.742	.000	.000	.000
5000	11.680	30.052	20.568	39.733	.000	.000	.000
5100	11.810	30.356	20.725	40.726	.000	.000	.000
5200	11.940	30.660	20.882	41.721	.000	.000	.000
5300	12.070	30.964	21.038	42.717	.000	.000	.000
5400	12.200	31.268	21.193	43.714	.000	.000	.000
5500	12.330	31.572	21.348	44.712	.000	.000	.000
5600	12.460	31.876	21.502	45.711	.000	.000	.000
5700	12.590	32.180	21.656	46.711	.000	.000	.000
5800	12.720	32.484	21.810	47.712	.000	.000	.000
5900	12.850	32.788	21.964	48.714	.000	.000	.000
6000	12.980	33.092	22.118	49.717	.000	.000	.000

TUNGSTEN (W)

GFW = 183.85

(REFERENCE STATE)

0 to 3680°K Crystal
3680 to 5936°K Liquid
5936 8000°K Ideal Monatomic Gas

See crystal, liquid and monatomic gas tables for details.

T, °K	Cp	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log Kp
0	0.000	INFINITE	-	1.180	0.00	0.00	0.00
100	3.932	2.297	12.164	1.533	0.00	0.00	0.00
200	5.235	5.262	8.437	0.593	0.00	0.00	0.00
298	5.807	7.806	8.406	0.000	0.00	0.00	0.00
300	5.811	7.802	7.802	0.011	0.00	0.00	0.00
400	5.958	8.036	8.414	0.600	0.00	0.00	0.00
500	6.061	10.875	1.201	1.201	0.00	0.00	0.00
600	6.164	11.989	8.970	1.812	0.00	0.00	0.00
700	6.269	12.947	9.471	2.433	0.00	0.00	0.00
800	6.374	13.791	9.959	3.066	0.00	0.00	0.00
900	6.480	14.529	10.428	3.709	0.00	0.00	0.00
1000	6.588	15.237	10.875	4.362	0.00	0.00	0.00
1100	6.696	15.969	11.301	5.026	0.00	0.00	0.00
1200	6.805	16.457	11.706	5.701	0.00	0.00	0.00
1300	6.914	17.006	12.093	6.387	0.00	0.00	0.00
1400	7.023	17.532	12.462	7.084	0.00	0.00	0.00
1500	7.137	18.031	12.816	7.792	0.00	0.00	0.00
1600	7.250	18.475	13.155	8.511	0.00	0.00	0.00
1700	7.363	18.918	13.481	9.242	0.00	0.00	0.00
1800	7.477	19.342	13.795	9.984	0.00	0.00	0.00
1900	7.592	19.749	14.096	10.737	0.00	0.00	0.00
2000	7.706	20.142	14.391	11.502	0.00	0.00	0.00
2100	7.824	20.521	14.673	12.279	0.00	0.00	0.00
2200	7.944	20.887	14.948	13.068	0.00	0.00	0.00
2300	8.063	21.243	15.214	13.868	0.00	0.00	0.00
2400	8.182	21.589	15.472	14.680	0.00	0.00	0.00
2500	8.302	21.925	15.724	15.504	0.00	0.00	0.00
2600	8.424	22.253	15.968	16.340	0.00	0.00	0.00
2700	8.550	22.575	16.207	17.193	0.00	0.00	0.00
2800	8.680	22.895	16.440	18.072	0.00	0.00	0.00
2900	8.810	23.215	16.668	18.977	0.00	0.00	0.00
3000	8.940	23.530	16.892	19.904	0.00	0.00	0.00
3100	9.070	23.840	17.112	20.952	0.00	0.00	0.00
3200	9.200	24.145	17.328	22.120	0.00	0.00	0.00
3300	9.330	24.458	17.542	23.414	0.00	0.00	0.00
3400	9.460	24.769	17.754	24.833	0.00	0.00	0.00
3500	9.590	25.079	17.964	26.380	0.00	0.00	0.00
3600	9.720	25.391	18.173	27.973	0.00	0.00	0.00
3700	9.850	25.705	18.382	29.613	0.00	0.00	0.00
3800	9.980	26.021	18.591	31.308	0.00	0.00	0.00
3900	10.110	26.337	18.801	33.068	0.00	0.00	0.00
4000	10.240	26.653	19.013	34.893	0.00	0.00	0.00
4100	10.370	26.970	19.227	36.785	0.00	0.00	0.00
4200	10.500	27.287	19.443	38.745	0.00	0.00	0.00
4300	10.630	27.604	19.661	40.773	0.00	0.00	0.00
4400	10.760	27.921	19.882	42.873	0.00	0.00	0.00
4500	10.890	28.239	20.106	45.043	0.00	0.00	0.00
4600	11.020	28.556	20.333	47.285	0.00	0.00	0.00
4700	11.150	28.873	20.563	49.598	0.00	0.00	0.00
4800	11.280	29.190	20.797	51.983	0.00	0.00	0.00
4900	11.410	29.507	21.031	54.443	0.00	0.00	0.00
5000	11.540	29.824	21.266	56.978	0.00	0.00	0.00

$\Delta H^\circ_{298} = 0$ kcal/mol
 $\Delta H^\circ_{298,15} = 0$ kcal/mol
 $\Delta H^\circ = [8.46 + 2.5] \text{ kcal/mol}$
 $\Delta H^\circ_{298,15} = 203.4 \pm 1.5 \text{ kcal/mol}$

Heat of Formation.

Zero by definition.

Heat Capacity and Entropy.

There have been several investigations of the low temperature heat capacity of tungsten: F. Lange, Z. Physik. Chem. **110**, 343 (1924), covered the range 28-91°K. M. Horowitz and J. G. Daunt, Phys. Rev. **91**, 1099 (1953), reported values in the range 1-77°K, while T. R. Waite, R. S. Craig, and W. E. Wallace, Phys. Rev. **104**, 1240 (1956), worked from 4-15° and W. DeSorbo, J. Phys. Chem. **62**, 965 (1958), from 15-90°K. C. Zwikker and G. Schmidt, Z. Physik. **52**, 668 (1928) covered the range from 90 to 2521°K. K. Clausius and P. Franzosini, Z. Naturforsch. **14a**, 99 (1959), made a thorough study of the heat capacity in the range 12-274°K, and their measurements were adopted leading to $S^\circ_{298} = 7.806$ eu based on $S^\circ_{12,5} = 0.0088$ eu. This value is in disagreement with the quoted value of 7.63 eu but agrees exactly with a separate integration by V. A. Kirillin, A. E. Sheindlin, V. Ya. Chekhovskoi and V. A. Petrov, Zhur. Fiz. Khim. **37**, 2249 (1963). In the intermediate temperature range the adiabatic heat capacity measurements of R. L. Bronson, H. M. Chisholm and S. M. Docketty, Can. J. Res. **B**, 282 (1953), from 253 to 773°K joined well with the low temperature measurements and were adopted. The high temperature enthalpies have been measured by several investigators from which were selected the values of P. M. Jaeger and E. Rosenblum, Rec. trav. chim. **51**, 1 (1932), from 273-1800°K; A. Magnus and H. Holzmann, Ann. Physik Ser. **5**, 585 (1929), who covered the range 373 to 1173°K; M. Hoch and H. L. Johnston, J. Phys. Chem. **65**, 855 (1961) who made measurements between 1382 and 2900°K; Kirillin et al., loc. cit., who have made several determinations over the range 600 to 3100°K, and have also analyzed the above data and have presented smooth functions from 0 to 3500°K. The present table agrees with that of Kirillin et al. up to 2700°K. Above this temperature the values of Cp adopted follow those reported by I. I. Novikov and P. G. Streikov, Vestnik. Akad. Nauk SSSR **34**, 26(1964), measured by an electric modulation method, up to the melting point. These values rise rapidly above 2700°K and are not inconsistent with the individual measurements of Kirillin et al. at their highest temperatures.

Melting Data.

I. Langmuir, Phys. Rev. **5**, 138 (1915), determined the melting point as 3540°K from intrinsic brilliance measurements; this was later corrected to 3655 ± 30°K by H. A. Jones, I. Langmuir and G. M. J. Mackay, Phys. Rev. **30**, 201 (1927). M. Firani and H. Alterthum, Z. Elektrochem. **29**, 5 (1923), from pyrometer measurements on a black body hole found 3660 ± 60°K. Using the same technique C. F. Zalabak, NASA Tech. Note D-761 (1961), reports 3680°K on a low carbon specimen; he reports a decrease of the melting point with increasing carbon content. E. Rudy and S. Windisch, Aerojet-General Tech. Rept. No. APWL-TR-65-2 Part 1, Vol. III July 1965, report a melting point of 3696 ± 20°K. The value adopted was 3680 ± 20°K. The heat of melting was obtained by assuming an entropy of melting of 2.3 eu obtained from a comparison of several high melting metals (Fe, Cu, Co, Mg, Al).

Sublimation Data.

See W(g) for details.

Tungsten (W)

(Liquid) GFW = 183.85

T, °K	C _p ^o	S ^o -(C _p ^o - H ₂₉₈ ^o)/T	H ₂₉₈ ^o - H ₂₉₈ ^o	ΔH ^o kcal/mol	ΔG ^o	Log K _p
0						
100						
200						
298	5.807	10.923	0.000	11.223	10.294	-7.545
300	5.810	10.923	0.011	11.223	10.288	-7.495
400	6.021	11.591	1.200	11.222	9.664	-6.224
500	6.164	12.087	1.812	11.223	9.353	-5.407
600	6.269	12.598	2.433	11.223	9.041	-4.823
700	6.374	13.077	3.066	11.223	8.729	-4.385
800	6.478	13.528	3.700	11.223	8.416	-4.000
900	6.581	13.952	4.362	11.223	8.100	-3.671
1000	6.696	14.418	5.026	11.223	7.793	-3.386
1100	6.805	14.823	5.701	11.223	7.482	-3.136
1200	6.914	15.210	6.387	11.223	7.171	-2.906
1300	7.023	15.583	7.073	11.223	6.860	-2.694
1400	7.132	15.933	7.769	11.223	6.547	-2.504
1500	7.250	16.273	8.511	11.223	6.236	-2.336
1600	7.363	16.599	9.242	11.223	5.924	-2.186
1700	7.477	16.912	10.000	11.223	5.612	-2.052
1800	7.591	17.210	10.787	11.223	5.300	-1.932
1900	7.709	17.508	11.502	11.223	4.989	-1.826
2000	7.826	17.791	12.279	11.223	4.677	-1.732
2100	7.944	18.065	13.068	11.223	4.363	-1.648
2200	8.062	18.331	13.868	11.223	4.054	-1.572
2300	8.180	18.586	14.677	11.223	3.743	-1.504
2400	8.300	18.831	15.504	11.223	3.431	-1.444
2500	8.420	19.066	16.354	11.223	3.118	-1.392
2600	8.540	19.292	17.224	11.223	2.805	-1.348
2700	8.660	19.508	18.114	11.223	2.495	-1.312
2800	8.780	19.715	19.024	11.223	2.186	-1.282
2900	8.900	19.912	19.954	11.223	1.876	-1.258
3000	9.020	20.097	20.904	11.223	1.567	-1.238
3100	9.140	20.274	21.874	10.875	1.257	-1.222
3200	9.260	20.446	22.864	10.557	0.948	-1.210
3300	9.380	20.612	23.874	10.239	0.640	-1.200
3400	9.500	20.774	24.904	9.924	0.332	-1.192
3500	9.620	20.931	25.954	9.606	0.026	-1.186
3600	9.740	21.083	27.024	9.290	-0.280	-1.182
3700	9.860	21.230	28.114	8.975	-0.586	-1.178
3800	9.980	21.372	29.224	8.660	-0.892	-1.174
3900	10.100	21.509	30.354	8.346	-1.200	-1.170
4000	10.220	21.641	31.504	8.032	-1.506	-1.166
4100	10.340	21.768	32.674	7.719	-1.812	-1.162
4200	10.460	21.890	33.864	7.406	-2.118	-1.158
4300	10.580	22.007	35.074	7.094	-2.424	-1.154
4400	10.700	22.120	36.304	6.782	-2.730	-1.150
4500	10.820	22.228	37.554	6.470	-3.036	-1.146
4600	10.940	22.332	38.824	6.158	-3.342	-1.142
4700	11.060	22.432	40.114	5.846	-3.648	-1.138
4800	11.180	22.528	41.424	5.534	-3.954	-1.134
4900	11.300	22.620	42.754	5.222	-4.260	-1.130
5000	11.420	22.708	44.104	4.910	-4.566	-1.126
5100	11.540	22.792	45.474	4.598	-4.872	-1.122
5200	11.660	22.872	46.864	4.286	-5.178	-1.118
5300	11.780	22.948	48.274	3.974	-5.484	-1.114
5400	11.900	23.020	49.704	3.662	-5.790	-1.110
5500	12.020	23.088	51.154	3.350	-6.096	-1.106
5600	12.140	23.152	52.624	3.038	-6.402	-1.102
5700	12.260	23.212	54.114	2.726	-6.708	-1.098
5800	12.380	23.268	55.624	2.414	-7.014	-1.094
5900	12.500	23.320	57.154	2.102	-7.320	-1.090
6000	12.620	23.368	58.704	1.790	-7.626	-1.086

Dec. 31, 1961, June 30, 1966

TUNGSTEN (W) (LIQUID)

OPW = 183.85

S_{298.15}^o = 10.923 gibbs/molΔH_{f298.15}^o = 11.223 kcal/molT_m^o = 3680 ± 20°KΔH_m^o = [8.46 ± 2.5] kcal/molT_b^o = [5936]°KΔH_v^o = [192.824] kcal/mol

Heat of Formation.

The heat of formation at 298°K was calculated from that of the crystal by adding ΔH_m^o and the difference between H₃₆₈₀^o - H₂₉₈^o for (c) and (l).

Heat Capacity and Entropy.

The heat capacity was estimated as 8.5 gibbs/g-atom by analogy with other monatomic metals. The entropy at 298°K was calculated in a manner analogous to that of the heat of formation. At 2500°K a glass transition was assumed, below which the heat capacity was that of the crystal.

Melting Data.

See crystal table for details.

Vaporization Data.

The boiling point and heat of vaporization were calculated from the adopted functions and heat of sublimation in order to maintain proper thermodynamic consistency.

Ground State Configuration $5d_0$

$\Delta H_f^\circ = 203.1 \pm 1.5$ kcal/mol

$\Delta H_f^{298.15} = 203.4 \pm 1.5$ kcal/mol

$S_{298.15}^\circ = 41.549$ gibbs/mol

Electronic Levels and Quantum Weights

E_i , cm ⁻¹	g_i	E_i , cm ⁻¹	g_i	E_i , cm ⁻¹	g_i
0.0	1	17701.14	7	20383.06	5
1670.3	3	17707.02	9	20427.81	3
3325.53	5	15459.99	7	20174.28	1
4830.00	7	14976.21	5	26035.67	35
6219.33	9	18082.80	3	26585.14	68
9521.29	7	18116.84	5	28413.86	60
9528.07	1	18974.47	7	30081.53	47
13307.08	3	19256.23	9	33420.02	44
19253.58	5	19535.04	11	34874.19	45
12161.95	9	19648.56	13	38611.26	277
15069.94	11	18280.48	5	43092.16	307
17008.50	13	19389.43	1	45985.57	309
13348.54	7	20756.53	8	48987.49	305
16431.28	9	23905.35	16	52348.75	321
19826.04	11	28159.77	24	55770.38	367
13777.70	5	19827.67	7	59180.98	183

Heat of Formation.

ΔH_f^{298} is the heat of sublimation of the crystal at 298°K; this has been obtained by 2nd and 3rd law analysis of the vapor pressure data of three investigators. The results are summarized below:

Ref.	Range*°K	Points	$\Delta H_f^{298.15}$ kcal/mol	3rd law drift eu
1	2511-3053	12*	200.9 \pm 3.6	0.1 \pm 1.4
2	2383-3123	14	214.8 \pm 1.4	202.17 \pm 2.5
3	2574-3183	10	202.4 \pm 2.7	203.35 \pm 1.2

*1 point rejected due to failure of a statistical test.

**All temperatures are taken from Ref. 3, in which the earlier measurements have been corrected.

References:

1. H. A. Jones, I. Langmuir and O. M. J. Mackay, Phys. Rev. **30**, 201 (1927).
2. C. Zwicker, Physica **5**, 249 (1925).
3. R. Szwarc, E. R. Plante, and J. J. Diamond, J. Res. Natl. Bur. Std. **69A**, 417 (1965).

The values are remarkably good, since even at the highest temperature the pressures are less than 10^{-6} atm; all workers used the Langmuir technique. Since the data of Refs. 1 and 3 do not drift, it may be assumed that the accommodation coefficient is unity or close to unity. The drift in the second set cannot be eliminated by assuming a non-unity accommodation coefficient, nor does there appear to be a constant pressure error. Most probably the drift is due to slight errors in temperature. For example, if the readings were 24° high at the low end and 10° low at the high end, the drift would be eliminated; errors of this magnitude are quite possible. The value adopted for $\Delta H_f^{298.15}$ is 203.4 ± 1.5 kcal/mol.

Heat Capacity and Entropy.

The electronic energy levels were taken from those listed by C. E. Moore, U. S. Natl. Bur. Std. Circular 467 (1958). Levels above 25000 cm⁻¹ were averaged.

Dec. 31, 1961; June 30, 1966

T, °K	C_p	$S^\circ - (C^\circ - H^{298})/T$	$H^\circ - H^{298}$	ΔH_f°	ΔG_f°	Log Kp
0	4.000	INFINITE	-1.486	203.103	INFINITE	
100	4.968	39.105	45.095	203.444	-437.238	
200	4.973	39.549	42.009	203.461	-214.804	
298	5.092	41.549	41.549	203.400	-141.722	
300	5.097	41.581	41.549	203.398	-140.802	
400	5.506	44.154	41.754	203.356	-103.763	
500	6.286	44.411	42.156	203.316	-81.345	
600	7.251	45.641	42.635	203.392	-66.731	
700	8.217	46.833	43.150	203.545	-56.144	
800	9.056	47.985	43.683	203.776	-48.196	
900	9.789	49.106	44.234	204.086	-42.006	
1000	10.455	50.109	44.762	204.386	-37.047	
1100	9.904	51.052	45.290	204.712	-32.983	
1200	9.787	51.910	45.807	205.023	-29.591	
1300	9.589	52.685	46.306	205.305	-26.717	
1400	9.349	53.391	46.786	205.562	-24.245	
1500	9.007	54.016	47.249	205.799	-22.110	
1600	8.721	54.588	47.690	205.926	-20.236	
1700	8.451	55.108	48.111	206.054	-18.581	
1800	8.205	55.584	48.513	206.144	-17.109	
1900	7.981	56.017	48.897	206.191	-15.791	
2000	7.786	56.427	49.264	206.224	-14.603	
2100	7.634	56.803	49.614	206.219	-13.532	
2200	7.499	57.155	49.949	206.186	-12.556	
2300	7.389	57.486	50.269	206.130	-11.666	
2400	7.299	57.799	50.573	206.053	-10.850	
2500	7.240	58.095	50.871	205.956	-10.100	
2600	7.197	58.378	51.155	205.841	-9.407	
2700	7.174	58.649	51.427	205.707	-8.767	
2800	7.167	58.910	51.690	205.545	-8.172	
2900	7.174	59.161	51.944	205.357	-7.619	
3000	7.200	59.405	52.188	205.150	-7.104	
3100	7.236	59.642	52.425	204.922	-6.622	
3200	7.264	59.872	52.654	204.680	-6.171	
3300	7.242	60.097	52.876	204.431	-5.748	
3400	7.249	60.318	53.092	204.177	-5.351	
3500	7.484	60.533	53.301	203.906	-4.978	
3600	7.565	60.745	53.505	203.623	-4.626	
3700	7.652	60.954	53.703	203.329	-4.297	
3800	7.744	61.159	53.897	203.029	-3.997	
3900	7.839	61.361	54.086	202.718	-3.712	
4000	7.937	61.561	54.270	202.395	-3.442	
4100	8.038	61.758	54.450	202.066	-3.184	
4200	8.140	61.953	54.627	201.732	-2.940	
4300	8.242	62.146	54.799	201.394	-2.706	
4400	8.345	62.337	54.968	201.053	-2.483	
4500	8.448	62.525	55.134	200.709	-2.270	
4600	8.550	62.712	55.297	200.362	-2.066	
4700	8.651	62.897	55.457	200.012	-1.871	
4800	8.750	63.080	55.614	199.659	-1.684	
4900	8.845	63.262	55.768	199.304	-1.505	
5000	8.943	63.441	55.920	198.947	-1.333	
5100	9.036	63.619	56.069	198.588	-1.168	
5200	9.127	63.796	56.216	198.227	-1.008	
5300	9.215	63.971	56.360	197.864	-0.855	
5400	9.301	64.144	56.500	197.500	-0.707	
5500	9.383	64.315	56.643	197.134	-0.565	
5600	9.463	64.485	56.782	196.766	-0.428	
5700	9.541	64.653	56.919	196.396	-0.295	
5800	9.615	64.820	57.053	196.024	-0.167	
5900	9.686	64.985	57.186	195.650	-0.044	
6000	9.755	65.148	57.318	195.276	0.000	

Tungsten Unipositive Ion (W⁺)
(Ideal Gas)

GFW = 183.8495

T, °K	C _p ^o	gibbs/mol S ^o - (C _p ^o - H ^o - TS ^o)/T	H ^o - H ^o 298	kcal/mol ΔH ^o	ΔG ^o	Log Kp
0						
100						
200						
298	5.108	42.931	42.931	0.000	388.918	- 276.318
300						
350	5.113	42.953	42.931	0.009	388.925	- 276.559
400	5.171	44.478	44.478	1.507	389.427	- 283.151
500	5.934	45.748	43.534	1.107	389.827	- 161.120
600	6.380	46.870	43.098	1.723	384.323	- 132.704
700	6.762	47.884	44.482	2.391	359.946	- 112.380
800	7.098	48.797	45.496	3.066	335.491	- 97.116
900	7.338	49.657	46.357	3.705	311.585	- 84.448
1000	7.553	50.442	45.902	4.250	288.583	- 73.701
1100	7.731	51.170	46.348	4.704	266.180	- 64.895
1200	7.877	51.849	46.779	5.085	244.783	- 57.381
1300	7.997	52.480	47.145	5.400	224.856	- 50.859
1400	8.081	53.080	47.453	5.652	206.790	- 45.159
1500	8.146	53.640	47.678	5.849	190.090	- 40.106
1600	8.189	54.167	48.348	6.001	174.278	- 35.541
1700	8.213	54.665	48.705	6.111	159.872	- 31.360
1800	8.222	55.137	49.042	6.186	146.454	- 27.514
1900	8.214	55.579	49.354	6.234	133.626	- 24.000
2000	8.202	55.991	49.702	6.257	121.000	- 20.849
2100	8.202	56.401	50.012	6.257	108.618	- 18.047
2200	8.190	56.782	50.311	6.236	96.481	- 15.585
2300	8.173	57.146	50.600	6.196	84.681	- 13.451
2400	8.152	57.496	50.875	6.144	73.314	- 11.614
2500	8.127	57.828	51.151	6.074	62.464	- 10.044
2600	8.119	58.148	51.414	5.991	52.220	- 8.726
2700	8.194	58.457	51.670	5.895	42.679	- 7.624
2800	8.258	58.756	51.917	5.797	33.846	- 6.721
2900	8.315	59.044	52.154	5.696	25.606	- 6.001
3000	8.292	59.325	52.392	5.592	17.956	- 5.455
3100	8.342	59.598	52.620	5.485	10.907	- 5.007
3200	8.399	59.863	52.843	5.376	4.515	- 4.668
3300	8.464	60.123	53.059	5.263	0.000	- 4.438
3400	8.537	60.377	53.267	5.147	- 4.495	- 4.315
3500	8.609	60.625	53.477	5.030	- 4.581	- 4.193
3600	8.688	60.869	53.679	4.911	- 4.658	- 4.071
3700	8.770	61.108	53.877	4.794	- 4.736	- 3.950
3800	8.857	61.343	54.070	4.673	- 4.815	- 3.830
3900	8.950	61.571	54.257	4.550	- 4.895	- 3.711
4000	9.020	61.801	54.445	4.425	- 4.976	- 3.593
4100	9.101	62.025	54.628	4.300	- 5.058	- 3.476
4200	9.180	62.245	54.806	4.174	- 5.141	- 3.360
4300	9.259	62.462	54.982	4.049	- 5.225	- 3.245
4400	9.338	62.676	55.154	3.925	- 5.310	- 3.130
4500	9.394	62.886	55.324	3.800	- 5.396	- 3.015
4600	9.455	63.093	55.490	3.675	- 5.483	- 2.900
4700	9.511	63.297	55.654	3.551	- 5.571	- 2.785
4800	9.564	63.496	55.816	3.426	- 5.660	- 2.670
4900	9.604	63.696	55.977	3.301	- 5.750	- 2.555
5000	9.641	63.890	56.131	3.176	- 5.841	- 2.440
5100	9.672	64.081	56.285	3.051	- 5.933	- 2.325
5200	9.696	64.269	56.437	2.926	- 6.026	- 2.210
5300	9.724	64.454	56.586	2.801	- 6.120	- 2.095
5400	9.752	64.634	56.732	2.676	- 6.215	- 1.980
5500	9.730	64.814	56.879	2.551	- 6.311	- 1.865
5600	9.729	64.990	57.022	2.426	- 6.408	- 1.750
5700	9.723	65.162	57.163	2.301	- 6.506	- 1.635
5800	9.711	65.331	57.303	2.176	- 6.604	- 1.520
5900	9.691	65.497	57.442	2.051	- 6.703	- 1.405
6000	9.674	65.659	57.576	1.926	- 6.803	- 1.290

Dec. 31, 1966

TUNGSTEN UNIPOSITIVE ION (W⁺)

(IDEAL GAS)

GFW = 183.8495

Ground State Configuration $5d_{1/2}$ $\Delta H_f^o = 387.139$ kcal/mol
 $S_{298.15}^o = 42.931$ gibbs/mol $\Delta H_f^{298.15} = 388.918$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_1, \text{cm}^{-1}$	ϵ_1	$\epsilon_1, \text{cm}^{-1}$	ϵ_1	$\epsilon_1, \text{cm}^{-1}$	ϵ_1
0	2	16553	10	28929	12
1518.8	4	17837	12	36185	2
3172.5	6	18001	10	39441	12
4716.3	8	18991	10	42256	18
6147.2	10	19071	10	44709	30
7420.4	6	19277	6	45522	6
8711.3	4	19404	6	46373	26
11301.1	6	19443	20	47397	14
13412.0	8	19637	10	48543	30
14857.2	10	[20000]	[30]	48176	28
8632.7	2	20040	8	50605	20
10592.5	4	20628	28	51443	38
13434.1	6	[21000]	[20]	52486	36
13173.4	2	[22000]	[20]	53323	34
14634.4	4	22187	40	54408	66
14967.8	6	23166	36	55342	20
15147.0	8	23921	36	56554	56
16234.8	6	25081	8	59910	194
16589.7	8	26189	18	63660	16

Heat of Formation.

The heat of formation is obtained by adding the heat of ionization at 0°K to the ΔH_f^o W(g). The heat of ionization, 184.056 kcal (7.98 eV), is obtained from C. E. Moore, Natl. Bur. Std. Circular 467, Vol. III, Washington D. C. (1958).

Heat Capacity and Entropy.

The electronic energy levels are obtained from C. E. Moore, loc. cit. In the low lying configuration [Xe] $4f^{14}5d^5$ the F_2, G_2, F_2, H and S multiplets have not been observed. The total degeneracy of these levels (70) is split among three estimated levels of 20000, 21000, and 22000 cm^{-1} , obtained by analogy with Mo^+ . A realistic uncertainty in these levels would produce a maximum uncertainty of 0.03 gibbs/mol in the free energy function and 0.09 gibbs/mol in the entropy at 6000°K.

The enthalpy at 0°K is -1.487 kcal/mol.

T, °K	C _p ^a	gibbs/mol S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	.000	.000	INFINITE	1.321	.000	.000	.000
100	4.466	3.352	14.443	1.109	.000	.000	.000
200	5.734	6.446	9.662	.563	.000	.000	.000
298	6.068	9.314	9.314	.000	.000	.000	.000
300	6.097	9.352	9.314	.011	.000	.000	.000
400	6.367	11.143	9.556	.634	.000	.000	.000
500	6.642	12.593	10.023	1.285	.000	.000	.000
600	6.919	13.428	10.557	1.963	.000	.000	.000
700	7.197	14.916	11.103	2.659	.000	.000	.000
800	7.475	15.895	11.642	3.402	.000	.000	.000
900	7.753	16.791	12.165	4.164	.000	.000	.000
1000	8.032	17.623	12.670	4.953	.000	.000	.000
1100	8.311	18.401	13.156	5.770	.000	.000	.000
1200	8.586	19.128	13.627	6.626	.000	.000	.000
1300	8.867	20.444	14.167	7.521	.000	.000	.000
1400	9.108	20.966	14.634	8.465	.000	.000	.000
1500	9.219	21.461	15.073	9.451	.000	.000	.000
1600	9.330	21.930	15.487	10.479	.000	.000	.000
1700	9.441	22.378	15.879	11.547	.000	.000	.000
1800	9.552	22.806	16.252	12.652	.000	.000	.000
1900	9.663	23.218	16.608	13.798	.000	.000	.000
2000	9.774	23.613	16.949	14.980	.000	.000	.000
2100	9.885	23.995	17.275	16.193	.000	.000	.000
2200	9.996	24.370	17.589	17.439	.000	.000	.000
2300	10.107	24.741	17.891	18.710	.000	.000	.000
2400	10.218	25.107	18.181	20.000	.000	.000	.000
2500	10.329	25.469	18.459	21.310	.000	.000	.000
2600	10.440	25.827	18.727	22.640	.000	.000	.000
2700	10.551	26.181	18.985	24.000	.000	.000	.000
2800	10.662	26.531	19.233	25.390	.000	.000	.000
2900	10.773	26.877	19.479	26.810	.000	.000	.000
3000	10.884	27.219	19.719	28.260	.000	.000	.000
3100	10.995	27.557	19.955	29.740	.000	.000	.000
3200	11.106	27.891	20.187	31.250	.000	.000	.000
3300	11.217	28.219	20.415	32.790	.000	.000	.000
3400	11.328	28.543	20.639	34.360	.000	.000	.000
3500	11.439	28.863	20.859	35.960	.000	.000	.000
3600	11.550	29.179	21.075	37.590	.000	.000	.000
3700	11.661	29.491	21.287	39.250	.000	.000	.000
3800	11.772	29.799	21.495	40.940	.000	.000	.000
3900	11.883	30.103	21.699	42.660	.000	.000	.000
4000	11.994	30.403	21.900	44.410	.000	.000	.000
4100	12.105	30.699	22.097	46.190	.000	.000	.000
4200	12.216	30.991	22.291	48.000	.000	.000	.000
4300	12.327	31.279	22.481	49.840	.000	.000	.000
4400	12.438	31.563	22.667	51.710	.000	.000	.000
4500	12.549	31.843	22.850	53.610	.000	.000	.000
4600	12.660	32.119	23.030	55.540	.000	.000	.000
4700	12.771	32.391	23.207	57.500	.000	.000	.000
4800	12.882	32.659	23.381	59.490	.000	.000	.000
4900	12.993	32.923	23.552	61.510	.000	.000	.000
5000	13.104	33.183	23.720	63.560	.000	.000	.000
5100	13.215	33.439	23.885	65.640	.000	.000	.000
5200	13.326	33.691	24.048	67.750	.000	.000	.000
5300	13.437	33.939	24.209	69.890	.000	.000	.000
5400	13.548	34.183	24.367	72.060	.000	.000	.000
5500	13.659	34.423	24.522	74.260	.000	.000	.000
5600	13.770	34.659	24.675	76.490	.000	.000	.000
5700	13.881	34.891	24.826	78.750	.000	.000	.000
5800	13.992	35.119	24.975	81.040	.000	.000	.000
5900	14.103	35.343	25.122	83.360	.000	.000	.000
6000	14.214	35.563	25.267	85.710	.000	.000	.000

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

See crystal, liquid and monatomic gas for details.

0 to 1135°K Crystal alpha
1136. to 2125°K Crystal beta
2126. to 4776.9°K Liquid
4776.9 to 6000°K Ideal Monatomic Gas

Zirconium, Alpha (Zr)
(Crystal)

ZIRCONIUM, ALPHA (Zr)

(CRYSTAL)

GFW = 91.22

GFW = 91.22

T, °K	Cp	S°	gibbs/mol -(C°-H°300)/T	ΔH° kcal/mol	ΔG°	Log Kp
0	0.00	0.00	INFINITE	0.00	0.00	0.00
100	6.046	3.25	1.321	0.00	0.00	0.00
200	5.754	6.446	1.583	0.00	0.00	0.00
298	6.068	9.314	1.862	0.00	0.00	0.00
300	6.097	9.352	1.870	0.00	0.00	0.00
400	6.367	11.453	2.556	0.00	0.00	0.00
500	6.542	12.593	3.023	0.00	0.00	0.00
600	6.919	13.828	3.557	0.00	0.00	0.00
700	7.197	14.916	4.000	0.00	0.00	0.00
800	7.475	15.995	4.402	0.00	0.00	0.00
900	7.753	16.911	4.765	0.00	0.00	0.00
1000	8.032	17.623	5.093	0.00	0.00	0.00
1100	8.311	18.401	5.370	0.00	0.00	0.00
1200	8.589	19.136	5.615	0.00	0.00	0.00
1300	8.868	19.835	5.835	0.00	0.00	0.00
1400	9.145	20.502	6.030	0.00	0.00	0.00
1500	9.423	21.143	6.201	0.00	0.00	0.00

S°_{298.15} = 9.314 ± 0.10 gibbs/mol

ΔH°_{298.15} = 0 kcal/mol

ΔH°_{298.15} = 0 kcal/mol

ΔH°_{298.15} = 0 kcal/mol

T_m = 1135 ± 5°K

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities, 1.1 - 298.2°K, have been measured by Todd (1), Skinner (2), Eastermann (3), Wolcott (4), Burk (5), and Kneip (6). Values of Cp_{298.15} were reported as 6.19 and 6.01 gibbs/mol by Todd (1) and Skinner (2), respectively. The difference (beginning at 180°K) is probably caused by different amounts of impurities (e.g. O₂, H₂, N₂) in the samples. Neither sample was analyzed for hydrogen and oxygen content. Small amounts of either of these impurities would cause important changes in Cp. Remeasurement of Cp using a high purity sample is desirable to resolve the difference. Tentatively, we adopt smooth Cp values which are intermediate between those of Todd and Skinner in the temperature range 200 - 298°K. The curve at lower temperatures is based on references 1, 2, 4, 5 and 6. S°_{298.15} is derived from the adopted Cp based on S°₁₁₆ = 0.0008 eu.

Enthalpies have been measured using drop calorimetry by Jaeger (7), Coughlin (8), Skinner (9), Redmond (10), Adenstedt (11) and Douglas (13). Cp above 298°K has been measured by Scott (12) and Vollmer (15) using adiabatic calorimetry and by Klein (14) using pulse heating. The data lead to differences in Cp which are even greater than those noted at 298°K. Observed Cp's are lower than the adopted curve by roughly 3 to 6 per cent, but the observed enthalpies are generally higher by 0 to 10 per cent. Impurities are partly to blame but there also may be a systematic difference between the methods. The purest and best-characterized samples are those of Douglas (13) and Vollmer (15). Even the high-purity sample of Douglas gives H values which are abnormally high at 573°K, suggesting the presence of thermal effects of solid solution and precipitation due to a small amount of hydrogen in the sample (12).

The adopted Cp is based mainly on Douglas (13), but references (7, 8, 9, 10, 11) were also given some weight. Deviations of (13) from the adopted values range from +3.3 per cent at 573°K to +0.3 at 1123°K. Other deviations (each in order of increasing T) are 3 to 0 per cent (7), 1.3 to -1.7 per cent (8), -4 to -6 per cent (9), -4 to -6 per cent (10), 5.4 to 1.7 per cent (11) and -1 to 9.5 per cent (14) in terms of enthalpy. Cp is extrapolated linearly above 1133°K.

Transition Data

See Zr(β) table for details.

Heat of Sublimation

ΔH°_{298.15} is calculated as the difference between ΔH°_{298.15} for Zr(g) and Zr(α).

References

1. S. S. Todd, J. Am. Chem. Soc. **72**, 2914 (1950), 53.2 - 296.8°K.
2. G. B. Skinner and H. L. Johnston, J. Am. Chem. Soc. **73**, 4549 (1951), 14.4 - 298.2°K. Purity is atom per cent.
3. I. Eastermann, S. A. Friedberg and J. E. Goldman, Phys. Rev. **87**, 582 (1952), 1.8 - 4.2°K.
4. N. M. Wolcott, Phil. Mag. **2**, 1246 (1957), 1.2 - 20°K.
5. D. L. Burk, I. Eastermann and S. A. Friedberg, Z. Physik. Chem. **16**, 183 (1958), 20 - 200°K.
6. G. D. Kneip, Jr., J. O. Betterton, Jr., and J. O. Scarbrough, Phys. Rev. **130**, 1687 (1963), 1.1 - 4.5°K.
7. F. M. Jaeger and W. A. Veenstra, Rec. Trav. Chim. **53**, 917 (1934), 670.6 - 902.4°K.
8. J. P. Coughlin and E. G. King, J. Am. Chem. Soc. **72**, 2262 (1950), 390 - 1371°K.
9. G. B. Skinner, Ph.D. Thesis, The Ohio State University, 1951, 1102 - 1798°K.
10. R. F. Redmond and J. Lones, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-1342, 1952, 404 - 1309°K.
11. H. K. Adenstedt, Trans. Am. Soc. Metals **44**, 949 (1952), 373.2°K.
12. J. L. Scott, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-2328, 1357, 333 - 1213°K.
13. T. B. Douglas and A. C. Victor, J. Res. Natl. Bur. Std. **61**, 13 (1958), 57A, 403 (1963), 373 - 1173°K.
14. A. H. Klein and G. C. Danielson, Iowa State University, Iowa, WP-14281, 1962, 298 - 2118°K. Cp given graphically.
15. O. Vollmer, M. Braun and R. Kohlhaas, Z. Naturforsch. **22**, 833 (1967), 300 - 1700°K.

$$S_{298.15}^{\circ} = 11.152 \text{ gibbs/mol}$$

$$\Delta H_{298.15}^{\circ} = 1.706 \text{ kcal/mol}$$

$$T_c = 1135 \pm 10^{\circ}\text{K}$$

$$\Delta H_c^{\circ} = 0.96 \text{ kcal/mol}$$

$$\Delta H_m^{\circ} = 5.0 \pm 0.3 \text{ kcal/mol}$$

Heat of Formation

The heat of formation is obtained from $\Delta H_{298}^{\circ}(\alpha)$ by adding ΔH° and the difference between H_{Tc}° - H_{298}° for Zr(α) and Zr(β).

Heat Capacity and Entropy

The enthalpies and Cp of Zr(β), at temperatures 1135 - 2118.2 °K, have been measured by many investigators (see Zr(α) table for details). The selected Cp values are based on the data reported by Douglas (2) and Skinner (2). Deviations from the adopted enthalpies are -1.4 to 0.8 per cent (1), -0.4 to 0.3 (2), and 0.2 to 3.0 per cent (3). Deviations of the measured Cp from the adopted values are -5 to -3 per cent (14) and about -6 per cent (10). The heat capacities below 1143.2 and above 1798°K are estimated by linear extrapolation.

The entropy is obtained in a manner analogous to that of the heat of formation.

Transition Data

Zirconium has two crystal forms, i.e., the hexagonal-close-packed α -form and the cubic-body-centered β -form (3, 4, 5). The value and range of Tt for $\alpha + \beta$ depends strongly on the kind and amount of impurities (5, 13). For example, nitrogen and oxygen increase Tt while hydrogen decreases it. The adopted value is Tt = 1135 \pm 10°K, although recent measurements using purer samples indicate a somewhat higher value. These are summarized below along with the data for ΔH_c° . The value $\Delta H_c^{\circ} = 0.96 \text{ kcal/mol}$ is derived from the adopted enthalpy and Cp data on Zr(α) and Zr(β).

Investigator	Tt, °K	ΔH_c° , kcal/mol	Purity, Percent	Method or Property Measured
3. Vogel (1931)	1135 \pm 5	-	unavailable	cooling and dilatometric curves
7. Coughlin (1950)	1135*	0.920	97.85	drop calorimetry
6. Komar (1957)	1135*	-	unavailable	Electron microscope
8. Hertzichen (1962)	1135	0.712 \pm 0.060	unavailable	differential calorimetry
1. Douglas (1958)	1136*	0.894	99.91	drop calorimetry
9. Duwez (1951)	1138 \pm 10	-	unavailable	cooling curve
10. Klein (1962)	1138 \pm 2	-	unavailable	resistivity
15. Kneip (1956)	1142 \pm 4	-	\approx 99.95	unavailable
2. Skinner (1951)	1143 \pm 5	1.042	99.05	drop calorimetry
12. Scott (1957)	1143 \pm 2	0.993 \pm 0.025	unavailable	adiabatic calorimetry
13. Rudy (1965)	1145 \pm 15	-	99.61	differential thermal analysis
11. Jaeger (1934)	<1150	-	unavailable	drop calorimetry
14. Vollmer (1967)	1155 \pm ?	0.950	99.8	adiabatic calorimetry

* Adopted by the original authors.

Melting Data

See the Zr(β) table for details.

References

1. T. B. Douglas and A. C. Victor, J. Res. Natl. Bur. Std. **51**, 13 (1958). The Tt value was evaluated from enthalpy data.
2. G. B. Skinner, Ph. D. Thesis, The Ohio State University, 1951. Sample purity is atom percent.
3. R. Vogel and W. Tonn, Z. Anorg. Allgem. Chem. **202**, 292 (1931).
4. W. G. Burgers, Physica **1**, 561 (1934).
5. A. P. Komar and V. N. Shrednik, Fiz. Metal. Metalloved. **5**, No. 3, 452 (1957).
6. A. P. Komar and V. N. Shrednik, Soviet Phys. JETP **5**, 127 (1957).
7. J. P. Coughlin and E. G. King, J. Am. Chem. Soc. **72**, 2262 (1950). The Tt value.
8. S. D. Hertzichen and B. F. Slyusar, Ukr. Fiz. Zhur. **7**, 339 (1962).
9. P. Duwez, Trans. AIME **191**, 765 (1951).
10. A. H. Klein and G. C. Danielson, Iowa State University, NP-14281, 1962.
11. F. M. Jaeger and W. A. Veenstra, Rec. Trav. Chim. **53**, 917 (1934).
12. J. L. Scott, Oak Ridge Natl. Lab. ORNL-1342, 1952 and ORNL-2228, 1957.
13. E. Rudy, D. P. Harmon and C. E. Brucki, Aerojet-General Corporation, AFM-TP-65-2, Part 1, Vol. II, 1965.
14. O. Vollmer, M. Braun and R. Kohlhaas, Z. Naturforsch. **22**, 833 (1967).
15. G. D. Kneip, Jr., and J. O. Betterton, Jr., J. Electrochem. Soc. **103**, 684 (1956).

Dec. 31, 1967

Zirconium (Zr)

(Liquid)

GFW = 91.22

T, °K	C _p	S°	-(G°-H° ₂₉₈)/T	H°-H° ₂₉₈	ΔH°	ΔG°	Log K _p
200							
250							
298	5.887	13.289	13.289	.000	6.351	5.166	- 3.787
300	5.889	13.325	13.289	.011	6.351	5.159	- 3.750
400	5.999	15.034	13.521	.605	6.372	4.766	- 2.008
500	6.110	16.385	13.763	1.211	6.277	4.391	- 1.915
600	6.221	17.509	14.463	1.827	6.215	4.007	- 1.460
700	6.332	18.476	14.969	2.455	6.137	3.645	- 1.138
800	6.443	19.329	15.462	3.094	6.043	3.295	- .900
900	6.554	20.076	15.935	3.743	5.935	2.956	- .716
1000	6.665	20.790	16.386	4.405	5.803	2.635	- .576
1100	6.776	21.431	16.816	5.077	5.658	2.325	- .462
1200	6.887	22.025	17.225	5.760	5.495	2.080	- .379
1300	6.997	22.581	17.616	6.454	5.318	1.867	- .314
1400	7.108	23.103	17.990	7.163	5.137	1.683	- .266
1500	7.219	23.635	18.349	7.889	4.959	1.437	- .209
1600	7.330	24.172	18.697	8.759	4.801	1.215	- .166
1700	7.441	24.657	19.034	9.559	4.663	.989	- .127
1800	7.552	25.114	19.359	10.359	4.513	.757	- .092
1900	7.663	25.556	19.673	11.159	4.363	.525	- .061
2000	7.774	25.957	19.977	11.959	4.213	.293	- .032
2100	7.885	26.347	20.271	12.759	4.063	.061	- .006
2200	7.996	26.717	20.556	13.559	3.913	.000	.000
2300	8.107	27.075	20.832	14.359	3.763	.000	.000
2400	8.218	27.415	21.099	15.159	3.613	.000	.000
2500	8.329	27.742	21.358	15.959	3.463	.000	.000
2600	8.440	28.056	21.610	16.759	3.313	.000	.000
2700	8.551	28.358	21.854	17.559	3.163	.000	.000
2800	8.662	28.649	22.092	18.359	3.013	.000	.000
2900	8.773	28.929	22.323	19.159	2.863	.000	.000
3000	8.884	29.201	22.547	19.959	2.713	.000	.000
3100	8.995	29.463	22.766	20.759	2.563	.000	.000
3200	9.106	29.717	22.980	21.559	2.413	.000	.000
3300	9.217	29.963	23.187	22.359	2.263	.000	.000
3400	9.328	30.202	23.390	23.159	2.113	.000	.000
3500	9.439	30.434	23.588	23.959	1.963	.000	.000
3600	9.550	30.659	23.782	24.759	1.813	.000	.000
3700	9.661	30.878	23.970	25.559	1.663	.000	.000
3800	9.772	31.092	24.155	26.359	1.513	.000	.000
3900	9.883	31.302	24.336	27.159	1.363	.000	.000
4000	9.994	31.502	24.512	27.959	1.213	.000	.000
4100	10.105	31.700	24.685	28.759	1.063	.000	.000
4200	10.216	31.892	24.854	29.559	.913	.000	.000
4300	10.327	32.081	25.020	30.359	.763	.000	.000
4400	10.438	32.264	25.183	31.159	.613	.000	.000
4500	10.549	32.444	25.342	31.959	.463	.000	.000
4600	10.660	32.620	25.499	32.759	.313	.000	.000
4700	10.771	32.792	25.656	33.559	.163	.000	.000
4800	10.882	32.961	25.802	34.359	.013	.000	.000
4900	10.993	33.126	25.948	35.159	.000	.000	.000
5000	11.104	33.287	26.095	35.959	.000	.000	.000
5100	11.215	33.446	26.238	36.759	.000	.000	.000
5200	11.326	33.601	26.378	37.559	.000	.000	.000
5300	11.437	33.753	26.516	38.359	.000	.000	.000
5400	11.548	33.903	26.651	39.159	.000	.000	.000
5500	11.659	34.050	26.784	39.959	.000	.000	.000

ZIRCONIUM (Zr)

(LIQUID)

GFW = 91.22

S°_{298.15} = [13.289] gibbs/mol

ΔH_f°_{298.15} = [6.351] kcal/mol

T_m = 2125 ± 5 °K

ΔH_m° = 5.0 ± 0.4 kcal/mol

T_b = [4776.9] °K

ΔH_v° = 141.13 kcal/mol

Heat of Formation

The heat of formation is obtained from ΔH_f°₂₉₈ (β) by adding ΔH_m° and the difference between H°₂₁₂₅ - H°₂₉₈ for Zr(β) and Zr(L).

Heat Capacity and Entropy

A glass transition temperature at 1400°K is assumed. The heat capacities below 1400°K are taken from those for Zr(β). The Cp value above 1400°K is estimated by comparison with that of Zr(β) at T_m and assumed to be constant in the temperature range 1400 - 5500°K. The entropy is obtained in a manner analogous to that of the heat of formation.

Melting Data

The melting point of Zr(β) has been determined by many investigators. The results reported show wide discrepancies, probably caused by the differences in purity of the samples used for determination. The T_m value adopted is obtained from Oriani and Jones. The other values of T_m reported are presented in the table below.

The adopted heat of melting was determined calorimetrically by V. P. Elyutin, M. A. Maurakh and G. M. Sverdlov, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. 10, No. 2, 87 (1967). Zirconium samples from two different sources were melted in an Arc-crucible furnace. The crucible contained an insert of graphite which had a thick lining (presumably of zirconium carbide) in order to minimize carbonization of Zr(L). The molten Zr was poured through an opening in the bottom of the crucible into a calorimeter containing molten Mg as the calorimetric fluid. The method of calculating the value of ΔH_m° was described in detail by V. P. Elyutin, M. A. Maurakh, V. Y. Mishuk, and G. M. Sverdlov, Izv. Vysshikh Uchebn. Zavedenii, Tsvetn. Met. 10, 60 (1967). The authors estimated the uncertainty as about 7 percent in ΔH_m°.

Reference

H. K. Adenstedt, Trans. Am. Soc. Metals 44, 943 (1952).
J. L. Scott, Oak Ridge Natl. Lab., Oak Ridge, Tenn., ORNL-2328, 1957.
R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 25, 248 (1954).
D. K. Deardorff and E. T. Hayes, Trans. AIME 208, 509 (1956).
J. H. deBoer, Ind. Eng. Chem. 49, 1256 (1957); J. H. deBoer, and J. D. East, Z. Anorg. Allgem. Chem. 187, 193 (1930); and F. H. Jaeger and W. A. Veenstra, Rec. Trav. Chim. 53, 917 (1934).
R. V. Sara, J. Am. Ceram. Soc. 48, 243 (1965).
R. A. Oriani and T. S. Jones, Rev. Sci. Instr. 27, 248 (1954). This value is not adopted.
E. Rudy and S. Windisch, Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. VIII, January 1965.
E. Rudy, D. P. Harmon, and C. E. Bruki, Aerojet-General Corporation, AFML-TR-65-2, Part I, Vol. II, May 1965.

Vaporization Data

T_b is the temperature at which the Gibbs energy change (ΔGr°) for the reaction Zr(L) = Zr(g) approaches zero. The difference between ΔH_f°(Zr, g) and ΔH_f°(Zr, l) at T_b is ΔH_v°.

GFW = 91.22

ZIRCONIUM (Zr)

(IDEAL GAS)

GFW = 91.22

T, °K	Cp*	gibbs/mol S°	(C°-H° ₂₉₈)/T	H°-H° ₂₉₈	kcal/mol ΔH°	ΔG°	Log Kp
0	5.000	37.221	INFINITE	-1.629	187.992	INFINITE	INFINITE
100	5.019	46.536	-	-1.132	186.277	184.651	-116.658
200	5.743	40.892	-	-0.598	181.466	181.466	-156.620
298	6.167	43.315	-	-	180.300	180.300	-101.276
300	6.175	43.358	-	-	180.301	180.300	-100.406
400	6.612	45.229	-	-0.664	186.330	184.625	-73.384
500	6.594	46.706	-	-1.326	186.341	181.284	-57.384
600	6.464	47.897	-	-1.979	186.316	182.875	-46.378
700	6.315	48.462	-	-2.619	186.284	184.653	-36.672
800	6.155	48.943	-	-3.259	186.247	186.247	-28.692
900	6.121	50.143	-	-3.859	187.195	187.195	-22.964
1000	6.121	51.068	-	-4.472	187.819	187.819	-18.492
1100	6.155	51.673	-	-5.085	187.615	187.615	-14.257
1200	6.225	52.211	-	-5.704	186.238	186.238	-10.106
1300	6.325	52.688	-	-6.328	184.653	184.653	-6.813
1400	6.428	53.165	-	-6.968	182.875	182.875	-3.478
1500	6.542	53.633	-	-7.617	180.300	180.300	-0.106
1600	6.655	54.059	-	-8.276	176.257	176.257	12.958
1700	6.763	54.465	-	-8.957	171.652	171.652	26.495
1800	6.859	54.829	-	-9.659	166.402	166.402	39.405
1900	6.946	55.158	-	-10.380	160.628	160.628	51.655
2000	7.046	55.568	-	-11.121	154.384	154.384	62.406
2100	7.127	55.934	-	-11.729	147.648	147.648	71.653
2200	7.202	56.266	-	-12.449	140.384	140.384	79.384
2300	7.274	56.569	-	-13.108	132.653	132.653	85.653
2400	7.341	56.843	-	-13.797	124.466	124.466	90.466
2500	7.408	57.201	-	-14.538	115.819	115.819	93.819
2600	7.475	57.492	-	-15.382	106.727	106.727	95.727
2700	7.542	57.826	-	-16.310	97.200	97.200	96.200
2800	7.609	58.119	-	-17.324	87.343	87.343	95.343
2900	7.678	58.366	-	-18.426	77.166	77.166	93.166
3000	7.749	58.561	-	-19.619	66.681	66.681	89.681
3100	7.821	58.836	-	-20.904	55.884	55.884	85.884
3200	7.894	59.086	-	-22.283	44.777	44.777	81.777
3300	7.969	59.269	-	-23.761	33.366	33.366	77.366
3400	8.045	59.384	-	-25.343	21.653	21.653	72.653
3500	8.121	59.463	-	-27.034	9.646	9.646	67.646
3600	8.198	60.033	-	-28.841	-12.757	-12.757	62.343
3700	8.275	60.220	-	-30.769	-26.000	-26.000	56.727
3800	8.354	60.498	-	-32.824	-39.384	-39.384	50.884
3900	8.426	60.848	-	-35.021	-52.819	-52.819	44.819
4000	8.500	61.223	-	-37.366	-66.300	-66.300	38.500
4100	8.573	61.633	-	-40.000	-79.834	-79.834	31.834
4200	8.644	62.073	-	-42.834	-93.419	-93.419	24.919
4300	8.716	62.543	-	-45.866	-107.050	-107.050	17.750
4400	8.789	63.043	-	-49.084	-120.727	-120.727	10.384
4500	8.864	63.573	-	-52.497	-134.446	-134.446	2.819
4600	8.906	64.129	-	-56.121	-148.200	-148.200	-4.346
4700	8.950	64.711	-	-60.000	-162.000	-162.000	-10.900
4800	9.073	65.321	-	-64.121	-175.834	-175.834	-17.834
4900	9.122	65.961	-	-68.584	-190.727	-190.727	-25.727
5000	9.172	66.641	-	-73.400	-206.681	-206.681	-34.681
5100	9.169	63.062	-	-36.296	-	-	-
5200	9.212	63.444	-	-39.466	-	-	-
5300	9.258	63.866	-	-42.919	-	-	-
5400	9.286	64.329	-	-46.653	-	-	-
5500	9.322	64.840	-	-50.684	-	-	-
5600	9.352	65.400	-	-55.021	-	-	-
5700	9.379	66.000	-	-59.666	-	-	-
5800	9.424	66.641	-	-64.619	-	-	-
5900	9.424	67.321	-	-70.000	-	-	-
6000	9.442	68.046	-	-75.834	-	-	-

Dec. 31, 1960; June 30, 1961; Dec. 31, 1967

Ground State Configuration $3p^2$ $S^{\circ}_{298.15} = 43.32 \pm 0.10$ gibbs/mol $\Delta H^{\circ}_{298.15} = 140.3 \pm 3.5$ kcal/mol

Electronic Levels and Quantum Weights

E_i , cm ⁻¹	g_i	E_i , cm ⁻¹	g_i	E_i , cm ⁻¹	g_i
0.00	5	8057.30	9	14348.78	5
570.41	7	10885.36	3	14697.03	7
1240.84	9	11016.65	5	14783.54	5
4186.11	5	11258.38	7	14791.28	9
4196.85	1	11640.72	5	14988.51	11
4376.28	3	11956.33	7	15119.66	13
4870.53	3	12342.37	9	15146.48	5
5023.41	5	12503.44	7	15201.26	7
5101.68	5	12760.66	9	15457.40	7
5249.07	7	12772.78	11	15699.86	9
5540.54	9	13141.76	1	15720.36	9
5888.93	11	14123.01	3	15932.10	9

Heat of Formation

Vapor pressures of Zr(β) and Zr(δ) were measured, using the Langmuir free-vaporization method, by Skinner (1) and Koch (3), respectively. Based on the reported results, the corresponding enthalpies of sublimation and vaporization are evaluated by the second and third law methods. See the table below for details. The values of evaporation rate and vapor pressure given by Koch in Table 2 on page 9 are too big by a factor of 10 due to typographical errors. The samples employed by Koch were prepared from iodide-process zirconium of 99.9 percent purity by tungsten-electrode melting in an inert atmosphere. The measured weight losses were in general more than one hundred times greater than those reported by Skinner. The value of ΔH°_{298} (Zr, g) adopted is 140.3 \pm 3.5 kcal/mol, which is derived using the data of Koch.

Truelsen (2) used a mass spectrometer with a high temperature Knudsen effusion source to obtain the vapor pressure for Zr(β) and Zr(δ). Based on the reported vapor pressures the values of heat of sublimation of Zr(β) are evaluated by the second and third law methods. The results are presented in the table below. Because of the uncertainties in obtaining absolute pressures from ion intensities, these results are not adopted.

Zwikker (4) determined the vapor pressures of Zr(β) by the Langmuir method. However, the zirconium sample was reported to be covered by an oxide layer during the measurement. Therefore, the pressures obtained are probably not the vapor pressures of pure zirconium and are not used for evaluation.

Investigator	Temperature, °K	No. of Points	ΔH°_{298} , kcal/mol	ΔH°_{298} , kcal/mol
1. Skinner (1951)	1951 - 2047	12	138.642.1	145.9
2. Truelsen (1965)	1968 - 2274	22	141.341.5	142.1
3. Koch (1968)	2229 - 2795	16	142.724.3	141.9

*Calculation based on the third law ΔH°_{298} , $\Delta H^{\circ}_{298}(\beta) = 1.706$ and $\Delta H^{\circ}_{298}(\delta) = 6.351$ kcal/mol.

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore (5). Above the level $E_i = 15932.10$ cm⁻¹, the values of E_i and g_i listed in the above table are average values calculated from those given by Moore. The entropy contributed by the unobserved electronic is estimated to be less than 0.1 eu at 6000°K.

References

1. G. B. Skinner, Ph. D. Thesis, The Ohio State University, 1951; and G. B. Skinner, J. W. Edwards and H. L. Johnston, J. Am. Chem. Soc. **73**, 174 (1951).
2. O. C. Truelsen and H. W. Goldstein, J. Phys. Chem. **69**, 2531 (1965).
3. R. K. Koch and W. E. Anable, U. S. Bur. Mines RI 7063, 1968.
4. C. Zwikker, Versl. Kon. Ak. van Wetenschappen, Amsterdam **35**, 336 (1926); Proc. Roy. Ac. Amsterdam **23**, 792 (1926); Physica **8**, 240 (1928); and J. H. DeBoer and J. D. Fact, Z. Anorg. Allgem. Chem. **187**, 193 (1930).
5. C. E. Moore, Natl. Bur. Std. Circ. **467**, Vol. II, 1952.

Zirconium Unipositive Ion (Zr⁺)

(Ideal Gas) GFW = 91.21945

ZIRCONIUM UNIPosITIVE ION (Zr⁺)

(IDEAL GAS)

Zr⁺

GFW = 91.21945

Ground State Configuration $4f_{3/2}^2$
 $S_{298.15}^\circ = 43.864 \pm 0.01$ gibbs/mol
 $\Delta H_f^\circ = 305.7 \pm 4$ kcal/mol
 $\Delta H_{298.15}^\circ = 306.2 \pm 4$ kcal/mol

Electronic Levels and Quantum Weights

$\epsilon_i, \text{cm}^{-1}$	g_i	$\epsilon_i, \text{cm}^{-1}$	g_i
0	4	15611.151	30
314.67	6	24311.416	46
763.44	8	30405.276	54
1322.91	10	31980.999	40
3003.126	18	34607.328	36
4080.140	20	37180.173	38
6466.284	26	38077.586	40
8624.116	36	40045.807	26
12983.250	40	41556.750	50

Heat of Formation

The heat of formation is calculated from the reaction $\text{Zr(g)} - e^-(\text{g}) = \text{Zr}^+(\text{g})$ with the JANAF auxiliary value for Zr(g) ; and an ionization potential = 6.84 eV or 157.737 kcal/mol, obtained from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. II, 1952 and Vol. III, 1958.

Heat Capacity and Entropy

The electronic levels and quantum weights are taken from C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ. 467, Vol. II, 1952 and Vol. III, 1958. The electronic levels above 2500 cm^{-1} are averaged. The $H^\circ - H_{298}^\circ$ value at 0°K is -1.786 kcal/mol.

T, °K	C_p°	$S^\circ - (C_p^\circ - H_{298}^\circ)/T$	$H^\circ - H_{298}^\circ$	ΔH_f°	ΔG_f°	Log K _p
0	6.759	43.864	0.000	306.200	294.412	-215.610
100	6.760	43.864	-0.13	306.211	294.339	-214.425
200	6.754	43.864	-0.53	306.761	290.281	-210.611
300	6.757	43.864	-1.386	307.278	286.121	-206.863
400	6.758	43.864	-2.021	307.758	281.844	-202.662
500	6.759	43.864	-2.673	308.200	277.488	-198.036
600	6.759	43.864	-3.322	308.613	273.073	-193.000
700	6.759	43.864	-3.970	308.996	268.607	-187.564
800	6.759	43.864	-4.621	309.355	264.100	-181.728
900	6.759	43.864	-5.275	309.689	259.559	-175.492
1000	6.759	43.864	-5.934	309.999	255.000	-168.856
1100	6.759	43.864	-6.596	310.284	250.411	-161.820
1200	6.759	43.864	-7.263	310.543	245.784	-154.384
1300	6.759	43.864	-7.933	310.778	241.128	-146.548
1400	6.759	43.864	-8.606	310.989	236.442	-138.312
1500	6.759	43.864	-9.282	311.177	231.726	-129.676
1600	6.759	43.864	-9.960	311.342	227.000	-120.640
1700	6.759	43.864	-10.640	311.484	222.274	-111.204
1800	6.759	43.864	-11.321	311.604	217.548	-101.768
1900	6.759	43.864	-12.004	311.704	212.822	-92.332
2000	6.759	43.864	-12.687	311.784	208.100	-82.896
2100	6.759	43.864	-13.371	311.844	203.374	-73.460
2200	6.759	43.864	-14.055	311.884	198.648	-64.024
2300	6.759	43.864	-14.740	311.904	193.922	-54.588
2400	6.759	43.864	-15.424	311.914	189.196	-45.152
2500	6.759	43.864	-16.109	311.914	184.470	-35.716
2600	6.759	43.864	-16.793	311.904	179.744	-26.280
2700	6.759	43.864	-17.477	311.884	175.018	-16.844
2800	6.759	43.864	-18.160	311.853	170.292	-7.408
2900	6.759	43.864	-18.844	311.803	165.566	2.028
3000	6.759	43.864	-19.525	311.733	160.840	11.492
3100	6.759	43.864	-20.206	311.643	156.114	20.956
3200	6.759	43.864	-20.887	311.533	151.388	30.420
3300	6.759	43.864	-21.568	311.403	146.662	39.884
3400	6.759	43.864	-22.249	311.253	141.936	49.348
3500	6.759	43.864	-22.930	311.083	137.210	58.812
3600	6.759	43.864	-23.611	310.893	132.484	68.276
3700	6.759	43.864	-24.292	310.683	127.758	77.740
3800	6.759	43.864	-24.973	310.453	123.032	87.204
3900	6.759	43.864	-25.654	310.203	118.306	96.668
4000	6.759	43.864	-26.335	310.003	113.580	106.132
4100	6.759	43.864	-27.016	309.753	108.854	115.596
4200	6.759	43.864	-27.697	309.453	104.128	125.060
4300	6.759	43.864	-28.378	309.103	99.402	134.524
4400	6.759	43.864	-29.059	308.703	94.676	143.988
4500	6.759	43.864	-29.740	308.253	89.950	153.452
4600	6.759	43.864	-30.421	307.753	85.224	162.916
4700	6.759	43.864	-31.102	307.203	80.498	172.380
4800	6.759	43.864	-31.783	306.603	75.772	181.844
4900	6.759	43.864	-32.464	305.953	71.046	191.308
5000	6.759	43.864	-33.145	305.253	66.320	200.772
5100	6.759	43.864	-33.826	304.503	61.594	210.236
5200	6.759	43.864	-34.507	303.703	56.868	219.700
5300	6.759	43.864	-35.188	302.853	52.142	229.164
5400	6.759	43.864	-35.869	301.953	47.416	238.628
5500	6.759	43.864	-36.550	301.003	42.690	248.092
5600	6.759	43.864	-37.231	300.003	37.964	257.556
5700	6.759	43.864	-37.912	298.953	33.238	267.020
5800	6.759	43.864	-38.593	297.753	28.512	276.484
5900	6.759	43.864	-39.274	296.503	23.786	285.948
6000	6.759	43.864	-40.000	295.203	19.060	295.412

Electron Gas (e⁻)

(Reference State) At. Wt. = 0.00054876

ELECTRON GAS (e⁻)

(REFERENCE STATE)

AT. WT. = 0.00054876

0 to 6000°K. IDEAL GAS

 $S_{298.15}^{\circ} = 4.988 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ $\Delta H_f^{\circ} 298.15 = 0$

Electronic Levels and Multiplicities

$$\frac{\epsilon_i \text{ cm.}^{-1}}{0} \cdot \frac{g_i}{2}$$

Heat of Formation.

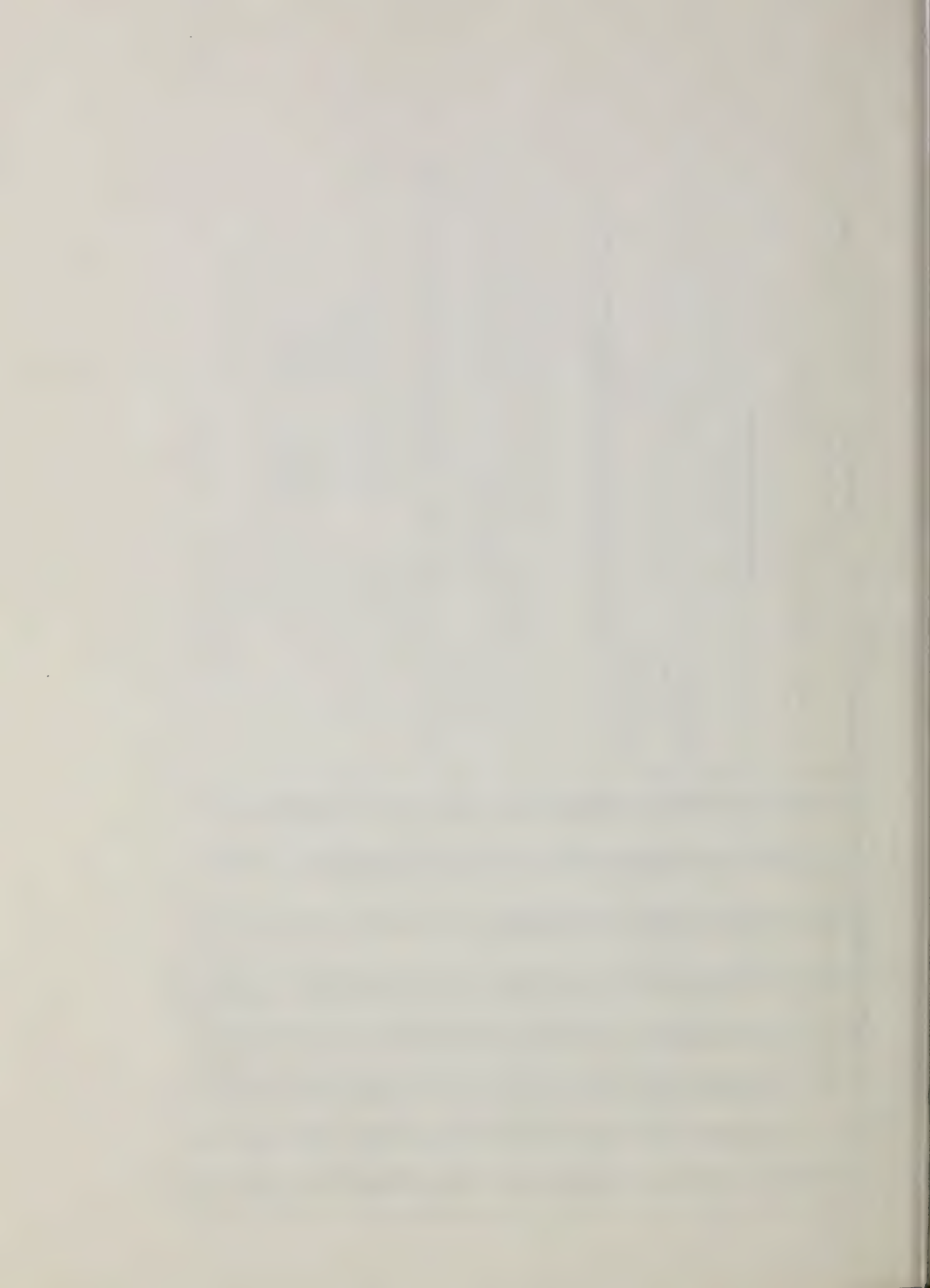
Zero by definition.

Heat Capacity and Entropy.

Calculated by assuming to be an ideal monatomic gas of mass 0.00054876 with two equivalent spin states. The enthalpy between 298 and 0°K. is 1.461 kcal. mole⁻¹ as for all unexcited monatomic gases.

T. °K.	C _p cal. mole ⁻¹ deg. ⁻¹	S° -(F°-H° ₂₉₈)/T	H°-H° ₂₉₈ kcal. mole ⁻¹	ΔH _f [°]	ΔF _f [°]	Log K _p
0	4.968	4.989	4.989	.000	.000	.000
100	4.968	5.019	.009	.000	.000	.000
200	4.968	5.184	.506	.000	.000	.000
300	4.968	5.552	1.003	.000	.000	.000
400	4.968	6.063	1.500	.000	.000	.000
500	4.968	6.637	1.996	.000	.000	.000
600	4.968	7.276	2.493	.000	.000	.000
700	4.968	7.977	2.990	.000	.000	.000
800	4.968	8.734	3.487	.000	.000	.000
900	4.968	9.549	3.984	.000	.000	.000
1000	4.968	10.424	4.480	.000	.000	.000
1100	4.968	11.360	4.977	.000	.000	.000
1200	4.968	12.357	5.474	.000	.000	.000
1300	4.968	13.415	5.971	.000	.000	.000
1400	4.968	14.534	6.467	.000	.000	.000
1500	4.968	15.714	6.964	.000	.000	.000
1600	4.968	16.955	7.461	.000	.000	.000
1700	4.968	18.257	7.958	.000	.000	.000
1800	4.968	19.620	8.455	.000	.000	.000
1900	4.968	21.044	8.951	.000	.000	.000
2000	4.968	22.528	9.448	.000	.000	.000
2100	4.968	24.071	9.945	.000	.000	.000
2200	4.968	25.673	10.442	.000	.000	.000
2300	4.968	27.334	10.939	.000	.000	.000
2400	4.968	29.054	11.435	.000	.000	.000
2500	4.968	30.833	11.932	.000	.000	.000
2600	4.968	32.670	12.429	.000	.000	.000
2700	4.968	34.564	12.926	.000	.000	.000
2800	4.968	36.514	13.423	.000	.000	.000
2900	4.968	38.519	13.919	.000	.000	.000
3000	4.968	40.578	14.416	.000	.000	.000
3100	4.968	42.690	14.913	.000	.000	.000
3200	4.968	44.854	15.410	.000	.000	.000
3300	4.968	47.070	15.907	.000	.000	.000
3400	4.968	49.336	16.403	.000	.000	.000
3500	4.968	51.652	16.900	.000	.000	.000
3600	4.968	54.017	17.397	.000	.000	.000
3700	4.968	56.431	17.894	.000	.000	.000
3800	4.968	58.894	18.390	.000	.000	.000
3900	4.968	61.405	18.887	.000	.000	.000
4000	4.968	63.963	19.384	.000	.000	.000
4100	4.968	66.567	19.881	.000	.000	.000
4200	4.968	69.216	20.378	.000	.000	.000
4300	4.968	71.909	20.874	.000	.000	.000
4400	4.968	74.645	21.371	.000	.000	.000
4500	4.968	77.423	21.868	.000	.000	.000
4600	4.968	80.243	22.365	.000	.000	.000
4700	4.968	83.103	22.862	.000	.000	.000
4800	4.968	86.002	23.358	.000	.000	.000
4900	4.968	88.939	23.855	.000	.000	.000
5000	4.968	91.914	24.352	.000	.000	.000
5100	4.968	94.926	24.849	.000	.000	.000
5200	4.968	97.974	25.346	.000	.000	.000
5300	4.968	101.057	25.842	.000	.000	.000
5400	4.968	104.174	26.339	.000	.000	.000
5500	4.968	107.324	26.836	.000	.000	.000
5600	4.968	110.507	27.333	.000	.000	.000
5700	4.968	113.723	27.830	.000	.000	.000
5800	4.968	116.971	28.326	.000	.000	.000
5900	4.968	120.250		.000	.000	.000
6000	4.968	123.560		.000	.000	.000

Mar. 31, 1965



Publications in the National Standard Reference Data Series

National Bureau of Standards

You may use this listing as your order form by checking the proper box of the publication(s) you desire or by providing the full identification of the publication you wish to purchase. The full letter symbols with each publication number and full title of the publication and author must be given in your order, e.g. NSRDS-NBS-17, Tables of Molecular Vibrational Frequencies, Part 3, by T. Shimanouchi.

Pay for publications by check, money order, or Superintendent of Documents coupons or deposit account. Make checks and money orders payable to Superintendent of Documents. Foreign remittances should be made either

by international money order or draft on an American bank. Postage stamps are not acceptable.

No charge is made for postage to destinations in the United States and possessions, Canada, Mexico, and certain Central and South American countries. To other countries, payments for documents must cover postage. Therefore, one-fourth of the price of the publication should be added for postage.

Send your order together with remittance to Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.

- ☐ NSRDS-NBS 1, **National Standard Reference Data System—Plan of Operation**, by E. L. Brady and M. B. Wallenstein, 1964 (15 cents), SD Catalog No. C13.48:1.
- ☐ NSRDS-NBS 2, **Thermal Properties of Aqueous Uni-univalent Electrolytes**, by V. B. Parker, 1965 (45 cents), SD Catalog No. C13.48:2.
- ☐ NSRDS-NBS 3, Sec. 1, **Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, Si II, Si III, Si IV**, by C. E. Moore, 1965 (35 cents), SD Catalog No. C13.48:3/Sec.1.
- ☐ NSRDS-NBS 3, Sec. 2, **Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, Si I**, by C. E. Moore, 1967 (20 cents), SD Catalog No. C13.48:3/Sec.2.
- ☐ NSRDS-NBS 3, Sec. 3, **Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, C I, C II, C III, C IV, C V, C VI**, by C. E. Moore, 1970 (\$1), SD Catalog No. C13.48:3/Sec.3.
- ☐ NSRDS-NBS 3, Sec. 4, **Selected Tables of Atomic Spectra, Atomic Energy Levels and Multiplet Tables, N IV, N VI, N VII**, by C. E. Moore, (in press).
- ☐ NSRDS-NBS 4, **Atomic Transition Probabilities, Volume I, Hydrogen Through Neon**, by W. L. Wiese, M. W. Smith and B. M. Glennon, 1966 (\$2.50), SD Catalog No. C13.48:4/Vol.1.
- ☐ NSRDS-NBS 5, **The Band Spectrum of Carbon Monoxide**, by P. H. Krupenie, 1966 (70 cents), SD Catalog No. C13.48:5.
- ☐ NSRDS-NBS 6, **Tables of Molecular Vibrational Frequencies, Part 1**, by T. Shimanouchi, 1967 (40 cents), SD Catalog No. C13.48:6/Pt.1.
- ☐ NSRDS-NBS 7, **High Temperature Properties and Decomposition of Inorganic Salts, Part 1, Sulfates**, by K. H. Stern and E. L. Weise, 1966 (35 cents), SD Catalog No. C13.48:7/Pt.1.
- ☐ NSRDS-NBS 8, **Thermal Conductivity of Selected Materials**, by R. W. Powell, C. Y. Ho, and P. E. Liley, 1966 (\$1), PB189698.
- ☐ NSRDS-NBS 9, **Tables of Bimolecular Gas Reactions**, by A. F. Trotman-Dickenson and G. S. Milne, 1967 (\$2), SD Catalog No. C13.48:9.
- ☐ NSRDS-NBS 10, **Selected Values of Electric Dipole Moments for Molecules in the Gas Phase**, by R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, 1967 (40 cents), SD Catalog No. C13.48:10.
- ☐ NSRDS-NBS 11, **Tables of Molecular Vibrational Frequencies, Part 2**, by T. Shimanouchi, 1967 (30 cents), SD Catalog No. C13.48:11/Part 2.
- ☐ NSRDS-NBS 12, **Tables for the Rigid Asymmetric Rotor: Transformation Coefficients from Symmetric to Asymmetric Bases and Expectation Values of P_z^2 , P_y^2 , and P_x^2** , by R. H. Schwendeman, 1968 (60 cents), SD Catalog No. 13.48:12.
- ☐ NSRDS-NBS 13, **Hydrogenation of Ethylene on Metallic Catalysts**, by J. Horiuti and K. Miyahara, 1968 (\$1), SD Catalog No. C13.48:13.
- ☐ NSRDS-NBS 14, **X-Ray Wavelengths and X-Ray Atomic Energy Levels**, by J. A. Bearden, 1967 (40 cents), SD Catalog No. C13.48:14.
- ☐ NSRDS-NBS 15, **Molten Salts, Vol. 1, Electrical Conductance, Density, and Viscosity Data**, by G. J. Janz, F. W. Dampier, G. R. Lakshminarayanan, P. K. Lorenz, and R. P. T. Tomkins, 1968 (\$3), SD Catalog No. C13.48:15/Vol.1.
- ☐ NSRDS-NBS 16, **Thermal Conductivity of Selected Materials, Part 2**, by C. Y. Ho, R. W. Powell, and P. E. Liley, 1968 (\$2), SD Catalog No. C13.48:16/Pt.2.
- ☐ NSRDS-NBS 17, **Tables of Molecular Vibrational Frequencies, Part 3**, by T. Shimanouchi, 1968 (30 cents), SD Catalog No. C13.48:17/Pt.3.
- ☐ NSRDS-NBS 18, **Critical Analysis of the Heat-Capacity Data of the Literature and Evaluation of Thermodynamic Properties of Copper, Silver, and Gold From 0 to 300°K**, by G. T. Furukawa, W. G. Saba, and M. L. Reilly, 1968 (40 cents), SD Catalog No. C13.48:18.
- ☐ NSRDS-NBS 19, **Thermodynamic Properties of Ammonia as an Ideal Gas**, by L. Haar, 1968 (20 cents), SD Catalog No. C13.48:19.
- ☐ NSRDS-NBS 20, **Gas Phase Reaction Kinetics of Neutral Oxygen Species**, by H. S. Johnston, 1968 (45 cents), SD Catalog No. C13.48:20.
- ☐ NSRDS-NBS 21, **Kinetic Data on Gas Phase Unimolecular Reactions**, by S. W. Benson and H. E. O'Neal, 1970 (\$7), SD Catalog No. C13.48:21.
- ☐ NSRDS-NBS 22, **Atomic Transition Probabilities, Vol II, Sodium Through Calcium, A Critical Data Compilation**, by W. L. Wiese, M. W. Smith, and B. M. Miles, 1969 (\$4.50), SD Catalog No. C13.48:22/Vol.II.
- ☐ NSRDS-NBS 23, **Partial Grottrian Diagrams of Astrophysical Interest**, by C. E. Moore and P. W. Merrill, 1968 (55 cents), SD Catalog No. C13.48:23.
- ☐ NSRDS-NBS 24, **Theoretical Mean Activity Coefficients of Strong Electrolytes in Aqueous Solutions from 0 to 100° C**, by Walter J. Hamer, 1968 (\$4.25), SD Catalog No. C13.48:24.
- ☐ NSRDS-NBS 25, **Electron Impact Excitation of Atoms**, by B. L. Moiseiwitsch and S. J. Smith, 1968 (\$2), SD Catalog No. C13.48:25.
- ☐ NSRDS-NBS 26, **Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions**, by J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 1969 (\$4), SD Catalog No. C13.48:26.
- ☐ NSRDS-NBS 27, **Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres**, by A. L. Gosman, R. D. McCarty, and J. G. Hust, 1969 (\$1.25), SD Catalog No. C13.48:27.
- ☐ NSRDS-NBS 28, **Molten Salts, Vol. 2, Section 1, Electrochemistry of Molten Salts: Gibbs Free Energies and Excess Free Energies From Equilibrium-Type Cells**, by G. J. Janz and C. G. M. Dijkhuis. **Section 2, Surface Tension Data**, by G. J. Janz, G. R. Lakshminarayanan, R. P. T. Tomkins, and J. Wong, 1969 (\$2.75), SD Catalog No. C13.48:28/Vol.2.
- ☐ NSRDS-NBS 29, **Photon Cross Sections, Attenuation Coefficients and Energy Absorption Coefficients From 10 keV to 100 GeV**, by J. H. Hubbell, 1969 (75 cents), SD Catalog No. C13.48:29.
- ☐ NSRDS-NBS 30, **High Temperature Properties and Decomposition of Inorganic Salts, Part 2, Carbonates**, by K. H. Stern and E. L. Weise, 1969 (45 cents), SD Catalog No. C13.48:30.
- ☐ NSRDS-NBS 31, **Bond Dissociation Energies in Simple Molecules**, by B. deB. Darwent, 1970 (55 cents), SD Catalog No. C13.48:31.
- ☐ NSRDS-NBS 32, **Phase Behavior in Binary and Multicomponent Systems at Elevated Pressures: *n*-Pentane and Methane-*n*-Pentane**, by V. M. Berry and B. H. Sage, 1970 (70 cents), SD Catalog No. C13.48:32.
- ☐ NSRDS-NBS 33, **Electrolytic Conductance and the Conductances of the Halogen Acids in Water**, by W. J. Hamer and H. J. DeWane, 1970 (50 cents), SD Catalog No. C13.48:33.
- ☐ NSRDS-NBS 34, **Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra**, by C. E. Moore, 1970 (75 cents), SD Catalog No. C13.48:34.

**Announcement of New Publications in
National Standard Reference Data Series**

Superintendent of Documents,
Government Printing Office,
Washington, D.C. 20402

Dear Sir:

Please add my name to the announcement list of new publications to be issued in the series: National Standard Reference Data Series—National Bureau of Standards.

Name_____

Company_____

Address_____

City_____ State_____ Zip Code_____

(Notification key N-337)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NSRDS-NBS 37	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE JANAF Thermochemical Tables, Second Edition		5. Publication Date	
		6. Performing Organization Code	
7. AUTHOR(S) D. R. Stull, H. Prophet, et al.		8. Performing Organization	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		10. Project/Task/Work Unit No.	
		11. Contract/Grant No. F04611-67-C-0009 F04611-70-0028	
12. Sponsoring Organization Name and Address The Thermal Research Laboratory Dow Chemical Company Midland, Michigan		13. Type of Report & Period Covered NA	
		14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES Superseding PB168-370 and Addenda 1, 2, and 3			
16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.) This monograph is the second edition of the JANAF Thermochemical Tables. It contains thermodynamic properties for some 1099 chemical species. The following properties are tabulated as functions of temperatures: C_p° , S° , $(F^\circ - H_{298}^\circ)/T$, $H^\circ - H_{298}^\circ$, ΔH_f° and Log Kp.			
17. KEY WORDS (Alphabetical order, separated by semicolons) Evaluated Data; Thermal Functions; Thermodynamic Properties of Materials; Thermodynamics.			
18. AVAILABILITY STATEMENT <input checked="" type="checkbox"/> UNLIMITED. <input type="checkbox"/> FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NTIS.		19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 1141
		20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price \$9.75

